



IMPERIAL COLLEGE LONDON

DOCTORAL THESIS

Modelling and Coarse-Grained Simulation of Polymers and Liquid Crystals

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*A thesis submitted in fulfilment of the requirements
for the degree of Doctor of Philosophy*

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November 16, 2019

Abstract

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This thesis explores the coarse-graining (CG) of complex fluids, namely polymers and liquid crystals, with a novel top-down approach using a molecular-based equation of state (EoS), SAFT- γ Mie. The EoS is employed to calculate the thermophysical properties of molecules provided their intermolecular interaction parameters and conversely, to obtain intermolecular interaction parameters from fits to experimental data.

Here, a systematic study of polymers is presented. Polymers are modelled as chains of homonuclear tangentially bonded spheres, with each sphere representing on average a monomer unit. Interaction parameters of six polymers are obtained by considering only small molecules containing the monomer units. A polymer of a particular molecular weight is modelled by repeating the number of spheres to match the experimental molecular weight. It is shown that the CG models proposed here are robust and can accurately predict both theoretically and in molecular dynamics simulations the correct thermodynamic behaviour of pure polymers, as well as mixtures of polymers with solvents and other polymers including lower and upper critical solution temperatures, the onset of miscibility and other complex phase behaviour. Polymer blends can be modelled using the same approach, indicating the extension of this work to studying block copolymers.

Polyphilic thermotropic liquid crystals are molecules which have functional groups that interact unfavourably with each other. The incompatibility between the groups within the same molecule leads to microphase separation and complex self-assembly.

In this work, T-shaped and swallow-tail bolaamphiphiles are modelled using a heteronuclear representation. CG models for these molecules are proposed and are used to predict and rationalize some of the most complex tiling patterns only recently discovered in experiments. It is shown that it is possible to predict the self-assembly structures, lattice dimensions and transition temperatures in quantitative agreement with experimental results. Extensions to surfactants, discotic liquid crystals and block copolymers are discussed.

Declaration of Authorship

I, Maziar FAYAZ-TORSHIZI, declare that this thesis titled, “Modelling and Coarse-Grained Simulation of Polymers and Liquid Crystals” and the work presented in it are my own. I confirm that where I have used the works of others, it is clearly stated and referenced accordingly.

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Acknowledgements

Words cannot describe my gratitude to my supervisor Erich A. Müller for inspiring me to pursue research in thermodynamics, statistical mechanics and molecular simulation following our first conversation in 2014. It would not be possible for me to pursue this path had it not been for his constant support and his caring nature. He has always been there whenever I needed him and I really appreciate our *ad hoc* meetings and the Lagunitas.

I am also grateful for being part of the Molecular Systems Engineering group and being enlightened by other academics, George Jackson, Claire Adjiman, Amparo Galindo and Andrew Haslam whose kind support and advice have always been useful. Doing a modelling PhD is a lot of long hours spent in the office and luckily for me I have been honoured to spend those long hours with some of the best people I have known in my life: Sadia, Gabriel, Dimitrios, Fred and Fabian, Karl, Jason, Jordan, Sara, Carlos, Isaac, Panos, Hajar, Stephanos, Spiros, Srikanth, David, Elliana, Silvia, Coni, Jonny and Clea have all been supportive and inspiring both in research and in my personal life. Special mention goes to Ed, with whom I have spent the 8 best years of of my life, and Harry, Naveed and Tom who have become some of my closest friends. I have to also acknowledge Paul Luckham who was the first person I met at Imperial and one of the reasons I considered academia.

I have to also thank other friends who have supported me in pursuing a PhD, even though sometimes it was hard for me to explain to them what I do or when I am done! Special mention goes to Tony Coton lads as our long sports and political discussions were pleasant distractions.

Finally, I have to thank my family who have always been supportive. Finishing this PhD was impossible without their caring support. My highest gratitude is to my mother, Behnaz Nejat, as without her presence in my life, it would be impossible for me to be the person I am.

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Dedicated to My Family.

Chapter 1

Motivation and Thesis Overview

The study of soft materials (highlighted in Figure 1.1 [1]) has become a burgeoning interdisciplinary research area, driven by the need to understand processes involving such materials over a hierarchy of scales, from interactions at quantum to continuum levels. To fully comprehend the behaviour of such processes, it is imperative to explore them at different scales.

There is a plethora of phenomena including self-assembly (e.g. colloidal and liquid crystalline packing [2–7], polymers phases [8–13], and DNA self-assemblies [14–16]), transport in confined systems [17, 18] (e.g. nano membranes and bio-capillaries), and fluid phase behaviour which involve the aforementioned materials.

Where the complexity of a given system is such that experimental studies are difficult, it is through modelling and simulation that a myriad of important details can be gathered from the careful study and observation of the molecular behaviour of fluids. [19] One would endeavour to have models that are reliable and rigorous, as well as having the capacity to deal with multicomponent mixtures. Ostensibly, in the context of molecular modelling, it is preferable to use theoretical models, such as equations of state (EoS), to describe system properties primarily due to ease of use and fast computation. However, the computer revolution and *in silico* experimentation via molecular simulations have opened new paths in predicting properties of materials, especially for complex systems where developing a theoretical framework is significantly challenging. Structural, transport and interfacial properties in bulk and confinement are only calculated using theory for the simplest of models, whereas in simulation more complicated models can be investigated. The constant

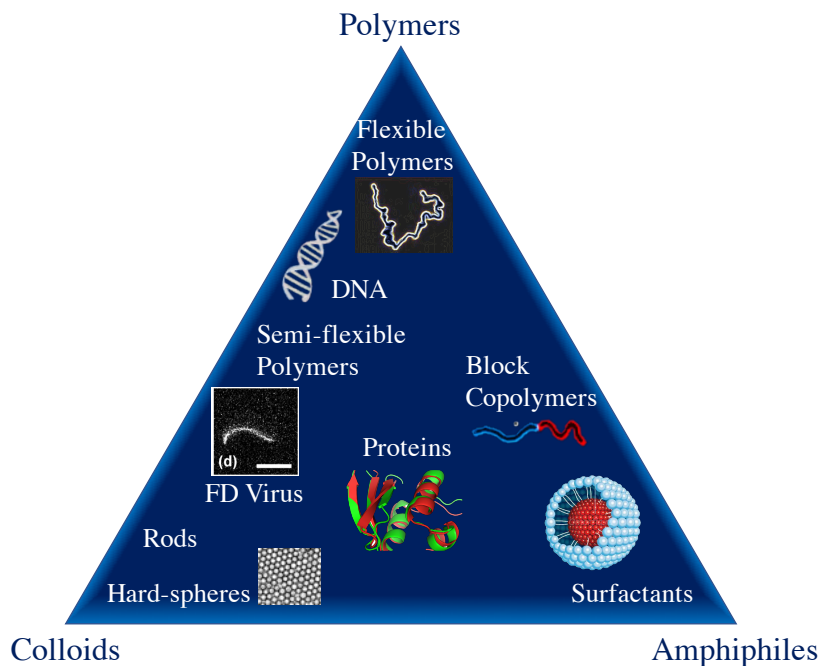


FIGURE 1.1: The triangle of soft matter, as adapted from [1]

increase in processing power (i.e. Moore's Law) coupled with improvements in simulation algorithms (largest simulations have more than 4 trillion particles [20]) render simulation as a useful complement to *in vitro* experimentation with ever more capacity.

While building blocks of some soft matter, such as colloids and biomaterials, are in the order of microns and can be modelled at continuum level, there are many examples where the shape and interaction of constituent materials are too small for a continuum description, yet too large for an all atom description. At this "in-between" scale, aptly named **mesoscale**, developing models by considering individual atoms is very computationally and theoretically intensive. To model such systems one would have to do coarse-graining (CG), i.e. consolidating groups of atoms into a pseudo-particle with an effective potential. Figure 1.2 is a schematic of the ranges where atomistic, continuum and CG models are applicable.

Coarse-graining is essential in mesoscale models and simulations that involve millions of atoms and times scales long enough to observe behaviour such as phase behaviour of complex systems, such as polymers and liquid crystals. [21] There are a variety of different mesoscale models that can at least qualitatively describe system

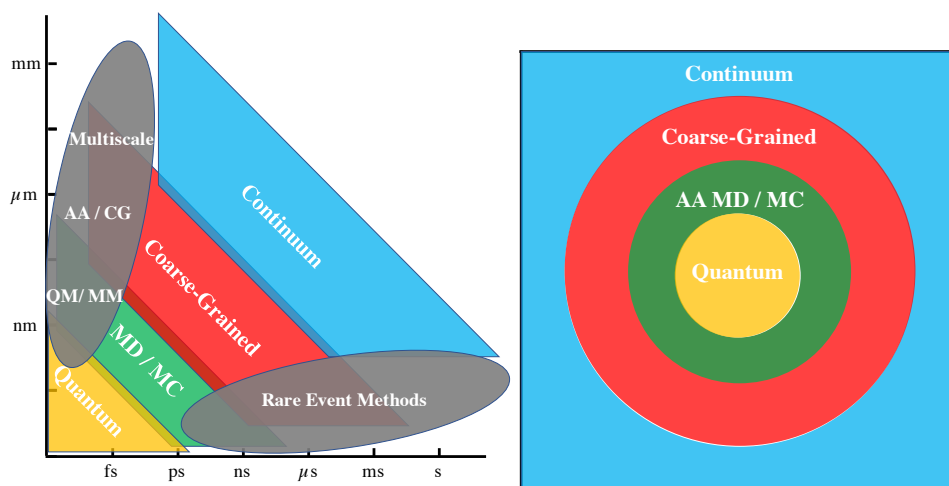


FIGURE 1.2: Scales where different modelling methods are valid, adapted from [1], MD/MC refers to atomistically detailed molecular simulations

properties by coarse-graining. These models follow either of two approaches. [22] The first approach can be described as "top down", where interaction parameters of the pseudo-particles are taken from macroscopic data. The data could be excess enthalpies, liquid density, vapour pressure etc. Provided that a robust model is used, this approach could be very useful for engineering purposes, as the model parameters are related to macroscopic experimental data. The seminal works of Flory are some of the first to employ "top down" approaches to investigate pseudo-particles with interactions that are top down in the sense that macroscopic properties such as mixing enthalpies and solubility parameters were used to obtain them, without knowledge of the atomistic detail. Conversely, the second approach is "bottom-up"; Starting with an atomistic (or fine-grained) description of the system, the redundant degrees of freedom, such as inter-atomic interactions, torsions and angles, are integrated out to provide a robust model to describe groups of atoms as a pseudo-particle.

There are three main challenges to mesoscale modelling:

- The development of reliable and robust coarse-grained models [23]:
 - It is significantly challenging to establish a link between the behavior of

the mesoscale representation of the system and the real molecular interactions (representability). This arises from loss of information from integrating out redundant degrees of freedom. The shape and range of interactions of the mesoscales might not be the same as that observed with atomistic representations. Moreover, many mesoscale models have parameters that can only be calculated from macroscopic properties (e.g. Flory-Huggins χ parameter [24, 25]). This has consequences for the robustness of the interaction parameters, and subsequently affects the predictive ability of CG models and their transferability between dissimilar systems.

- Direct link between experiments, theoretical models and *in silico* simulations:
 - Although there are many models that can qualitatively capture the phase behaviour of complex materials, developing an accurate molecular based thermodynamic model is still a difficult challenge, and there are very few of these models with realistic molecular interaction parameters for them to be able to reproduce the same calculations via simulations.
- No individual method to model transport, structural and thermodynamic properties altogether:
 - Coarse-graining can have significant effects on dynamic properties, given that the shape and interaction between coarse-grained particles are different to the real moieties they are representing. Modelling transport properties such as diffusion and viscosity accurately can be challenging using CG potentials.

It can be seen that in order to overcome the challenges in mesoscopic modelling, bottom-up approaches seem more reliable, as there is a clear link between the CG representation and atomistic detail. However, bottom up approaches are time consuming, as there is a need to model microscopic details first. Furthermore, the CG representation obtained from atomistic detail is generally dependent on the state of the atomistic representation (e.g. density ρ , temperature, pressure, composition etc).

Over the last few years, a novel top-down CG methodology based on the statistical associating fluid theory equation of state (SAFT- γ Mie EoS) [22, 27] has been developed to use a highly accurate molecular based equation of state to find intermolecular potentials for different molecular moieties (or functional groups). The input parameters of the EoS are the parameters of the Mie potential [28] (a more general form of the Lennard-Jones potential). For a given molecule with a given set of Mie potential parameters, the EoS could predict its thermodynamic properties. Thus intermolecular parameters can be directly fitted to experimental data using numerical techniques. Knowing the interaction parameters allows one to predict properties that were not used in the fitting for pure components, as well as applying the parameters in mixtures or designing new molecules. Moreover, the same set of interaction parameters can be used in molecular simulations to study interfacial and transport properties.

The first study using the mentioned methodology was done on CO₂ [29], with extremely promising results, reducing the complex molecule with local partial charges and quadruple moments into a single sphere. Vapour-liquid equilibrium data of pure CO₂ were used to fit intermolecular interactions of CO₂ using the equation of state. Then a wide range of properties, such as heat capacity, surface tension, speed of sound, Joule-Thomson coefficient and isothermal compressibility were predicted using simulations and theory. It was shown that the predictions of the equation of state match those of simulations and experimental data for a wide range of conditions. This approach has since been extended to greenhouse gases [30], benzene [31], alkanes up to C₂₀ [32], and perfluoroalkanes [33]. Moreover Müller and Mejía have also developed a methodology to efficiently estimate force fields for many small molecules, using the method of corresponding states. The library of force-field parameters for more than 23,000 molecules can be found in ref [34]. However, in terms of soft matter, the only materials that have been extensively studied are non-ionic surfactants [35] and ionic surfactants [36].

Although the theory alone has been extended to systems of associating fluids, it has not been tested for systems with long chains. Also the limits of coarse-graining are not yet well known, especially for prediction of complex structures, such as those found with liquid crystals.

The objective of this thesis is to develop a framework based on SAFT- γ Mie methodology to study the properties of soft matter, namely polymers and liquid crystals over a range of conditions. This would entail the use of both the EoS and the corresponding simulations using the same potential parameters.

Polymers are versatile and unique materials. Their unique mechanical and chemical features render them very useful for a large variety of applications, as evident from their ubiquity in nature (e.g. DNA) and their presence in almost all objects we utilise daily.

Although polymeric systems have been studied for decades, it has been a challenge to develop a molecular based model of polymers that can describe their structure, dynamics, phase equilibria in pure melts, solutions and blends as well as glass transition temperatures. Interactions in polymeric systems span many spatio-temporal orders of magnitude depending on the polymer regime, concentration and molecular weight. Individual atoms interact in the order of angstroms, yet end to end distances of polymers are typically in the order of tens of nanometres. Similarly, diffusion of individual monomers can be much faster than the diffusion of the centre of gravity of its constituent molecule.

As for all mesoscale soft matter, this wide spatio-temporal span in description makes bridging between atomistic descriptions of polymers and their bulk properties, such as mesophase separation, dissolution, mixing etc., a particular challenge.

In terms of polymers, the key objective of this thesis is to predict properties of polymers, from pure components, to mixtures with solvents, blends and finally testing the limit of the theory to study mesophase separation in block copolymers. The **novelty** of this work is that first the interaction parameters of the monomer are fitted to experimental data from small molecules containing the monomer. Once the parameters are fitted, monomers could be replicated to any size and the properties of polymers containing the monomer will be found. This means that the parameters will not be state dependent (i.e. the size of monomer or their attraction or repulsion will not be a function of temperature or density). Moreover, the phase map exploration will be fully predictive once the interaction parameters are known. This is particularly useful in the study of polymers in solution, as many common polymer theories are not accurate in describing phase behaviour of polymers in solution

predictably.

Due to the fact that polymers can have very high molecular weights, the main aim will be to show the robustness of the EoS in modelling thermodynamic behaviour of polymers, whilst simulations will be restricted to the systems of lower molecular weights, as particle based simulations become impractical as polymers become larger. As far as the authors are aware, there are no simulation techniques where the thermodynamics of polymers in solution can be accurately and predictably captured, especially for lower critical solution temperature behaviour of common polymers.

Another key objective is to apply the SAFT- γ methodology to systems of rod-like and discotic polyphilic liquid crystals, especially for cases where there is limited theory to predict the structures of polyphilic liquid crystals. Liquid crystals have a wide variety of applications from their use in optical devices, photovoltaics, CO₂ capture and electronics. Bolaamphiphilic molecules are excellent candidates to test our CG parameters to study the self-assembly of liquid crystals. Complex columnar phases (square, pentagonal, hexagonal) as well as bicontinuous phases have been discovered in experiments, however thermodynamically robust modelling of such systems has remained a significant challenge.

The advantages of the SAFT- γ approach of using both simulations and theory is therefore highlighted.

To summarise the objectives:

- The development of reliable and robust coarse-grained models:
 - Polymers: Prediction and estimation of pure component properties (PVT data), phase behaviour of polymers in solution and blends, and microphase separation, with one set of unadjusted monomer interaction parameters, transferable to any system size (from oligomers to high Mw polymers) for all ranges of temperature and pressure
 - Rod-like Liquid Crystals: Predicting the previously unobserved complex morphologies of bolaamphiphilic liquid crystals by employing an accurate molecular based methodology of coarse-graining,

- Disk-like Liquid Crystals: Providing the initial foundations for a robust coarse-graining methodology to model polycyclic aromatic
- Direct link between experiments, theoretical models and *in silico* simulations:
 - Both theory (EoS) and simulations will provide a full phase diagram from different moieties studied in this thesis, with simulations testing the validity of interaction parameters used in the EoS for complex systems, with predictions from both methods compared to experimental data
- Capturing phase equilibrium properties as well as structural and dynamic properties of complex systems

1.1 Thesis Overview

Chapter 2 is a summary of all fundamental concepts in the study of polymers and liquid crystals. Key definitions are provided. Specifically for polymers, different polymer solvent phase behaviours highlighted in Figure 2.7 will be extensively used in this work. For liquid crystals the concept of the director is also important. In Chapter 3, the theoretical background of finding reliable molecular interaction parameters is explained, with the concepts behind the theory of SAFT- γ Mie EoS explained without going into the specific details, as the development of the theory is beyond the scope of this thesis.

Chapter 4 is the first results chapter in this work, where for the first time the viability of the EoS to model polymeric systems is assessed. Like-interaction parameters for 6 polymers are calculated using a novel way, and unlike interaction parameters are obtained from experimental data of binary mixtures. It is shown that the theory is robust in modelling homopolymer melts, polymer-solvent mixtures and polymer-polymer blends.

The same set of parameters is then used directly in MD simulations in Chapter 5. It is shown for the first time that it is possible to simulate all phases observed in Figure 2.7 with quantitative accuracy, with parameters that are state independent.

In the first two results chapters, the molecules are modelled as homonuclear chains, where all the beads in each molecule are the same as the other beads. In

Chapter 6, the focus is on trying to assess the viability of SAFT- γ methodology proposed in this thesis in modelling heteronuclear molecules. For this purpose, for the first time realistic models are developed to predict the self-assembly of polyphilic liquid crystals. Predictions are found to be in remarkable agreement with experimental results for some of the most complex two and three dimensional structures.

The final Chapter is the conclusions and the future outlook of this thesis.

Chapter 2

Polymers and Liquid Crystals

2.1 Fundamental Concepts in Polymer Theory

The word polymer comes from the Greek *πολυ*- "many" and *-μερος* "parts". As the name suggests, polymers refer to macromolecules that are composed of covalently bonded repeat units, called monomers, to form long chains. [37]

A small sample of different types of polymers can be seen in Figure 2.1. The versatility of polymers comes from the fact that they can have structural as well as chemical variety. Linear homopolymers are naturally the simplest of polymers, composed of the same monomer in a single strand. By having two or more monomers that can covalently bond, there are infinite possibilities of polymers that could be synthesised. Polymers composed of different building blocks are called copolymers. Some examples of typical monomers, which will be modelled in later chapters are presented in Figure 2.2. It is important to note that the existence of double bonds or side chain phenyl groups causes difference in the properties of these monomers. One could exploit these different chemistries to make macromolecules that have different properties. Different functional groups have different interactions at the molecular level, which lead to different entropic and enthalpic contributions affecting properties such as blend and solvent miscibility, glass transition, as well as mechanical properties due to chain rigidity. [38]

Since sizes of polymers are typically much larger than the size of the monomers, a general assumption has been that local interactions average out and polymers can be characterized by a handful of quantities, such as structure, stiffness, and the repulsion/attraction between the moieties. The sheer difference in the size of the polymer

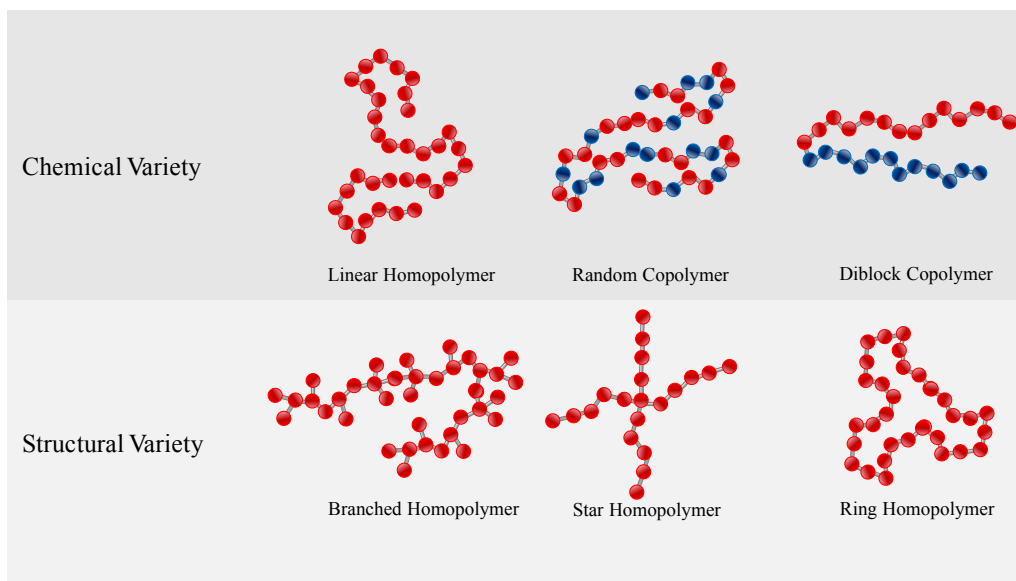


FIGURE 2.1: Different varieties of polymers, homo refers to polymers made up of a single type of monomer, and copolymer are those that are composed of a variety of different monomers (e.g. red and blue)

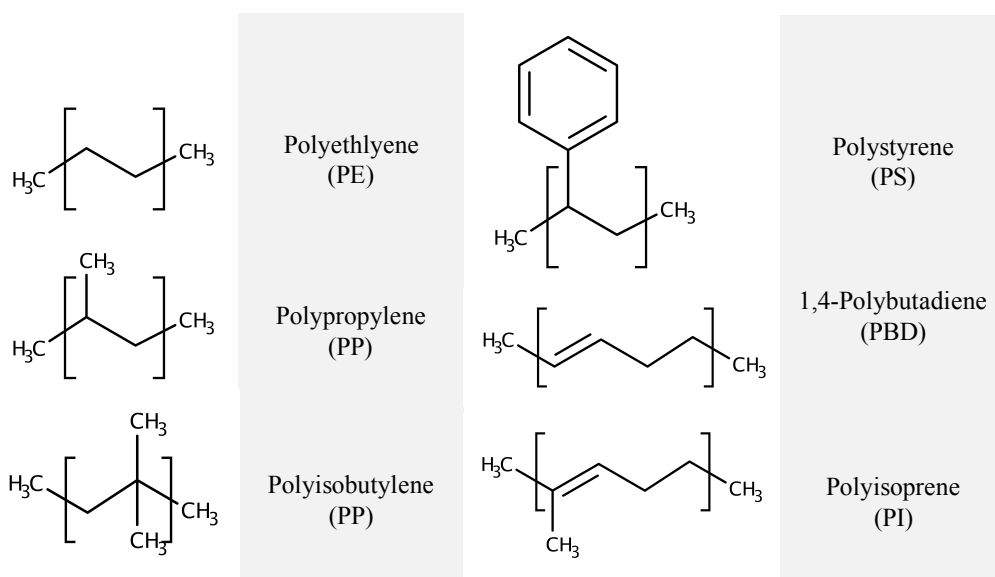


FIGURE 2.2: Examples of common monomers used in polymer synthesis

in comparison with its building blocks inevitably leads to universal properties for all polymers. This has been fundamental in the theories developed by Flory, De Gennes [39] and Edwards [40] where redundant atomistic degrees of freedom of polymers are integrated out and they are modelled with a coarse-grained description. [38, 41]

2.1.1 Chemically Independent Coarse-Grained Representations

There is no general rule as to how many atoms can be represented by a CG segment. However, if one assumes that coarse grained segments (i.e. CG monomers) are so much larger than the real monomeric units in a polymer, then the polymer chain can be represented as a random walk with segments at positions that are not correlated to each other. Although this representation has led to many significant discoveries in polymeric systems, atomistic interactions are in essence filtered out. This has connotations in terms of predictive modelling of fluid mixtures, be it mixtures with solvents or polymer blends. However, most theoretical and simulation frameworks of polymeric materials are based on this perspective.

In this subsection, the full variety of *chemically independent* coarse-grained models of polymers will be discussed.

Geometric Models in Continuous Space

Continuous models are those where monomers can take any position in real space (off-lattice) subject to their bonding constraints to other monomers. There are three main categories of such models [41], with the only difference being the type of bonding between the monomers, as shown in Figure 2.3:

- *Freely-jointed chain* is a self-avoiding random walk with beads that are connected to each other with rigid bonds of a fixed length,
- *Bead-spring chain* is a model where beads are connected to each other with springs, so that the bond lengths are not fixed, but the equilibrium bond length is; this model was first presented by Kremer and Grest [42] and is popular in molecular simulations, as molecules can get closer and further away from each other, being more flexible than a self-avoiding random walk

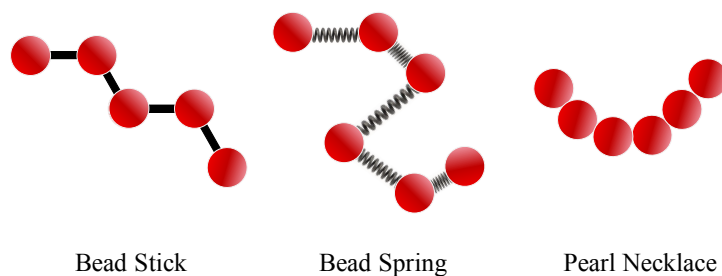
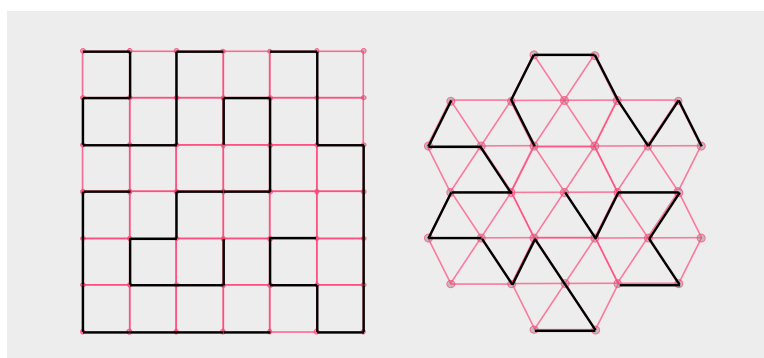


FIGURE 2.3: Models of polymers in continuous space

FIGURE 2.4: two-dimensional lattice models, *left* square lattice, *right* triangular lattice

- *Pearl-necklace* is the same as the freely-jointed chains, for the case where all segments are tangentially bonded to each other

An advantage of these off-lattice models is that extra constraints such as angles and dihedrals can be easily imposed for different groups. A bead stick model with an imposed angle between every three neighbouring segments is called a freely rotating chain. Moreover, off-lattice models are better capture excluded volume effects than lattice models, as the monomer positions are no longer confined to the sites of a lattice and depending on functional group, monomers can have different volumes. [43]

Geometric Models in Discrete Space

Lattice models are an alternative to the model discussed previously, and are commonly used in some of the oldest and the most popular models to study phase behaviour of polymer solutions. Here, polymer segments are only allowed to sit on certain positions in space called **grids**. These grids are positioned at fixed distances

to neighbouring grids so that bond distances between segments are fixed. Figure 2.4 is a schematic of lattice models in two-dimensions. Note that lattice models can be both in two and three dimensions. Common three dimensional lattices are cubic and diamond (tetrahedral) lattices. It could be seen that, on a lattice all segments have the same volume (or size) and that the total volume of the box is fixed, i.e. there are no fluctuations of volume. An advantage of such models is that analytical expressions of energy can be easily calculated, based on the coordination number, which is quite difficult for off-lattice models. Coordination number is the number of closest neighbours surround a segment on a lattice. Square lattices have a coordination number of 4, and triangular lattices have a coordination number of 6. In three dimensions, cubic lattices have 6 nearest neighbours and diamond lattices have 4.

Real vs Ideal Chains

If the segments of a polymer are small enough where excluded volume effects are significant, segments cannot overlap. At this scale, polymers have to be modelled as real chains, consisting of repulsive segments. At the most fundamental level, a real chain is composed of the constituent atoms with bonding, angle and dihedral constraints describing the chain stiffness. Above a certain level of coarse graining, chains become more flexible and lose their stiffness. The minimum distance at which polymers segments become uncorrelated is called the *Kuhn length* or ($2 \times \text{persistence length}$). This length is related to the local rigidity of the polymer, which is a function of its chemistry. Freely-jointed chains as described above are also represented as real chain, with beads representing a size greater than the Kuhn length of polymer. However, for higher levels of coarse-graining, if segments are orders of magnitude larger than atomistic scales, then it can be shown that the coarse-grained segments become "soft" and they can overlap. [44] In terms of lattice models, this means that different segments can occupy the same grid point. At this scale, molecules can be described as ideal random walk chains. Although full overlap is not strictly true in a real system, it is an assumption that greatly helps in understanding fundamental behaviour of polymers. Again by assuming a system of ideal chains, one loses the connection to the underlying molecular interactions.

Interesting analytical expressions can be derived for an ideal chain. The probability distribution of finding the position of the N th segment of an ideal chain in position $\mathbf{r}_N$, given the position of the first segment $\mathbf{r}_0$, follows the normal distribution:

$$P(\mathbf{r}_N) = (2\pi Nb^2/3)^{-3/2} \exp\left(-\frac{3}{2} \frac{(\mathbf{r}_N - \mathbf{r}_0)^2}{b^2 N}\right) \quad (2.1)$$

$$\langle (\mathbf{r}_N - \mathbf{r}_0) \rangle = 0 \quad \text{and} \quad \langle (\mathbf{r}_N - \mathbf{r}_0)^2 \rangle = b^2 N \quad (2.2)$$

Here b refers to the inter-segment distance and the angle brackets refer to averages. The second equation in Equation 2.2 refers to the mean squared end-to-end distance, R_{End} , of an ideal chain. Although end-to-end distances are a measure of the size of the polymer, a more common measure of the size of a polymer is usually given by the radius of gyration, R_g , which is the average distance of a segment from the centre of mass of the polymer. These two measures are defined below [41]:

$$R_{End}^2 = \langle (\mathbf{r}_N - \mathbf{r}_0)^2 \rangle \quad (2.3)$$

$$R_g^2 = \frac{1}{N+1} \sum_{i=0}^N \langle (\mathbf{r}_i - \mathbf{r}_{com})^2 \rangle = \frac{1}{2(N+1)^2} \sum_{i,j=0}^N \langle (\mathbf{r}_i - \mathbf{r}_j)^2 \rangle \quad (2.4)$$

For an ideal chain (and assuming isotropy) the radius of gyration is given as:

$$R_g = \frac{1}{\sqrt{6}} b N^{1/2} \quad (2.5)$$

As mentioned before, ideal chains are constructs of the assumption that segments can overlap. Also segments in an ideal chain do not interact with each other. For some instances, such as in pure component liquid phase (known as pure *melt*), polymers can behave like ideal chains with the radius of gyration being proportional to $N^{1/2}$. This ideal behaviour in melts arises due to segments interacting equally with all other segments surrounding them, whether these are from the same polymer or from others. This causes the polymers to swell in dense melts. This swelling in turn causes the displacement of chains from other molecules, which then exert a pressure on the polymer and cause it to contract. These two countering effects lead to the ideal behaviour.

Ideal behaviour is also seen in some cases of polymers in solutions (known as θ solvents). However, for most cases, solutions of polymers do not behave ideally. Equation 2.5 can be generalised for real polymers:

$$R_g \propto N^\nu \quad (2.6)$$

Where ν is the Flory exponent. For cases where $\nu \gg 1/2$, the polymer is more swollen, indicating it is attracted to the surrounding environment. For a *good solvent* $\nu \approx 3/5$ and the polymer is called a *coil* [39]. When $\nu \ll 1/2$, the polymer does not like its surrounding environment and it collapses onto itself to form a *globule*. In a poor solvent $\nu \approx 1/3$, which can be understood intuitively:

$$N \propto R_g^3 \quad (2.7)$$

It can be seen from equation 2.7 that in a poor solvent, a polymer with a given size N has a size that corresponds to the volume of a sphere of radius of R_g . This is because molecules want to arrange themselves in a perfect spherical packing, which maximises the shielding of the segments from the surrounding environment. It is important to notice that for a real polymer in a real solvent, the polymer can be a coil and a globule at different conditions. This leads to a wide array of liquid phase behaviour that polymers can have, making it difficult for models to predictably model all behaviour of polymeric systems.

2.1.2 Fluid Phases of Polymers

Flory-Huggins Theory

In section 2.1.1, the effect of interactions between different types of beads present in the system were not discussed. The most popular model to describe interactions in a system containing different types of segments in polymers is given by Flory [45] and Huggins [46]. The Flory-Huggins (FH) theory starts with a lattice model of a binary blend of two homopolymers, A and B, with with number of segments N_A and N_B and volume fractions ϕ_A and ϕ_B . For an incompressible system ($\phi_A + \phi_B = 1$), with no interactions between A and B, the free energy of the system is only determined

by the entropy:

$$\frac{A}{k_B T} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B \quad (2.8)$$

In this case, no phase separation can be observed. If one introduces interactions between neighbouring beads on a lattice, with like beads experiencing an average energy of ϵ_{AA} and ϵ_{BB} and the unlike beads experiencing an average energy of ϵ_{AB} , one could define an average energy parameter χ ,

$$\chi = \frac{z-2}{k_B T} (\epsilon_{AB} - 1/2(\epsilon_{AA} + \epsilon_{BB})) \quad (2.9)$$

where z is the coordination number. If $\epsilon_{AB} = \epsilon_{AA} = \epsilon_{BB}$, the mixture behaves ideally. A positive value of χ indicates that different beads are incompatible and do not favour mixing as the energy cost of two unlike beads being neighbours is higher than that of two like beads. Thus χ is a measure of repulsion. An important assumption in Equation 2.9 is the inverse proportionality of χ to temperature. The lower the temperature, the higher the value of χ .

The free energy including interaction between the monomers is given,

$$\frac{A_{FH}}{k_B T} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \chi \phi_A \phi_B \quad (2.10)$$

In this model phase separation occurs for all values of χ higher than the critical value of χ_c ,

$$\chi_c = \frac{1}{2} (1/\sqrt{N_A} + 1/\sqrt{N_B})^2 \quad (2.11)$$

$$\phi_{A,c} = 1/(1 + \sqrt{N_A/N_B}) \quad (2.12)$$

Figure 2.5 is the phase diagram for a 2 component polymer blend for components with equal size. The phase envelope where there is coexistence is called the binodal curve. As mentioned the lower the temperature, the higher the value of χ .

As mentioned before, the FH theory is based on lattice model. However, it can be applied to off-lattice models, assuming the following assumptions [38, 47]:

- Incompressibility: the mixture has to be incompressible,
- Lattice size assumption: Each segment of A and B should have the same size,

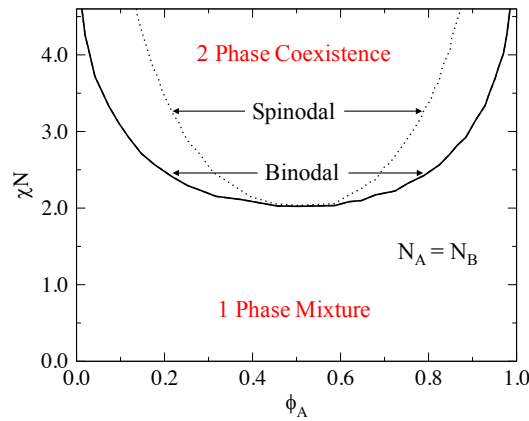


FIGURE 2.5: FH phase diagram for a 2 component polymer blend for components with equal size

- Chains have to be ideal
- Mean field approximation: No fluctuations in local compositions

None of these assumptions are strictly valid for a real system. Segments of polymers do not usually have the same volume due to different chemistry. Moreover, the conformation of polymer in a mixture does not follow the ideal chain assumptions. Finally, local fluctuations do exist especially for short chains and polymers in solution. This means in reality, real polymers deviate from the FH description of polymer mixtures. There have been attempts to improve the modelling using FH theory by correlating χ to properties of the mixtures under study, such as structure, composition and chain length [48].

One way to calculate the χ parameter is by using the random phase approximation (RPA) [39] to extract the χ parameter from SANS data, be it from experiments or from atomistic simulation. This approach is robust due to its direct link to underlying molecular interactions. However, such measurements are state dependent (i.e. function of composition, molecular weight, pressure, temperature etc) and it has been experimentally shown [49, 50] that this state dependency should not be ignored. This lack of a robust understanding of the χ parameter at different conditions hinders the predictive applicability of the FH theory.

Since the FH theory, there have been major advances in lattice models, with one example, the lattice cluster theory (LCT) [51–53] being able to reproduce many

phases of polymers. LCT takes into account the composition of monomers by representing them with a united atom description. For some cases, such as high pressure (limit of incompressibility) and high molecular weight (no local fluctuations in composition), the theory is the same as the FH theory, with a composition and molecular structure dependent χ parameter.

As can be seen from the assumptions of the theory, it is obvious that the connection of χ to real molecular interactions is not tangible. Prediction of phase behaviour of polymeric systems, with parameters that are independent of composition, molecular weight, temperature and pressure could be very useful, both in simulations and in theoretical modelling. In order to do this, a mean field macroscopic view of the interactions is not robust enough, and one would have to capture the underlying physics at the molecular level.

Yet to this day, due to decades of polymers research founded upon the theories set by Flory, χ parameter is the backbone of most polymer theory.

Homopolymer Pure Melts

A *melt* is the liquid state of the polymer above its glass transition temperatures. The behaviour of linear homopolymer and diblock copolymer melts are well known. [8] In order to have realistic models, as is the aim of this thesis, one should have to capture the correct thermodynamic behaviour of polymers. In realistic homopolymer melts, the Pressure-Volume-Temperature (PVT) relationship is key [54]. Dynamical properties of polymer melts have also been studied, with revolutionary works of de Gennes [39] and Edwards and Doi [40]. However, dynamical properties of polymers (Rouse model [55], Zimm model [56] and reptation [57]) are beyond the scope of this thesis, and it is something that will have to be investigated in the future.

Block Copolymer Melts

Moving away from pure homopolymer melts, the next step is to look at more complicated melts. Block copolymers display a great variety of phases. When the different building blocks on the same molecules are incompatible with each other, the blocks become immiscible. If these blocks were not connected to each other, macroscopic

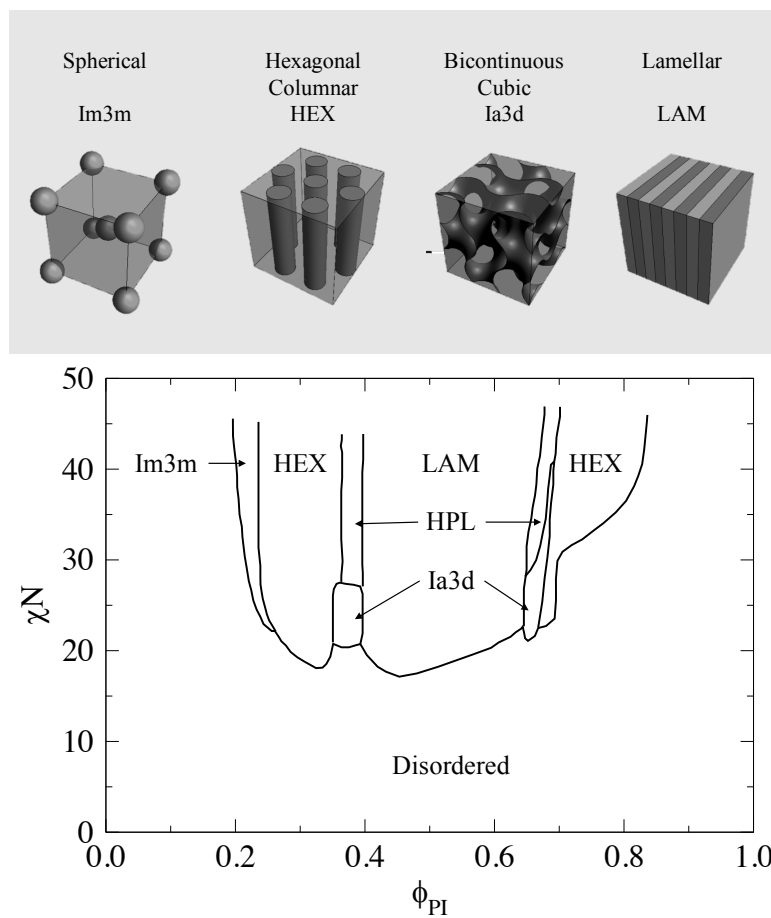


FIGURE 2.6: **Top** common phases in diblock copolymer melts, **Bottom** χN vs polyisoprene volume fraction ϕ_{PI} experimental phase diagram for poly(styrene-co-isoprene) diblock copolymer, adapted from [11]

phase separation would be observed. This is not possible due to the connectivity of these different blocks, and instead phase separation occurs over periodic domains at the microscale. This phenomenon is called *microphase separation*. For the case where the blocks are highly immiscible, called *strong segregation limit* (SSL), Matsen and Bates [58] showed the following spacing between the microphase domains, D :

$$D \propto N^{2/3} \quad (2.13)$$

The most commonly studied phase map of block copolymer melts is that of the diblock copolymer. Khandpur et al. [11] produced one of the first such phase diagrams with poly(styrene-*b*-isoprene) copolymer, as can be seen in Figure 2.6. When the volume fraction of isoprene is similar to polystyrene, a lamellar phase is observed. Increasing the volume fraction of either of the components first leads to the bicontinuous cubic phase, or commonly known as gyroid, where two independent networks of the same polymer are formed with 3D periodicity. This is followed by hexagonal columnar phase and finally spherical body centred cubic (bcc) phase for the largest differences in the sizes of the blocks. The lamellar and hexagonal columnar phases observed are periodic in two dimensions, whereas the spherical and cubic phases are periodic in three dimensions. When the blocks are more miscible due to attractive molecular interactions, microphase separation is not observed. This usually happens at high temperatures where entropy has the dominant contribution to the free energy.

Since the aforementioned study, there have been many studies, both experimental or with theory and simulations, on the morphology of ever more complex copolymer melts. For a review on linear ABC triblock and star triblock copolymers melts the reader can be referred to ref [59] and ref [60] respectively. Triblock copolymers generally have microphases that can be constructed by a combination of the microphases seen in the diblock copolymers.

Block copolymers with different structures have also been studied. The reader could refer to [61] for the study of bottle-brush copolymers, with one block being a branched polymer and the other being linear, as well as rod-coil block copolymers where one block is rigid and the other is flexible. [62]

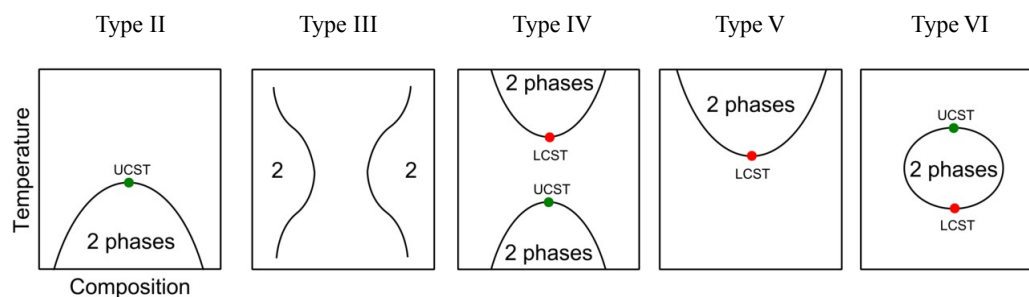


FIGURE 2.7: Phases of binary liquids as characterised by van Konyenburg and Scott [63], all the phase envelopes correspond to coexistence curves

Blends and Solutions

Copolymer melts cannot fully phase separate due to the connectivity of incompatible chains. However, for mixtures of polymers, also known as *blends*, as well as solutions of polymers, macroscopic phase separation can be observed. The most common phases observed in a binary mixture of any fluids are shown in Figure 2.7. For simplicity, type I phase of binary fluids is not shown as it corresponds to vapour-liquid equilibrium of a binary mixture, which only occurs for mixtures of light gases and polymers. Figure 2.7 is an almost universal phase diagram of binary mixtures of polymers, be it in blends or in solution. Type II phase is the most common phase in the study of polymers, and is the only phase behaviour that can be explained by the FH theory. Equation 2.9 clearly demonstrates that with decreasing temperature, the value of χ should increase and therefore the binary fluids become less miscible. One of the first studies of FH theory fluid theory was used to investigate the phase behaviour of polystyrene in cyclohexane near the θ temperature, i.e. the temperature at which the polymer behaves like an ideal chain. [64] The critical temperature at which the fluids in the mixture becomes immiscible is called the **upper critical solution temperature** (UCST). Phase separation here occurs due to enthalpic reasons, where it is energetically more favourable for molecules of each component to interact with themselves.

Type III to VI cannot be observed using the FH theory, unless the value of χ parameter becomes a phenomenological variable, correlated directly with experiments at different conditions. This again means that mean field theories are not predictive

in capturing phase behaviour of polymer solutions.

Type V is the exact opposite of type II phase behaviour, where by increasing the temperature of the system, phase separation is observed and the fluids in the mixture become immiscible. The critical temperature where phase separation occurs is called **lower critical solution temperature** (LCST). This phase separation at high temperatures cannot be due to enthalpic reasons, unless the fluids are associating. For systems where a solvent can form hydrogen bonds with the polymer, at low temperatures it is enthalpically favourable for the polymer to be dissolved in solution. By increasing the temperature, hydrogen bonds are broken and phase separation occurs. LCST behaviour also exists for common non-polar mixtures [65]. This is due to entropic effects. At higher temperatures, solvents are much more compressible than the polymer making it entropically favourable for the mixtures to phase separate. [66]

From a combination of two extreme types, other phases can be formed. Phase IV occurs when both LCST and UCST critical points exist, with the LCST being at a higher temperature than the UCST. If the two critical points approach each other and the coexistence regions merge, type III phase behaviour is observed, with a phase diagram that looks like an hour glass. Finally type VI occurs for hydrogen bonding mixtures, such as poly(ethylene oxide) in water [67]. However, simulation studies of closed-loop behaviour with associative toy models exist [68]. In this thesis, in order to robustly model polymers predictably, only non-polar solvents are studied. It is important to mention that mean field lattice models that have vacant sites, and therefore can capture effects of compressibility, with polymers being able to have expanded as well as contracted conformations, can capture the LCST behaviour. Famous lattice models are lattice cluster theory as well as lattice based equations of state such as Sanchez-Lacombe EoS. Phase diagrams of polymers in solution are usually calculated with the help of equations of state.

Ternary mixtures and vapour-liquid equilibrium (VLE)

Lattice and Off lattice models such as bead-spring models have been previously used to study of VLE of pure Lennard-Jones chains [69]. In general, polymer VLE can only

be modelled with EoS or with simulation techniques.

Polymers have extremely low vapour pressures, and therefore modelling vapour liquid equilibrium of pure polymers is not interesting for experimental temperatures and pressures. However gases can dissolve in polymers and especially in ternary mixtures this can significantly affect the LCST behaviour.

2.1.3 Perspective

In this brief overview, the aim was to show that the phase behaviour of polymers is complicated. Depending on the system (melts, blends, solutions) polymers can behave differently. In the melt, polymers behave like ideal chains and therefore a mean-field treatment of polymers is to some extent valid. However, for polymer in solution, mean field assumptions break down. Moreover, the χ parameter used to model phase behaviour in polymers is a function of many different variables (i.e. state dependent) hindering mean field theories' ability to quantitatively predict phase behaviour of polymers, especially those in solution.

A predictive tool to accurately model phase behaviour requires input parameters that are state independent. No matter what the size of the polymer is or the composition of the mixture, a predictive model should be able to measure the phase behaviour of polymer. This is achieved if the underlying physics of the molecular interactions can be correctly captured. This is a particular advantage of the SAFT- γ methodology as will be outlined in the next chapter.

2.2 Fundamental Concepts in Liquid Crystals

2.2.1 Phases of Liquid Crystals

Liquid crystals (LC) are compounds that have characteristic properties that can be found in crystalline solids as well as liquids. They are liquid in that they can flow, yet the orientational ordering of each molecule (*mesogen*) is reminiscent of a crystal. Since the seminal works of Friedel in characterising liquid crystals almost a century ago [70], these materials have found their way into all fields of engineering.

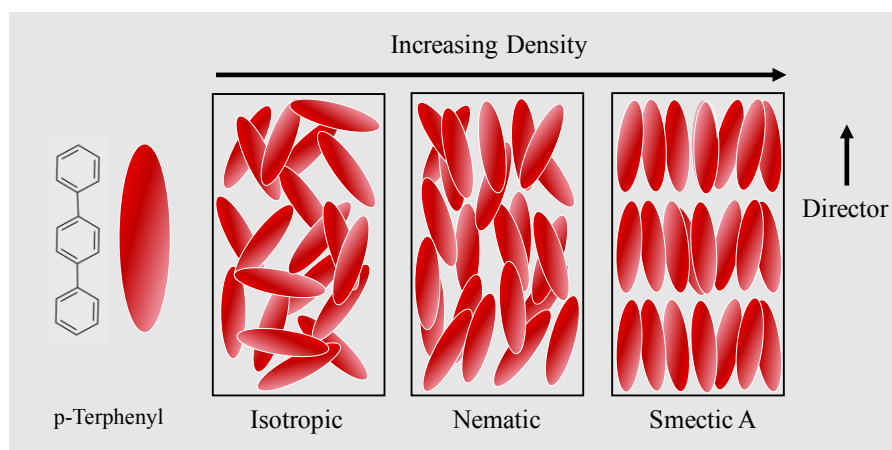


FIGURE 2.8: Classic phases of calamitic (hard-rod) liquid crystals

Shape anisotropy of the liquid crystalline molecules is sufficient to induce ordering in the mixture of mesogens [71]. This geometric anisotropy leads to anisotropic interactions between the molecules, with repulsive interactions leading to excluded volume effects (molecules cannot overlap), while attractive interactions induce aggregation.

Hard Systems

The simplest representation of a liquid crystal is an anisotropically shaped molecule which has no attractive interactions with any other liquid crystal molecules so that molecules become "hard". Anisotropically shaped molecules can have an array of shapes such as rods, disks and rings. Hard-rods or *calamitic* liquid crystals were some of the first LCs to be described theoretically, with the seminal works of Onsager [72].

Ignoring attractions and by only considering a system of hard-rods in a box, the classic phases of liquid crystals can be observed (Figure 2.8). For mesogens with anisotropic shapes, decreasing the volume of the system forces closer packing, and molecules start aligning themselves in a certain direction, with the vector defining the direction of the orientation being the *director*. In the nematic phase, molecules are oriented in the direction of the director, with their positions being random in space. Decreasing the volume of the box even more causes molecules to pack ever

closer and molecules start to have positional as well as orientational order. Hard-rods arrange themselves in layers to maximise their entropy. By minimising their movements to a two-dimensional plane perpendicular to the director, hard rods can have a higher intra-layer diffusion than a positionally isotropic phase and thus have a higher entropy. This layered phase is called the smectic phase. Liquid crystals that are discotic have similar phase behavior to calamitics, as shown in Figure 2.9.

One key definition in this field is the nematic order parameter, P_2 , which is defined as [73]:

$$P_2 = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad (2.14)$$

where θ is the angle between the principal vector of the mesogen with the director. P_2 measures the average value of the alignment of mesogens with respect to the director. If all mesogens are aligned parallel to the director, the nematic order parameter approaches 1. This definition is useful in the study of calamitic liquid crystals, as they align themselves in the direction of the director. For discs stacking on top of each other, the director is perpendicular to the principal axis, and the nematic order parameter approaches -0.5. The planar order parameter, S_2 , is used to describe discotics:

$$S_2 = \frac{1}{2} \langle 3 \sin^2 \theta - 1 \rangle \quad (2.15)$$

For nematic discs, S_2 approaches one if they are all oriented perpendicular to the director.

Hard systems have been extensively studied in literature, especially with simulations. Examples of simulations of hard systems are rod-like molecules [74–76], disc like molecules [73, 77], ring molecules [78]. One particularly interesting case is that of the hard-pear liquid crystal model of Schönhöfer et al, where the structure of the mesogen is pear shaped. Three-dimensional periodic gyroid phases were observed without the presence of any attractive interactions [7], something that is very rare to observe for rigid molecules. This shows the extent of the applicability of simulations of hard rods for capturing the phenomenological behaviour of liquid crystalline systems.

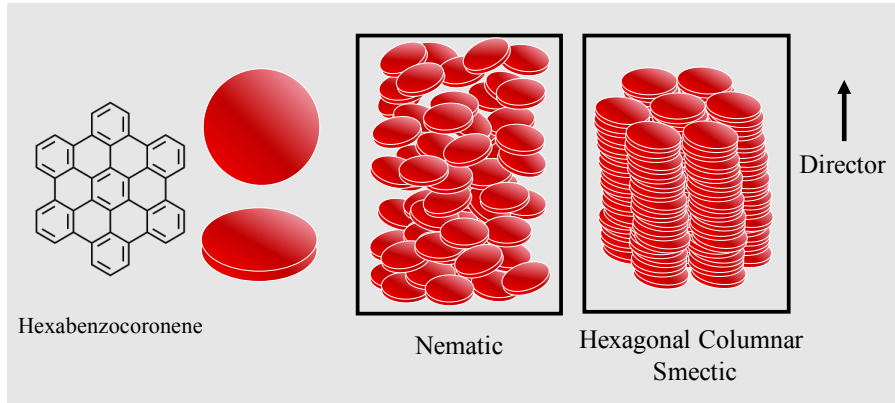


FIGURE 2.9: Classic phases of discotic liquid crystals

Onsager's hard rod theory [72] is a perturbation theory, adding contributions due to excluded volume effects and orientational entropy to the ideal gas free energy, to study the phase behaviour of liquid crystals. By minimising the free energy, an isotropic nematic phase transition is observed solely due to entropic effects. Onsager's theory gives a qualitative description of phase transitions in liquid crystals.

Thermotropic Liquid Crystals

The description above excludes attractions and molecules only arrange themselves due to excluded volume effects and shape anisotropy. In reality many liquid crystalline mesogens have sizes in the sub 10 nm scale, and thus attractions, especially π - π interactions, play an important role in the stability of these phases. Liquid crystals that become ordered due to enthalpic effects are called *thermotropic*. At high temperatures, the system is isotropic. As temperature is decreased a phase transition to nematic or smectic phase is observed. There are many studies on the theory of thermotropic liquid crystals such as the Maier-Saupe mean field treatment [79], Landau-de Gennes theories [80] and vdW type perturbation theories, with most models aiming to describe the isotropic nematic phase transition. The Maier-Saupe mean field theory is a theory where the intermolecular potential, U , between two molecules is given only by their orientation [81, 82]:

$$U(\cos(\theta_{1,2})) = -u_0 \frac{a^3}{V} P_2(\cos \theta_{1,2}) \quad (2.16)$$

Where $\theta_{1,2}$ is the angle between two molecules, $P_2(\cos \theta_{1,2})$ is given by Equation 2.14 and u_0 and a are constants; The potential energy is minimised if the directions of the principal axes of two molecules are parallel to each other. If the principal axes are not aligned, the potential energy is maximised. Such a simple theory, which even ignores short range effects (i.e. repulsions) has been successful in observing order disorder transition temperatures. However, with added complexity it becomes significantly more difficult to develop models describing the phase behaviour of liquid crystals. One such case is that of the polyphilic liquid crystals.

Polyphilic Liquid Crystals

Most theories of liquid crystals are developed for simple geometries. Due to the orientational contributions to the free energy, it is very challenging to develop models when there is added complexity. Polyphilic liquid crystals are materials that behave like liquid crystals, due to the presence of highly anisotropic functional groups (such as a rigid backbone, or a central disk), but the molecule is composed of many different functional groups that are incompatible with each other. Figure 2.10 shows two examples of the polyphilic liquid crystals that will be discussed in this thesis.

Although theoretical modelling of these systems has not been possible to date, molecular simulations can provide great insight into the phase behaviour of such systems. However, quantitatively accurate forcefields for simulating such systems has been a great challenge. One particularly interesting success story is that of modelling of janus dendrimers by Percec et al. [83], where several properties such as surface/interfacial tension, densities, hydration free energy and structural data (from AA-MD) were used to coarse-grain the polyphilic liquid crystals. The robustness of the parameters led to discovery of stable vesicles that were observed experimentally. In this thesis, it will be shown that thermodynamically accurate description of such systems is possible and could be useful in predicting phase behaviour of complex fluids.

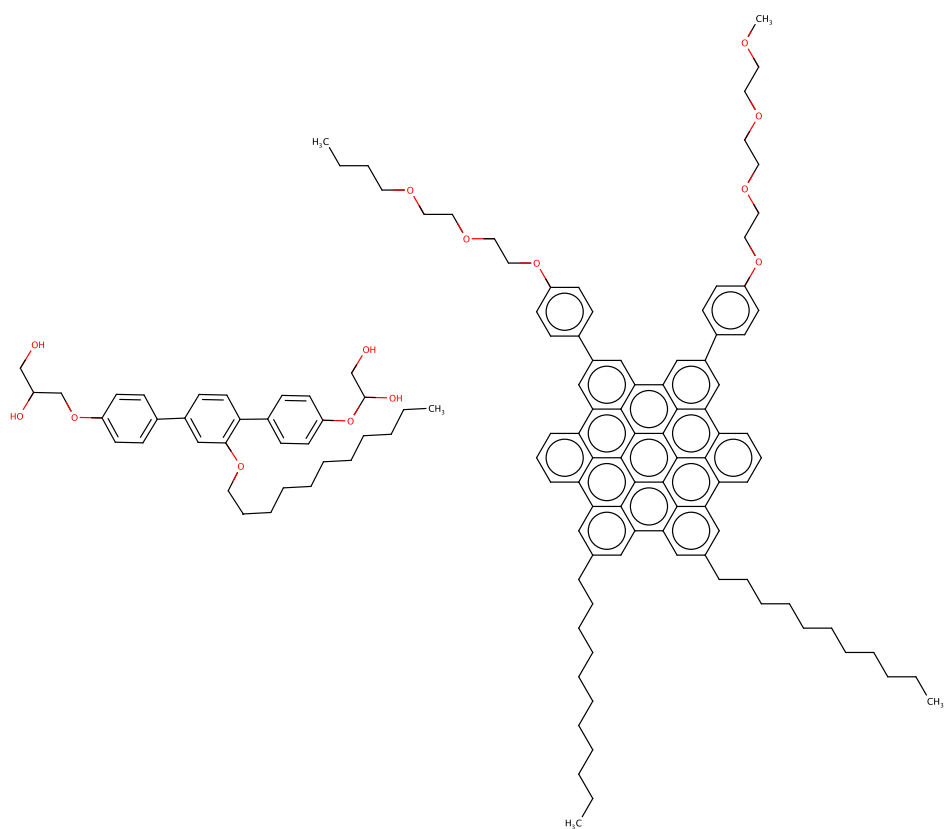


FIGURE 2.10: Examples of polyphilic molecules: **Left** p-Terphenyl backbone with glycerol end groups and a lateral alkyl side-chain, **Right** Hexabenzocoronene discs with alkyl and tetraglyme side chains

Lyotropic Liquid Crystals

Lyotropic liquid crystalline systems are those where the mesogen is in a solvent. The concentration of the mesogen in solvent and its interactions with its surroundings, as well as temperature and pressure effects, determine the phases formed. Amphiphilic molecules, such as surfactants, fall into this category of liquid crystalline phases. If polyphilic liquid crystals are put into a solvent where only one of the functional groups is attracted to the solvent, other moieties will phase separate from the fluid which causes mesophase ordering. Typical phases of these systems are micellar phases and lamellar phases where the solvent-liking functional groups form the interface between the solvents and solvent-hating moieties.

2.2.2 Perspective

In this section, fundamental concepts in liquid crystalline phases have been discussed. The overwhelming literature on liquid crystals involves assuming a certain molecular geometry and trying to understand the phenomenological phase behaviour of liquid crystals. A main reason for this is that, due to a lack of accurate theories, there are many phenomena that are still undiscovered. However, much less focus has been on developing quantitatively accurate models, which again arises from the fact that it is very difficult to obtain mesoscopic forcefield parameters that can accurately capture the phase behaviour of the functional groups.

Accurate forcefield development for mesoscale will be the main topic of the next chapter.

Chapter 3

Development of Accurate Molecular Based CG Potentials

3.1 Intermolecular Forces and Potentials

The need to understand microscopic behaviour of molecules first arose from observations of the macroscopic thermodynamic properties. Non-ideal behaviour of gases as determined by the second virial coefficient, condensation of gases into liquids, surface tension and viscosity underlined the need to understand intermolecular forces.

By the end of the nineteenth century it was known from a classical Newtonian description that there are two types of interactions describing intermolecular forces. One is the short range repulsive interactions, with its macroscopic manifestation being the volume occupied by a solid or a liquid state, and the other being long range attractive interactions that could explain condensation of gases. It was not yet clear how to mathematically describe the intermolecular forces. Given an interaction potential $u(r)$, the force, F , acting on two particles can be calculated:

$$F = -\frac{du(r)}{dr} \quad (3.1)$$

Development of quantum mechanics helped with a rigorous description of the electrostatic interactions of atoms. It was shown that the repulsive force experienced between two atoms is the result of the Pauli exclusion principle, while the attractions between non-polar atoms being due to fluctuating dipoles [31, 84].

Electrostatic forces are due to the presence of ions, dipoles, quadrupoles etc. In the simplest case, the electrostatic interaction between two point charges is given by:

$$u^{Coulomb}(r) = \frac{q_1 q_2}{4\pi\epsilon_0\epsilon_r} \frac{1}{r} \quad (3.2)$$

where q_1 and q_2 are the charges, ϵ_0 is permittivity of free space and ϵ_r is the dielectric constant and r the inter-charge distance. For an interaction between two dipoles, both distances and the orientation of the dipoles are needed to define the interaction potential. It has been shown that the angle-averaged potential between two dipoles is given by [84]:

$$u^{dipole}(r) = -\frac{2}{3} \frac{\mu_1^2 \mu_2^2}{k_B T (4\pi\epsilon_0)^2} \frac{1}{r^6} \propto -\frac{1}{r^6} \quad (3.3)$$

Equation 3.3 is the interaction between two permanent dipoles, i.e. polar molecules. Non-polar molecules have attractions due to the fluctuating induced dipole moments. For attraction between induced dipoles, the proportionality of $u(r) \propto -1/r^6$ is still valid [85]. This exponent of 6 is what is used for the description of the attractive term in common intermolecular potentials such as the Sutherland, Lennard-Jones and Buckingham potentials. This is in contrast with the repulsive term, whose exact analytical form is only known for the simplest of molecules [86].

So far only interactions between pairs have been considered. For a N component mixture things become much more complex, as the total potential, $\mathcal{V}$, is not only a sum of the pair potentials, but also the sum of many body potentials [87]:

$$\mathcal{V} = \sum_i u_1(r_i) + \sum_i \sum_{j>i} u_2(r_i, r_j) + \sum_i \sum_{j>i} \sum_{k>j} u_3(r_i, r_j, r_k) + \dots \quad (3.4)$$

In the above equation u_1 is the potential due to external fields, u_2 is the pair potential, and u_3 is the potential induced between two molecules in the presence of a third particle. In the absence of external fields, the biggest contribution to the total particle-particle interactions is the sum of the pair potentials. In this light, Equation

3.4 can be rewritten in terms of an effective pair potential, u_2^{eff} :

$$\mathcal{V} = \sum_i \sum_{j>i} u_2(r_i, r_j) + \sum_i \sum_{j>i} \sum_{k>j} u_3(r_i, r_j, r_k) + \dots = \sum_i \sum_{j>i} u_2^{eff}(r_i, r_j) \quad (3.5)$$

where $u_2^{eff}(r_i, r_j)$ is the effective pair potential. The rationale behind doing this is to simplify the mathematical form of the potential, as calculating many body potentials can be a very laborious task, given that their contribution to the total potential is not as high as the pair potential.

Assuming the potential of a system of N components can be represented by a sum over all the pair potentials, the mathematical function describing $u_2^{eff}(r_{ij})$ has to be chosen carefully, to ensure a robust representation of the intermolecular potentials. For example $u_2^{eff}(r) = 0$ is the correct description of an ideal gas, but it is not valid for real liquids. A range of commonly used potentials to study molecular systems is presented in Figure 3.1.

Discontinuous Potentials

The simplest of all potentials is the hard-sphere potential (Equation 3.6), where below a certain distance, σ , the potential is infinity, meaning the particles cannot overlap. σ represents the centre to centre distance of two hard spheres. In other words it is the distance at which two hard spheres are touching. Hard sphere potentials are useful in the study entropic packing of particles, where attractive interactions can be ignored. In fact the first molecular dynamics simulations ever run were on the phase transitions of hard spheres [88]. As will be shown later, hard spheres are commonly used in statistical mechanics as the reference fluid in perturbation theories, where extra contributions to the free energy, such as attractive potentials, are added to a reference hard sphere system to derive accurate free energy expressions for real systems.

$$u^{HS}(r) = \begin{cases} \infty & (r < \sigma) \\ 0 & (r \geq \sigma) \end{cases} \quad (3.6)$$

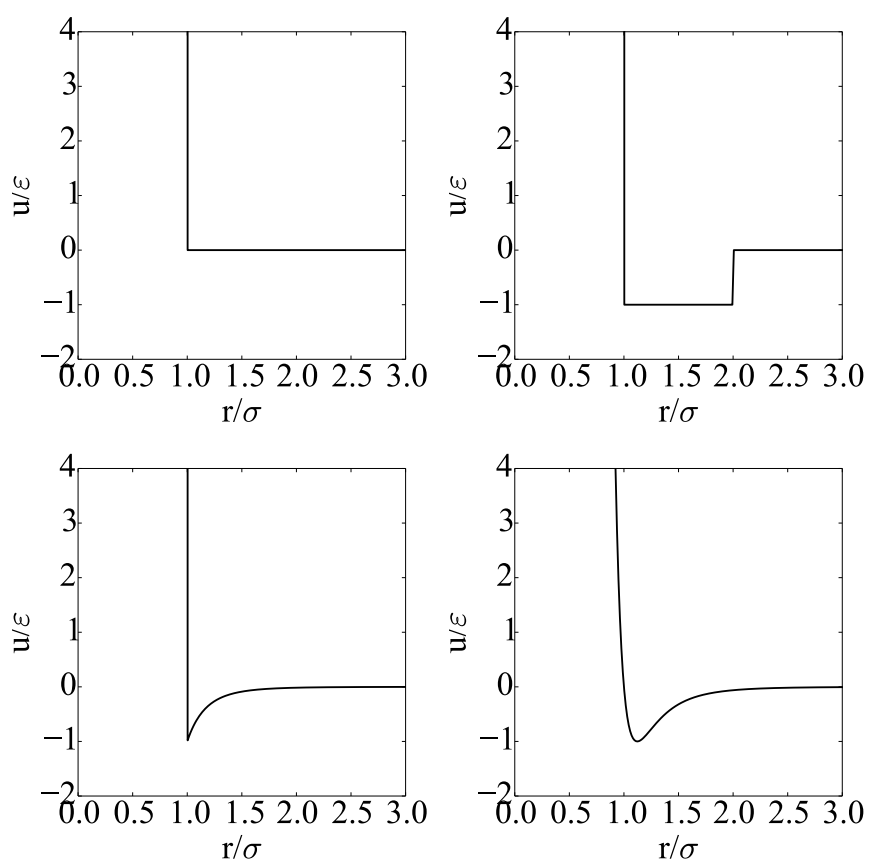


FIGURE 3.1: Different types of possible intermolecular potential models, from top left clockwise: hard sphere potential, square well potential, Lennard-Jones potential and Sutherland potential

Assuming a hard sphere reference fluid for attractive molecules, there are two potentials that can be used as perturbations of this hard sphere potential. One is the square well potential (Equation 3.7), which is a hard sphere with an additional attractive potential that is constant for an intermediate ranges. When particles are close to each other, they are at a lower energy state, with no force acting on them. At far away distances, particles do not experience any forces due to attractive or repulsive energies.

$$u^{SW}(r) = \begin{cases} \infty & (r < \sigma) \\ -\varepsilon & (\sigma \leq r < \sigma_2) \\ 0 & (r \geq \sigma_2) \end{cases} \quad (3.7)$$

where $-\varepsilon$ is the minimum of the potential well. The simplicity of this potential in modelling real fluids makes it very common in statistical mechanical studies as analytical expressions are easy to derive for such simple functional form. It has been shown that a square well fluid can accurately model vapour-liquid (VLE) and liquid-liquid (LLE) equilibria of real systems. However, second derivative properties such as speed of sound and heat capacities are not correctly captured with square well potentials [86].

The other potential that is a perturbation of the hard sphere potential is the Sutherland potential:

$$u^{suth}(r) = \begin{cases} \infty & (r < \sigma) \\ -\epsilon \left(\frac{\sigma}{r}\right)^6 & (r \geq \sigma) \end{cases} \quad (3.8)$$

A particular disadvantage of hard sphere, Sutherland and square well potentials is that they cannot be used in conventional deterministic simulations, due to the discontinuities in the potentials. Also as shown in Equation 3.3, a robust mathematical form of the attractive part of the potential should be proportional to $-r^{-6}$. Apart from the Sutherland potential, the aforementioned discontinuous potentials do not have this mathematical form for the attractive part.

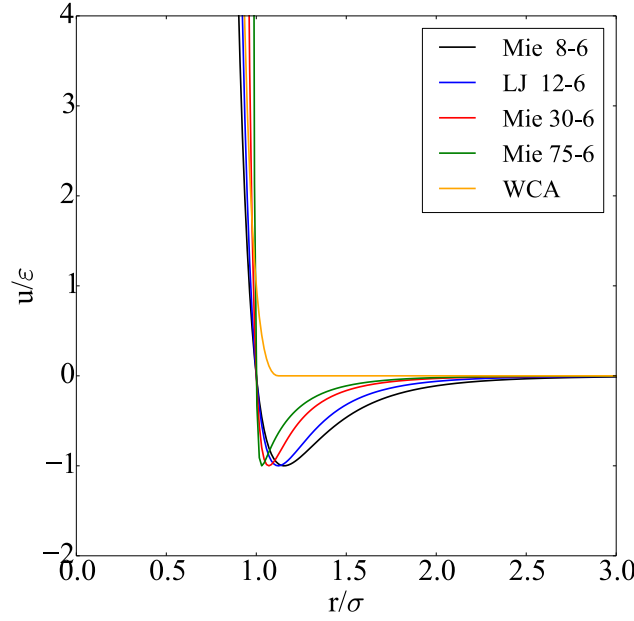


FIGURE 3.2: Different types of continuous potentials

Continuous Potentials

Continuous potentials have proven to be very successful in capturing the correct phase behaviour of real fluids in molecular simulations. The most general form of a continuous potential was first proposed by Mie [28]:

$$u^{Mie}(r) = \mathcal{C}\epsilon \left[\left(\frac{\sigma}{r} \right)^{\lambda_r} - \left(\frac{\sigma}{r} \right)^{\lambda_a} \right] \quad (3.9)$$

with,

$$\mathcal{C} = \left(\frac{\lambda_r}{\lambda_r - \lambda_a} \right) \left(\frac{\lambda_r}{\lambda_a} \right)^{\lambda_a / (\lambda_r - \lambda_a)} \quad (3.10)$$

Like before, σ defines the distance between the centres of two spherical particles when their surfaces are touching. $\mathcal{C}$ is a prefactor that ensures the minimum of the potential well is at $-\epsilon$. The two exponents λ_r and λ_a control the shape of the potential curve. λ_r is the repulsive exponent that controls the hardness of repulsive forces, and λ_a is the attractive exponent, determining the range of the attractions. Figure 3.2 shows different types of Mie potentials. For one case where $\lambda_r = 12$ and $\lambda_a = 6$, the potential is called Lennard-Jones [89], named after the scientist who proposed this

model twenty years after Mie had proposed its general form. The Lennard-Jones model of the dispersion interactions is by far the most commonly intermolecular potential for real fluids and is given by the formula:

$$u^{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3.11)$$

A continuous potential representing molecules with no attractions, similar to the discontinuous hard sphere potential was proposed by Weeks, Chandler and Anderson (WCA) [90]. It is based on the Lennard-Jones model, where the potential is shifted up by ϵ and cut-off at the distance where ϵ is at the minimum. The potential can be seen in Figure 3.2.

$$u^{WCA,rep}(r) = \begin{cases} u^{LJ}(r) + \epsilon & r < r_{min} \\ 0 & r \geq r_{min} \end{cases} \quad (3.12)$$

Although the use of Lennard-Jones type equations is ubiquitous in the scientific community, the use of the Mie potential, at least with a $\lambda_a = 6$, can have certain advantages. Intuitively, it could be seen that it is a much more flexible potential in terms of the hardness of the repulsive term. This can be advantageous in the parametrisation of potentials for polymeric monomers, where differences in functional groups, shapes and sizes of monomers make it more difficult to fit intermolecular potentials using only two parameters σ and ϵ . Moreover, it has been shown that the Mie potential is considerably better at capturing second derivative properties, such as isothermal compressibility and heat capacity, than other types of potentials [29].

Anisotropic Potentials

One particular model that is extensively used for the study of anisotropic molecules is that of the Gay-Berne (GB) potential [91]. It is a further extension of the Lennard-Jones model. When two anisotropic molecules are in a end-to-end position experience a different force to where they are side-by-side. This is achieved by introducing an angular dependence term to the Lennard Jones model. The advantage of this

model, is that the side-by-side energy is lower than the end to end, promoting alignment of the GB potential. GB potential models have been studied extensively, with isotropic, nematic and smectic A phases being observed for the calamitic type.

This potential has also been extended to discotics by Bates and Luckhurst [92, 93] With higher interaction energies, and high aspect ratios, discotic GB potential models are known to exhibit hexagonal columnar phases. Further studies of these columnar phases has led to the discovery of with chiral nanowires [94] and nanosheets [95] from achiral GB molecules in bulk. A new study of the phases behaviour of GB model in cylindrical confinement has discovered layered annular bent columns inside a cylinder [96], which qualitatively correspond to experimental predictions.

Gay-Berne potentials are useful in phenomenological study of liquid crystals. However, as a technical side note, their difficult implementation in deterministic molecular simulations has made them less popular than isotropic models.

3.2 Fundamentals of Statistical Mechanics

With an understanding of the mathematical form of the intermolecular forces, the question now is what values should one use for parameters of a given potential in order to accurately calculate macroscopic properties of a target molecule? At the atomistic level, one could use quantum mechanical calculations to predict accurate dispersion interactions. This is not quite possible at the mesoscale. At this level, statistical mechanics is key to understanding interactions between beads.

Statistical mechanics links average of microscopic state, *microstates*, to macroscopic properties. A microstate is defined by the positions, $\mathbf{q}$, and momenta, $\mathbf{p}$ of all particles in the system, with the Hamiltonian, $\mathcal{H}$:

$$\mathcal{H}(\mathbf{p}, \mathbf{q}) = \mathcal{K}(\mathbf{p}) + \mathcal{V}(\mathbf{q}) \quad (3.13)$$

with $\mathcal{K}$ being the kinetic given by:

$$\mathcal{K}(\mathbf{p}) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} \quad (3.14)$$

$\mathcal{V}$ is the potential energy defined in Equation 3.5.

Macroscopic properties are time averages over a large number of microscopic states with system sizes in the order of 10^{23} particles. For example temperature is directly proportional to the average value of the kinetic energy of the system, and therefore the momenta of all particles. At this scale, differences in the macroscopic observations of each microstate is negligible. A fundamental breakthrough in statistical mechanics is the concept of ergodicity, where instead of describing macroscopic observables in terms of different microstates in time, one could have many replicas, or an ensemble, of microstates that can reproduce the macroscopic observable. The most common ensemble is that of canonical (or NVT) ensemble, where temperature, volume and the number of particles are fixed. Other common ensembles are microcanonical (NVE) where instead of constant temperature, the internal energy is conserved, grand canonical ensemble (μ VT) where instead of fixing the number of particles, chemical potential is conserved with a fluctuating number of particles, isothermal-isobaric ensemble (NPT) where pressure is conserved instead of volume, and finally constant stress-temperature $N\sigma T$ where elements of the stress tensor are conserved.

The probability of a given microstate with energy E_i in the canonical ensemble is given by:

$$P(E_i) = \frac{\exp(-\beta E_i)}{\sum_{i=1}^N \exp(-\beta E_i)} \quad (3.15)$$

where $\beta = 1/(k_B T)$ and k_B is the Boltzmann constant. The denominator is the sum over all states and is called the canonical partition function, Q :

$$Q = \sum_{i=1}^N \exp(-\beta E_i) \quad (3.16)$$

$$\frac{\partial Q}{\partial \beta} = \sum_{i=1}^N E_i \exp(-\beta E_i) \quad (3.17)$$

Knowing the probability of a microstate, the average values of a thermodynamic variable A in the canonical ensemble could be calculated:

$$\langle A \rangle = \frac{\sum_{i=1}^N A_i \exp(-\beta E_i)}{\sum_{i=1}^N \exp(-\beta E_i)} \quad (3.18)$$

The internal energy of a system in the canonical ensemble is therefore given by:

$$U = \frac{\sum_{i=1}^N E_i \exp(-\beta E_i)}{\sum_{i=1}^N \exp(-\beta E_i)} = \frac{\sum_{i=1}^N E_i \exp(-\beta E_i)}{Q} = -\frac{1}{Q} \frac{\partial Q}{\partial \beta} = -\frac{\partial \ln Q}{\partial \beta} \quad (3.19)$$

This is an important derivation, as it clearly shows that individual probabilities of each microstate is not necessary if one has access to Q . Knowing the partition function, it is possible to also calculate the Helmholtz free energy for an NVT ensemble:

$$A = U - TS \quad (3.20)$$

$$\frac{A}{T} = \frac{U}{T} - S \quad (3.21)$$

$$\frac{\partial}{\partial T} \left(\frac{A}{T} \right) = \frac{\partial}{\partial T} \left(\frac{U}{T} \right) = -\frac{U}{T^2} = -\frac{1}{T^2} \frac{\partial \ln Q}{\partial \beta} = -k_B \frac{\partial \ln Q}{\partial T} \quad (3.22)$$

$$A = -k_B T \ln Q \quad (3.23)$$

Access to the free energy allows access to all thermodynamic variables. For example pressure is:

$$P = -\left(\frac{\partial A}{\partial V} \right)_{NT} \quad (3.24)$$

The chemical potential of species i is:

$$\mu_i = \left(\frac{\partial A}{\partial N_i} \right)_{N_{j \neq i} VT} \quad (3.25)$$

The bridge between statistical mechanics and thermodynamics comes from the definition of the partition function. From a continuum description of the Hamiltonian, the partition function could be written as:

$$Q = \frac{1}{N! h^{3N}} \int \dots \int \exp(-\beta \mathcal{H}(\mathbf{q}^N, \mathbf{p}^N)) d\mathbf{q}^N d\mathbf{p}^N \quad (3.26)$$

Due to the definition of the Hamiltonian ($\mathbf{q}$ and $\mathbf{p}$ are independent), the partition function can be split into two terms:

$$Q = \frac{1}{N! h^{3N}} \int \exp(-\beta \mathcal{K}(\mathbf{p}^N)) d\mathbf{p}^N \int \exp(-\beta \mathcal{V}(\mathbf{q}^N)) d\mathbf{q}^N = Q^{ideal} Z \quad (3.27)$$

The first term Q^{ideal} is the ideal gas partition function (energy distribution due to absence of interactions) and it has a direct mathematical form:

$$Q^{ideal} = \frac{\Lambda^{-3N}}{N!} \quad (3.28)$$

where Λ is the *thermal de Broglie wavelength* and is equal to $(\frac{\beta h^2}{2\pi m})^{1/2}$.

Z in Equation 3.27 is the *residual partition function* which is given by:

$$Z = \int \exp(-\beta \mathcal{V}(\mathbf{q}^N)) d\mathbf{q}^N \quad (3.29)$$

It is the contribution to the partition function due to the presence of interactions in the system. It is an impossible task to carry out the integration of the partition function over all variables $\mathbf{q}^N$.

However, it is possible to reduce the dimensionality of the integral by introducing the concept of *residual energy*, by assuming a system of particles interacting with **pair potentials** [97]:

$$U^{residual} = \langle \mathcal{V}(\mathbf{q}^N) \rangle = 2\pi\rho N \int_0^\infty g(r)u(r)r^2 dr \quad (3.30)$$

where $g(r)$ is the radial distribution function, and $u(r)$ is the pair potential.

An interesting conclusion can be drawn from this exercise; the free energy of the system can be rewritten in the following form:

$$A = -k_B T \ln Q = -k_B T \ln Q^{ideal} - k_B T \ln Z = A^{ideal} + A^{residual} \quad (3.31)$$

The key point that can be drawn from this is that provided one can define a free energy for a reference system, here the reference is ideal gas, extra terms can be added to the system to refine the calculation of the free energy. It is also shown that the residual term can be simplified for a system of particles interacting with pair potentials. The residual Helmholtz free energy itself can be a summation of different contributions to the free energy. This forms the foundation of free energy perturbation theories.

3.2.1 Equation of State and Free Energy Perturbation Theory

An equation of state is one that uses a definition of the free energy (or its derivatives) to calculate macroscopic observables. The ideal gas EoS and the van der Waals (vdW) EoS were some of the first to describe gases and liquids using the relationship between pressure, temperature and volume. It is possible however to derive these equations using the statistical mechanical notions discussed above. The ideal gas equation of state can be exactly derived for a monoatomic molecule:

$$\begin{aligned}
 A &= -k_B T \ln Q^{ideal} \\
 &= -k_B T \ln \frac{\Lambda^{-3N}}{N!} \\
 &= -k_B T (N \ln V - \ln N! - \ln \Lambda^{3N}) \\
 &\approx Nk_B T (\ln \frac{N\Lambda^3}{V} - 1)
 \end{aligned} \tag{3.32}$$

$$P = -\frac{\partial A}{\partial V} = \frac{Nk_B T}{V} \tag{3.33}$$

The theory developed by vdW EoS is based on the concepts of Equation 3.31. Starting with a reference fluid (ideal gas), in vdW theory two additional contributions to the free energy are defined. First is the excluded volume effect. Ideal gases are point particles that only interact with each other by having elastic collisions. Particles that have a volume behave like hard spheres (refer to Equation 3.6). The free energy of a hard sphere can therefore be written as:

$$\frac{A^{HS}}{Nk_B T} = \ln \frac{V - Nb}{V} \tag{3.34}$$

Equation 3.34 describes an entropic term, which is due to excluded volume effects. b is the excluded volume for a pair of hard sphere particles of size σ ($b = 2/3\pi\sigma^3$). Particles cannot access some of the volume inside the box as that volume is occupied, and therefore the entropy is lowered, causing an increase in the value of the Free energy relative to that of the ideal gas.

The second contribution to the free energy from vdW EoS is addition of an attractive term, which is perturbation of the free energy of a hard sphere:

$$A^{Total} = A^{ideal} + A^{HS} + \Delta A^{attract} = A^0 + \Delta A^{attract} \quad (3.35)$$

Equation 3.35 could be rewritten as,

$$\Delta A^{attract} = A^{Total} - A^0 = -k_B T \ln \frac{Q^{Total}}{Q^0} = -k_B T \ln \frac{Z^{Total}}{Z^{HS}} \quad (3.36)$$

With Q^{Total} being the total partition function of a system with attractions, and Q^0 being the partition function of the hard sphere reference system. Using Equation 3.29:

$$\Delta A^{attract} = -k_B T \ln \frac{\int \dots \int \exp(-\beta \mathcal{V}^{Total}(\mathbf{q}^N)) d\mathbf{q}^N}{\int \dots \int \exp(-\beta \mathcal{V}^{HS}(\mathbf{q}^N)) d\mathbf{q}^N} \quad (3.37)$$

Where $\mathcal{V}^{HS}$ is the potential energy of the hard sphere reference system and $\mathcal{V}^{Total}$ is given by:

$$\mathcal{V}^{Total} = \mathcal{V}^{HS} + \Delta \mathcal{V} \quad (3.38)$$

$\Delta \mathcal{V}$ is the residual potential energy accounting for attractive interactions in a real system. Using equation 3.38 in 3.37, and the definition of ensemble averaging in Equation 3.18:

$$\begin{aligned} \Delta A^{attract} &= -k_B T \ln \frac{\int \dots \int \exp[-\beta(\mathcal{V}^{HS}(\mathbf{q}^N) + \Delta \mathcal{V}(\mathbf{q}^N))] d\mathbf{q}^N}{\int \dots \int \exp[-\beta \mathcal{V}^{HS}(\mathbf{q}^N)] d\mathbf{q}^N} \\ &= -k_B T \ln \frac{\int \dots \int \exp[-\beta \Delta \mathcal{V}(\mathbf{q}^N)] \exp[-\beta \mathcal{V}^{HS}(\mathbf{q}^N)] d\mathbf{q}^N}{\int \dots \int \exp[-\beta \mathcal{V}^{HS}(\mathbf{q}^N)] d\mathbf{q}^N} \\ &= -k_B T \ln \langle \exp[-\beta \Delta \mathcal{V}(\mathbf{q}^N)] \rangle_0 \end{aligned} \quad (3.39)$$

This means the free energy contribution due to attractions is an ensemble average of the attractive potential energy for a reference hard sphere system: First assume a given microstate that is composed of a system of hard spheres at fixed positions, then turn on the attractive energies and measure the change in the energy of the system, repeat the same process over many microstates, and use the final term in Equation 3.39 to calculate the attractive contribution to the free energy, $\Delta A^{attract}$. Equation 3.39 can be further simplified using Equation 3.30:

$$\Delta A^{attract} \approx \langle \Delta V(\mathbf{q}^N) \rangle_0 = 2\pi\rho N \int_{\sigma}^{\infty} g(r)u(r)r^2 dr \quad (3.40)$$

The significance of Equation 3.40 is that it provides an analytical expression for the free energy due to attractions. Here, the free energy is no longer defined as the potential due to particles being in positions $\mathbf{q}^N$, and the potential is the sum of all pair potentials. It should be noted that Equation 3.40 is different to Equation 3.30 as the bounds of the two integrals are different. In Equation 3.40 presented here, the lower limit of the integral is σ . When $r > \sigma$, the only interaction between two spheres is attractive, and thus the integral only measures the total attractive energy. Van der Waals equation of state uses Equation 3.40 to define the attractive contribution to the free energy:

$$A^{Total} = A^{ideal} + A^{HS} + 2\pi N\rho \int_{\sigma}^{\infty} g(r)u(r)r^2 dr \quad (3.41)$$

vdW theory uses the mean field assumption, defining the radial distribution function as that of a reference hard sphere fluid, $g_{HS}(r) = 1$. One can rewrite Equation 3.41 as:

$$A^{Total} = Nk_B T \left(\ln \frac{N\Lambda^3}{V} - 1 - \ln \frac{V - Nb}{V} \right) - \frac{N^2}{V} a \quad (3.42)$$

Where a is a mean-field energy attractive energy:

$$a = -2\pi \int_{\sigma}^{\infty} u(r)r^2 dr \quad (3.43)$$

The final form of the vdW EoS can be written as the contributions of three terms:

$$\frac{A^{Total}}{Nk_B T} = \frac{A^{Ideal}}{Nk_B T} + \frac{A^{residual}}{Nk_B T} = \frac{A^{Ideal}}{Nk_B T} + \frac{A^{HS}}{Nk_B T} + \frac{A^{Attr}}{Nk_B T} \quad (3.44)$$

If Equation 3.42 is differentiated with respect to V , the vdW cubic equations of state in terms of the pressure is derived:

$$P^{vdW} = \frac{RT}{v - b} - \frac{a}{v^2} \quad (3.45)$$

Where $v = V/N$.

It is interesting that this equation which lays the foundation of a family of EoS commonly used in the engineering community has an underlying statistical mechanical justification. The robustness of the assumptions in the derivation of the EoS means that all the phases shown in Figure 2.7 in the previous chapter can be observed for binary mixtures. However, due to the assumptions in the vdW theory, namely the mean-field assumption with $g(r) = 1$ and the incompressibility of the hard spheres, the theory tends to overpredict pressure and critical compressibility [97]. If particles are hard even for high densities, they cannot overlap and therefore at high packing fractions, the system has a high pressure. This is why the vdW EoS overpredicts pressures.

vdW type equations of state are called cubic EoS, as the equation is third order in terms of the volume. There have been many advances in thermodynamic modelling using cubic equations of state, both in trying to refine the hard sphere term and the mean field energy term. Carnahan-Starling (CS) EoS [98] is highly successful in capturing the correct thermodynamic properties of hard spheres in terms of their fraction. However replacing the hard sphere term of cubic EoS with Carnahan-Starling is not possible, as the equation would become none cubic. More successful cubic EoS have a different mathematical form for the description of the attractive term in vdW equation of state. For example for Peng-Robinson [99]:

$$p^{PR} = \frac{RT}{v - b} - \frac{a\alpha(\omega)}{v^2 + 2bv - b^2} \quad (3.46)$$

It could be seen that the the hard sphere terms is untouched and the attractive term is significantly altered. The α term is a correction factor which is a function of the acentric factor and the denominator is a quadratic term which is empirical in nature. Although such cubic equations are highly successful in predicting phase equilibria, these equations are all empirical in form. The attractive term is a mean-field assumption with no underlying statistical mechanical justification.

This justifies the need for a more robust equation of state which can improve upon the perturbation theories as proposed by vdW. Certain assumptions can certainly improve the modelling aspects of fluids:

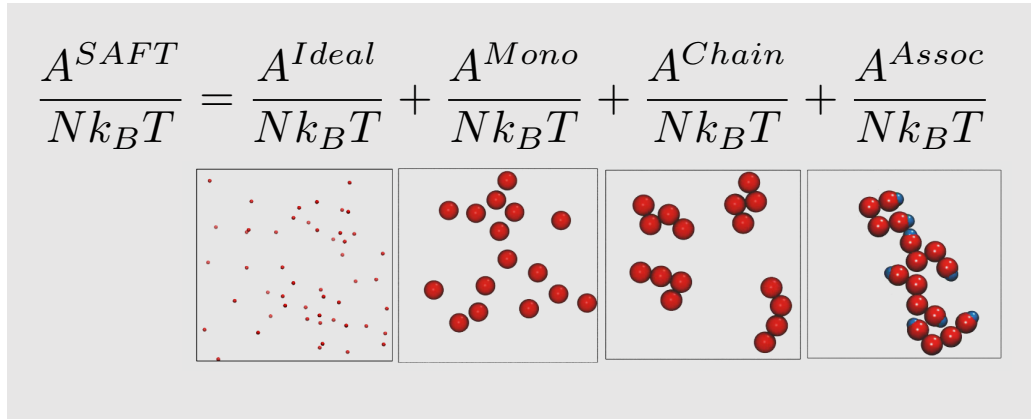


FIGURE 3.3: Schematic representation of each perturbation term in SAFT model

- The hard sphere term can be replaced by a more accurate formula, such as Carnahan-Starling EoS
- vdW assumed particles are spherical in shape with a diameter σ , what happens for anisotropically shaped molecules, like polymers and liquid crystals?
- Another major improvement could be made with improving the mean field assumption of the attractive term, by incorporating $g(r)$
- Using an accurate form of intermolecular potentials in the EoS, which can be then used in simulations to calculate the same maroscopic properties

SAFT type equations were developed to address all these issues.

3.3 SAFT- γ Mie Equation of State

SAFT stands for statistical association fluid theory, and this family of EoS was developed to address the main problems associated with most equations of state as already discussed. The foundations of SAFT could be found in the associating theory developed by Wertheim [100–103]. It was Jackson, Chapman and Gubbins who managed to "decipher" Wertheim's complex theory in two foundation papers [104, 105] which lead to the publication of the first SAFT type paper [106]. Ever since then, all SAFT models follow the same framework, which is given by:

$$\frac{A^{SAFT}}{Nk_B T} = \frac{A^{Ideal}}{Nk_B T} + \frac{A^{Mono}}{Nk_B T} + \frac{A^{Chain}}{Nk_B T} + \frac{A^{Assoc}}{Nk_B T} \quad (3.47)$$

The total Helmholtz free energy is given as the sum of four components. First is the contribution of the ideal gas to the free energy, as previously discussed. The next perturbation is a vdW type perturbation, which assumes the system is composed of monomers with excluded volume and attractive energies. New perturbations were added to account for the free energy contribution due to monomers forming chains of a certain size. The final perturbation is due to presence of associating interactions, such as hydrogen bonding. Figure 3.3 is a schematic of the main contributions to the free energy within the SAFT framework.

Since the original SAFT paper by Chapman et al. [106], there has been an explosion in the different flavours of SAFT, with the main difference between each model being the modelling of the monomer term [107]. The original SAFT model as well as the model of Huang and Radosz [108], surprisingly published in the same issue of *Molecular Physics*, have slightly different equations using a square-well fluid of fixed size to describe the monomer term. Huang and Radosz, who were employed by Exxon, were the first to model polymeric materials with SAFT [108]. However, their models were not realistic as the number of segments representing a chain was only a correlation. Simplified-SAFT of Fu and Sandler [109] was an attempt to simplify the model of Huang and Radosz, with yet another adjustment to the monomer term, but still retaining the fixed square-well nature of the interactions. LJ-SAFT proposed by Kraska and Gubbins [110, 111] was the first attempt to replace the square-well attraction of the monomer term with a more realistic continuous potential. An accurate equation of state for Lennard-Jones was used to model such system. The SAFT-VR EoS [112], using the square well potential with a square-well that could have different widths was developed to study different systems, from alkanes to solvents for carbon capture and polymers. Parameters from SAFT-VR square well were shown to overpredict the critical points of the VLE curve for pure components, and simulation results could not be reproduced for the same set of parameters.

PC-SAFT [113] is yet another popular flavour of the EoS that is widely use in

industry and in the scientific community. Unlike all other flavours of SAFT, PC-SAFT EoS does not have a hard sphere reference fluid, but a hard chain, so that the $g(r)$ in its dispersion terms (refer to Equation 3.41) is that of a reference hard sphere chain. This was done to improve the model for long chains, and is different to all other models of SAFT which have hard sphere as their reference fluid. However, due to its use of the hard chain as its reference fluid, PC-SAFT does not have parameters that can be used as intermolecular potentials.

In this thesis, parameterisation of the force field is done using the highly accurate SAFT- γ Mie EoS. Mie EoS has already been published in literature and for the full explanation of the theory the reader should refer to ref [27]. There are certain advantages to using this flavour of SAFT in modelling real systems. Firstly, the equation of state is highly accurate up to second order derivatives properties. Secondly the interaction parameters can be directly used in molecular simulation packages, as it is based on the continuous Mie potential. Thirdly, SAFT- γ Mie EoS is a group contribution method, where intermolecular potential of functional groups can be parametrised. Below is a short explanation for each term in the SAFT- γ Mie potential, and is not given in great detail, as the original paper explains things in much greater depth than the author of this thesis ever could.

For a brief summary, we can start by defining a system composed of a mixture of N_C components, with N_G distinct functional groups. Monomers in the system interact with each other with a Mie potential (Equation 3.9). Each functional group has its own distinct intermolecular potential $u(r)$. For this system the A^{Ideal} term in SAFT- γ Mie EoS is given by:

$$\frac{A^{Ideal}}{Nk_B T} = \left(\sum_{i=1}^{N_C} x_i \ln(\rho_i \Lambda_i^3) \right) - 1 \quad (3.48)$$

where $\rho_i = N_i/V$.

This term contains all contributions to the ideal gas free energy (translational, rotational and vibrational degrees of freedom).

The monomer contribution is given as a Barker-Henderson perturbation expansion to third order [114, 115]. The reference fluid, A_0 , is that of a hard sphere:

$$\frac{A^{Mono}}{Nk_B T} = \frac{A_0}{Nk_B T} + \frac{A_1}{Nk_B T} + \frac{A_2}{Nk_B T} + \frac{A_3}{Nk_B T} \quad (3.49)$$

With:

$$\frac{A_n}{Nk_B T} = \left(\frac{1}{k_B T} \right)^n \left(\sum_{i=1}^{N_C} x_i \sum_{k=1}^{N_G} v_{ki} \right) a_n \quad (3.50)$$

where $n = 0, 1, 2, 3$, x_i is the mole fraction of component i and v_{ki} is the number spheres of type k in component i . It could be seen that the dispersion terms (i.e. $n = 1, 2, 3$) are temperature dependent. a_n is the n^{th} order term of the Barker Henderson perturbation [114, 115], and is obtained by summing the pairwise contributions between all the monomers in the system:

$$a_n = \sum_{k=1}^{N_G} \sum_{l=1}^{N_G} x_{mono,k} x_{mono,l} a_{n,kl} \quad (3.51)$$

where $x_{mono,k}$ is a mole fraction term, describing the ratio of all spheres of functional group k in the system, relative to the total number of spheres.

Just like the vdW EoS described above, the first term of the monomer contribution is a hard sphere term, with an accurate expressions for hard sphere mixtures being used. However, a fundamental difference in using a soft potential as the reference fluid, is that the hard sphere diameter is not constant, and an effective diameter has to be calculated using the equation for a Barker-Henderson diameter. Barker Henderson diameter approaches the value of σ at low temperatures, and decreases as temperature is increased.

The second contribution to the monomer term, is again identical to the second term in Equation 3.41, and can be written as:

$$a_{1,kl} = 2\pi\rho_s \int_{\sigma}^{\infty} g^{HS}(r) u_{kl}^{Mie}(r) r^2 dr \quad (3.52)$$

Here however, $g(r)$ is not assumed to be one, and the structure of the fluid is directly incorporated into the perturbation term, along with the correct contribution of the intermolecular interaction to the free energy. The third contribution to the monomer term, a_2 is based on modified compressibility approximation (MCA)

proposed by Zhang [116]:

$$a_{2,kl} = -\pi\rho_s K^{HS}(1 + \chi_{kl}) \int_{\sigma}^{\infty} g^{HS}(r)(u_{kl}^{Mie}(r))^2 r^2 dr \quad (3.53)$$

with K^{HS} being the isothermal compressibility of the reference fluid, which is obtained from the density derivative of the Carnahan and Starling expression for the compressibility factor. χ_{kl} is a correction factor from simulation of hard spheres to minimise the mismatch between simulations and the theory.

The final contribution to the monomer term, a_3 was evaluated by means of Monte Carlo simulations. Having the monomer up to third order expansion term allows for an accurate description of the system near the critical point and for second derivative properties.

Finally the chain term is given by the following:

$$\frac{A^{chain}}{Nk_B T} = - \sum_{i=1}^{N_C} x_i \sum_{k=1}^{N_G} (v_{ki} - 1) \ln g_i^{Mie}(\bar{\sigma}, \zeta_x) \quad (3.54)$$

where $\bar{\sigma}$ is the average of all the σ s in compound i and ζ_x is the packing fraction. For a pure component system of a homonuclear molecule, Equation 3.54 reduces to:

$$\frac{A^{chain}}{Nk_B T} = -(m_s - 1) \ln g(\sigma) \quad (3.55)$$

where m_s is the number of segments in each molecule.

The association contribution to the free energy is not discussed here, because associating species in the EoS cannot be directly modelled in molecular simulation. There are correction factors for associating molecules that cannot be directly linked to a real physical system. Besides, most of the systems studied in this work are non-associating, so that there is no hydrogen bonding contribution to the free energy.

Perspective

The aim of this section was by no means a full theoretical explanation of SAFT- γ Mie EoS. It was to highlight the fundamental concepts of this perturbation theory for the reader to have a basic understanding. It is to be reiterated that for a full explanation of this EoS, the reader should refer to [27, 86]. However, what could

be appreciated from this is that the equation of state attempts to calculate thermodynamic behaviour of a system, solely based on its local structure, $g(r)$ and the pair potential, $u(r)$. Accurate representation of these two variables means that for a given pair potential, the theory and simulations can produce the same results.

3.3.1 Coarse-Graining with SAFT- γ Mie

SAFT- γ Mie EoS is a group contribution methodology, where each functional group is in essence a coarse-grained representation of a group of neighbouring atoms. The choice of the functional groups is arbitrary. If one wants to simulate a mesoscale molecule, it is natural to maximise the number of atoms per CG bead, without loss of accuracy. However, if one wants to predict the phase behaviour of a pharmaceutical compound, it might be best to use very fine-grained functional groups [117]

For mixtures in this framework, every group has a self-interaction potential, given by the Mie Potential:

$$u^{Mie}(r) = C\varepsilon \left[\left(\frac{\sigma}{r} \right)^{\lambda_r} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3.56)$$

with,

$$C = \left(\frac{\lambda_r}{\lambda_r - 6} \right) \left(\frac{\lambda_r}{6} \right)^{6/(\lambda_r - 6)} \quad (3.57)$$

For cross interactions between different species, combining rules can be used. An arithmetic mean is used for σ_{ij} , between two different species:

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \quad (3.58)$$

A geometric mean, with an adjustable parameter (k_{ij}) is used to find inter-species energy:

$$\varepsilon_{ij} = (1 - k_{ij}) \frac{(\sigma_{ii}^3 \sigma_{jj}^3)^{1/2}}{\sigma_{ij}^3} \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \quad (3.59)$$

k_{ij} is state-independent adjustment parameter. When $k_{ij} = 1$ there is no interaction between the segments.

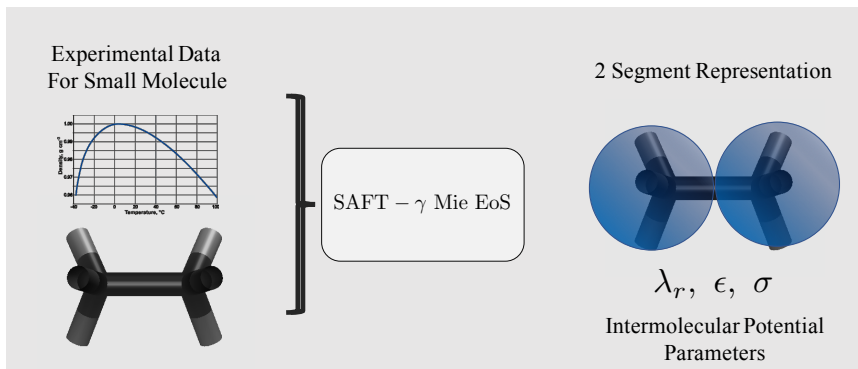


FIGURE 3.4: SAFT- γ Mie Process of fitting parameters for small molecules

Similar to ϵ , a geometric mean is used to find the cross $\lambda_{r,ij}$:

$$\lambda_{r,ij} = 3 + \sqrt{(\lambda_{r,ii} - 3)(\lambda_{r,jj} - 3)} \quad (3.60)$$

Here, an example is given of coarse-graining a linear alkane, so that the concept could be more easily understood. We use the example of hexacosane, $C_{26}H_{54}$. The aim is to coarse-grain every four CH_2 groups into one segment, so that a CG polyethylene molecule can be represented by a chain of CG segments. Hexacosane is made of six $(CH_2)_4$ groups and two CH_3 groups. In order to calculate intermolecular potential parameters of the CG beads, one would first have to find the intermolecular parameters of the terminal CH_3 groups.

This can be done, for example, by fitting the parameters of CH_3 groups to that of a two bead representation of ethane using the EoS. This is shown in Figure 3.4. Knowing the parameters for the CH_3 group, experimental data for hexacosane could now be used to fit the intermolecular parameters of the $(CH_2)_4$ group. The final picture of the coarse-graining can be seen in Figure 3.5.

The advantage of this methodology is that there is no ambiguity in what each coarse-grained bead is representing, with an intermolecular potential that is fitted to match experimental data. The coarse-grained beads can now be replicated, with the help of the chain term in the EoS to predict the properties of any polymer. For example, a polyethylene of Mw of 10 kDa can be represented by ≈ 180 $(CH_2)_4$ CG beads.

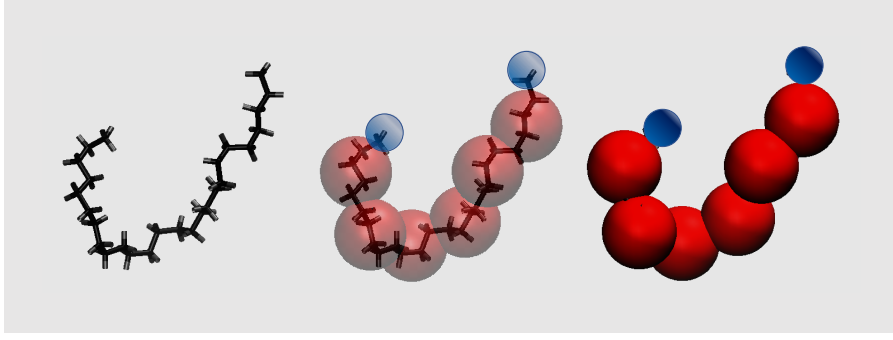


FIGURE 3.5: Heteronuclear CG representation of hexacosane, blue represents the terminal CH₃ group, and each red beads represents four CH₂ groups

3.3.2 Phase Equilibria and Parameter Estimation

The requirement for N phase equilibrium is given by :

$$T_1 = T_2 = \dots = T_N \quad (3.61)$$

$$P_1 = P_2 = \dots = P_N \quad (3.62)$$

$$\mu_1 = \mu_3 = \dots = \mu_N \quad (3.63)$$

For a pure component system, experimental data such as vapour pressures and saturation liquid densities can be used to estimate parameters for intermolecular potentials. Parameters are estimated by minimising the difference between the experimental and EoS calculated values for given properties. For the cases where the properties are vapour pressure and saturation liquid density, the objective function is given by:

$$\min_{\alpha} F_{obj}(\alpha) = \min_{\alpha} \left[w_P \sum_{i=1}^{N_P} \left(\frac{P_v^{Calc}(T_i, \alpha) - P_v^{Exp}(T_i)}{P_v^{Exp}(T_i)} \right)^2 + w_{\rho} \sum_{i=1}^{N_{\rho}} \left(\frac{\rho_l^{Calc}(T_i, \alpha) - \rho_l^{Exp}(T_i)}{\rho_l^{Exp}(T_i)} \right)^2 \right] \quad (3.64)$$

where α is the vector of parameters of the intermolecular potential ($m_{segments}$, ϵ , σ , λ_r). N_P and N_{ρ} are the number of data used for pressure and density respectively. w_P and w_{ρ} are weights given to each type of experimental data.

Now that the framework to parametrise intermolecular potentials is outlined, once parameters are estimated, it is possible to use them in molecular simulations.

3.4 SAFT- γ Mie Force Field for Simulations

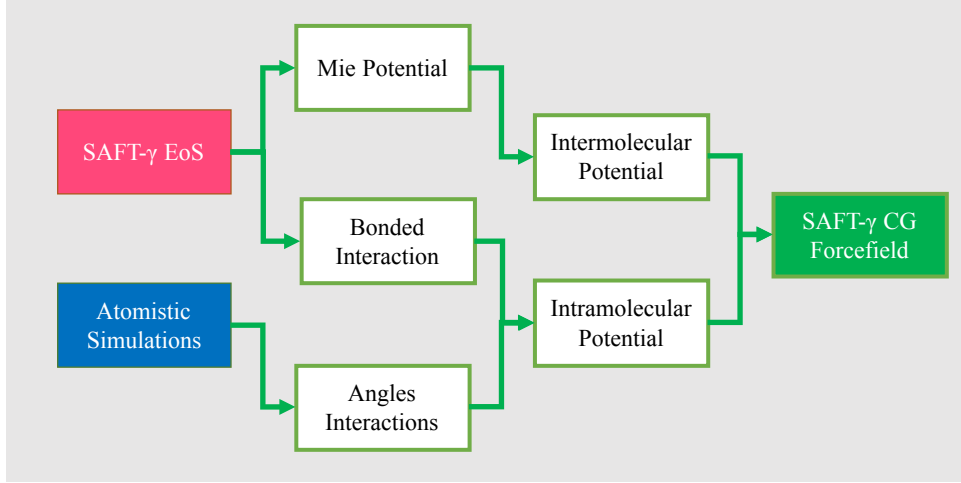
3.4.1 Intramolecular Potentials

The most general description of the potential energy of a system composed of chains is,

$$\begin{aligned}
 U_{Total}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = & \sum_{bonds} \frac{1}{2} k_{bond} (d_i - d_{i,0})^2 + \sum_{angles} \frac{1}{2} k_{angle} (\theta_i - \theta_{i,0})^2 \\
 & + \sum_{torsions} \sum_n c_{i,n} \cos(\omega_i n)^n + \sum_{ij} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \\
 & + \sum_{ij} C\epsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^n - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^m \right]
 \end{aligned} \quad (3.65)$$

In the above equation, the bonding constraint between two particles is taken into effect by the *bonds* term, where the bonds $d_{i,0}$ is the equilibrium bond length and k_{bond} is a harmonic bond constant. The angle θ_i formed between three bonded particles is constrained using the second term, with $\theta_{i,0}$ being the equilibrium angle and k_{angle} being the bond constant. Both k_{bond} and k_{angle} describe the stiffness of the potential. The lower their value, the more flexible the molecule. Finally the dihedral torsion between four bonded particles is taken into account by the fourth term. The last two terms are the intermolecular interactions.

Within the SAFT- γ framework, molecules are tangentially bonded spheres with intermolecular Mie potentials. They are tangentially bonded, so that the distance between the centre of mass of two tangentially bonded spheres is given by σ_{ij} . In essence a SAFT chain can be thought of a pearl necklace model described in Chapter 2. However, the effect of angles and chain stiffness cannot simply be ignored. For example, a liquid crystalline molecule with a rigid backbone cannot be modelled as a freely-jointed chain. Rahman et al. [32] have recently published a study highlighting the importance of considering the effect of chain stiffness in modelling alkanes with SAFT- γ Mie, in order to capture the correct conformation of the molecules. It is shown that the centre of mass radial distribution function (RDF)

FIGURE 3.6: SAFT- γ Mie force field Framework

of dodecane cannot be accurately represented with a fully flexible chain, given that each CG bead contains three CH_2 groups. For an accurate description of molecules in this work, angular potentials have to be fitted to atomistic simulations using the following equation [32, 118]:

$$u(\theta) = \frac{1}{2}k_{\text{angle}}(\theta - \theta_0)^2 \approx -k_B T \ln(P(\theta) / \sin(\theta)) \quad (3.66)$$

where $P(\theta)$ is the probability of three neighbouring particles in a chain having an angle θ . Assuming a Gaussian distribution for the probability of angles:

$$P(\theta) / \sin(\theta) = \frac{1}{\sqrt{2\pi}s^2} \exp\left(-\frac{(\theta - \theta_0)^2}{2s^2}\right) \quad (3.67)$$

where s is the standard deviation, it could be seen that:

$$\frac{1}{2}k_{\text{angle}}(\theta - \theta_0)^2 \approx \frac{1}{2} \frac{k_B T}{s^2} (\theta - \theta_0)^2 \quad (3.68)$$

Thus:

$$k_{\text{angle}} \approx \frac{k_B T}{s^2} \quad (3.69)$$

3.4.2 SAFT- γ Force Field Framework

Given the above description of the SAFT framework, the parametrisation of a CG potential can now be summarised in Figure 3.6.

3.5 Other Coarse Graining Methodologies

There are different philosophies of obtaining the interaction parameters for coarse-graining. The derivations could target at reproducing thermodynamic properties, for example partitioning data used by Marrink et al. for the MARTINI force field [119]. For complex systems this approach has proven very successful as will be discussed later. However, it can be proven via statistical mechanics that thermodynamically accurate CG results in loss of structural accuracy and vice versa [35, 120, 121]. This means that there would be discrepancy between atomistic levels of radial distribution function of molecules and coarse grained ones. This prevents the bridging of coarse-grained simulation properties and atomistic level, as the coarse-grained particles would be in a different location than their atomistic constituent atoms. If instead of thermodynamic data, one wants to use atomistic level detail to map the correct structure, then this might be achievable by structure-matching methods where the CG force field is manipulated to give the correct structure. This has the benefit of ensuring the coarse grained particles are in the same location as their atomistic particles. However, again by enforcing structure matching it would not be possible to guarantee that properties are thermodynamically consistent.

Coarse-graining methods can be categorised in to the following two main branches, top-down approaches and bottom-up approaches [120, 122, 123]. In top-down models, the interactions are parametrised to reproduce certain emergent structural or thermodynamic properties on macroscopic level. This requires the knowledge of experimental thermodynamics properties, such as VLE data, liquid density and vapor pressure that could be used to parametrise the models. In bottom-up approaches, information obtained from *ab initio* or atomistic simulations are used to map coarse-grained parameters.

3.5.1 Bottom Up Approaches

Structure Based Methods

Structure matching coarse-graining aims to reproduce structural properties, obtained experimentally or through more detailed atomistic simulations.

Once high resolution simulations are run, structural properties, such as radial distribution functions, could be used as a reference point to the CG models. Perhaps the easiest method is to use the potential mean force (PMF) on the molecule at its centre of mass [124]. PMF is the force a molecule a at $\mathbf{r}_a$ experiences due to another molecule b being at position $\mathbf{r}_b$. The PMF of n particles acting on particle j for a system with N particles is calculated by integrating the average multibody force over the remaining $N - n$ particles, whilst keeping the particles from 1 to n fixed [125].

$$-\nabla_j w = \frac{\int -\nabla_j H_w e^{-\beta H_w} dq^{N-n}}{\int e^{-\beta H_w} dq^{N-n}} \quad (3.70)$$

for $j = 1, 2, \dots, n$.

The PMF between two particles is given by

$$w^{(2)} = -k_B T \ln g(r) \quad (3.71)$$

Equation 3.71 could be used to calculate the potential mean force between two particles which is the effective intermolecular potential between two beads. This is strictly valid at low densities of homogeneous systems. For non-homogeneous dense fluids, this becomes less accurate as multibody interactions affect the value of the PMF and the effect of a third particle on the pair interactions also needs to be considered. There are methods of improving the calculations through Ornstein-Zernicke type equations using the Percus-Yervik closure by obtaining the total pair distribution function. However, this is still not very accurate and the correct distribution function is not quite achieved [126]. Although Ornstein-Zernicke equation can give exact results for the RDF, it is impossible to solve without closure relations, which leads to inaccuracies in the prediction of the RDF.

More accurate methodologies for structure matching have been proposed, in particular the iterative Boltzmann inversion (IBI) by Müller-Plathe et al. [124]. It is popular for its straightforward nature, and that it could be applied to a broad range of systems. As the name suggests, this method is an iterative method to estimate the effective pair potential, which can be described as below:

$$U_{i+1}(r) = U_i(r) + \alpha(w_{ref}(r) - w_i(r)) \quad (3.72)$$

$$U_{i+1}(r) = U_i(r) + \alpha k_B T \ln \frac{g_i(r)}{g(r)} \quad (3.73)$$

i denotes the iteration number, and α is a convergence parameter to suppress large changes in the potential update [127]. $w_{ref}(r)$ is the reference pair potential calculated using atomistic simulation. A starting point in this method is guessing a pair potential by using Equation 3.71. This method iteratively solves for a new pair potential until the change in the magnitude of the potential term is negligible. For complex systems, this method ensures that the final potential gives the correct RDF, unlike PMF calculations. However, a significant disadvantage of this method is that it is not state-independent [127]. The potential is dependent on β (i.e. temperature), density and composition [128]. As temperature changes, the radial distribution function also changes and therefore for every temperature or density change, an iterative calculation of the pair potentials is necessary. This makes parameter estimation using this method very slow. Having said that, the overall concept is very simple and it is this reason why it is extensively used in simulating polymer melts [129–132]. A particular advantage of the IBI method is that by assuming intermolecular, bonding and angle potentials are independent, one could apply this method to find independent potentials for intermolecular, bonded and angles interactions.

In general, as highlighted in a review in ref [133], the primary issue with structure matching techniques is the transferability over thermodynamic states different from that used in the parametrisation. There have been attempts to improve this problem by introduction of multistate iterative Boltzmann inversion techniques, as proposed by the group of McCabe [127]. In this study, propane was used to derive parameters for n =alkane chains. For every iteration multiple state points (temperatures) were simulated and the the potential was updated using the summation of the ratio of the RDFs for all states. The parameters were the then used to predict the radius of gyration of dodecane up to 98 percent accuracy. However, the number of iterations had increased 3 times. Polymers in solvents have also been modelled using single state IBI [134]. Polystyrene in toluene at different concentrations were used to fit potential parameters. It was shown that the IBI method could capture the correct phase behaviour for the most concentrated solutions. Even the autocorrelation of the end to end distances matched that of atomistic simulations. However, for each

state point 43 iterations had to be run to fit the potentials. It is important to note that this method is state dependent, and to sample different state points many iterations are required to accurately model to full phase diagram.

Force Matching Methods

A different method of matching atomistic data to coarse-grained ones is by the force-matching method, developed by Voth and coworkers [135]. In this method the force field is determined by minimising the difference between the CG forces and AA forces. Although this method seems different to structure matching, it is similar to structure matching in that a multibody potential of mean force is determined which is related to pair potentials of mean force used in structure matching [136].

Multiscale Coarse Graining (MS-CG) was first implemented for complex fluids by Izvekov and Voth [135]. The classical forces of a preselected form, which are dependent on parameters $\mathbf{g}$, are optimized by minimising the parameter χ , which is defined as the difference between CG forces and a predetermined database of forces calculated by atomistic simulations. For clarification, the CG forces are written as:

$$\mathbf{F}^{\text{CG}} = \mathbf{F}^p(\{\mathbf{g}\}) \quad (3.74)$$

The objective function would be to minimise χ^2 :

$$\chi^2(\{\mathbf{g}\}) = \frac{1}{3LN} \sum_{l=1}^L \sum_{i=l}^N \left\| \mathbf{F}_{il}^{\text{ref}} - \mathbf{F}_{il}^{\text{CG}} \right\|^2 \quad (3.75)$$

which is a minimisation of L different configurations generated by the atomistic simulations, with N being the number of atoms, $\mathbf{F}^{\text{ref}}$ is the force acting on the centre of mass of the groups of atoms that will be coarse-grained in atomistic simulations and $\mathbf{F}^{\text{CG}}$ is the force acting on the CG bead that is representing the group of atoms. This function is very difficult to solve in this form. If the coarse-graining force field depends linearly on the fitting parameters, $\mathbf{g}$, Izvekov and Voth showed that the least squares fit can be performed by solving an overdetermined system of linear equations. Force matching using pairwise forces gives the optimal solution to the exact many body force [121]. This is because the force acting on a particle is the sum of

forces acting on that particle due to two, three, four, ..., N body forces in the system. Thus this is a major improvement relative to the iterative Boltzmann inversion where multibody interactions are not taken into account.

Top Down Approaches

Top down approaches aim to eliminate the problems associated with integrating the degrees of freedom discussed in the previous section. The main problems with the bottom-up coarse-graining is that iterative and heuristic approaches are necessary to perform the parameter estimation. Furthermore, the solutions for the parameters are optimised for a single data point, e.g. radial distribution function or energy, and it is not optimised globally. Thus to simulate a whole phase map of self-assembling systems, bottom-up parameter estimation for different states could be very painful and time consuming. Müller and Jackson found a wide range of values for the variables of the Lennard-Jones interaction parameters (σ and ϵ) that are used for CO₂ at different conditions from literature [22].

At this point, it could be seen that an alternative approach is required if an efficient method of parameter estimation is to be implemented. This alternative is the top-down approach, which is the exact opposite to bottom-up approaches: Thermodynamic properties are used to estimate optimal force field parameters for a broad range of states. The pre-requisite to this is having an equation of state (EoS) that could accurately bridge the link between the force field and thermodynamic properties.

Many top-down methods have been developed. Commonly, group contribution theory is used to represent a molecule as an assembly of functional groups that always have the same interaction regardless of the system. Of particular interest is the MARTINI force field, established by Marrink et al. [119] to model biomolecules. In this force field, a four-to-one mapping is used (e.g. every four CH₂ groups form one CG bead) and the IBI method is used for the intermolecular potentials, bonds and angles. Lennard-Jones potentials are used to model intermolecular interactions fitted to hydration energies and densities of the different groups. An advantage of the MARTINI force field is its simple form of the potential and the fact that many of the

parameters for different functional groups are very similar. This makes it useful to build large biomolecules such as proteins [137] and DNA [138] with little complexity. The model is successful in capturing fundamental behaviour of biomolecules, such as area per head group of lipids, densities and stress across bilayers. The MARTINI force field has been used to study polymers, namely polyethylene and polypropylene [139], polystyrene [140] and pluronic (PEO-PPO-PEO) triblock copolymers in water. The polystyrene and polyethylene models were shown to capture the correct conformation in melt, with qualitative agreement of dynamic properties with atomistic simulations. The triblock copolymer simulations were run by the independent group of Carbone, and it was shown that MARTINI force field parameters for pluronics were accurate for the systems the parameters were fitted to. The models for PEO were not as accurate for temperatures outside the fitted region. For example, increasing the temperature did not increase the radius of gyration of polyethylene oxide. Overall, radius of gyration of the pluronic triblock copolymers were also underestimated. MARTINI force fields are also solely parametrised for the liquid phase, so there is not guarantee that vapour-liquid equilibria can be accurately calculated with such models.

Other group contribution methods that are of particular interest are the force fields introduced by Klein et al. [83, 118, 141, 142]. This model is one of the first to use the Mie potential to model fluids. Interfacial tension, densities, hydration free energy and structural data (from AA-MD) are used to fit pure component parameters. Solvation free energy is used to fit cross interactions. This model is a quantitatively accurate model to study lyotropic liquid crystals like non-ionic surfactants [118], as well as janus dendrimers [83]. Experimentally observable phases such as micelles, hexagonal columnar, lamellar and vesicles are all observed using this model. This model has not been applied to polymers yet.

The aforementioned top down methods have all been used to model many complex systems, however the methodology of finding the parameters is not efficient. Moreover, it is not possible to predict interesting phase behaviour given a set of potentials, such as LCST phase behaviour, before simulations are run, so that simulations can be run in more interesting areas of the phase diagram. SAFT- γ Mie force fields have this advantage.

3.6 Simulations at Mesoscale

Unlike theories that can solve statistical mechanical problems with the help of analytic expressions, simulations find solutions of these problems numerically. If it is not possible to find reliable models to describe complex systems, it is with the help of simulations that one can find interesting insights into these. There are two families of simulation techniques for mesophase, particle based models, and field theoretic models.

3.6.1 Mesoscale Modelling Techniques: Particle-Based Simulations

Molecular Dynamics

Molecular dynamics is a simulation technique where for a system of particles interacting in a box, the classical equations of motion are solved numerically,

$$\mathbf{f}_i = m\mathbf{a}_i = -\frac{\partial U}{\partial \mathbf{r}_i} \quad (3.76)$$

Positions of particles are updated every time step, based on the forces acting on the particles. Starting from a random configuration, the system evolves deterministically into an equilibrium state where it could be assumed that the system is ergodic, i.e. all the statistical mechanical microstates can be visited with equal probability. At this equilibrium, time averages correspond to ensemble averages and thermodynamic properties can be calculated. Common numerical integrators can be used to solve the equations of motion. The leapfrog algorithm is commonly used [87]:

$$v(t + \delta t/2) = v(t - \delta t/2) + \frac{f(t)}{2m} \delta t \quad (3.77)$$

$$r(t + \delta t) = r(t) + v(t + \delta t/2) \delta t \quad (3.78)$$

This type of numerical integration is more accurate than Euler's method as it uses half the time step δt to evolve the system. Temperature can be calculated by calculating the total kinetic energy, and pressure can be calculated from the virial theorem. If the system is modelled with the only interactions being from the kinetic energy and potential energy, then the simulation is in the microcanonical ensemble (NVE). In

order to simulate the system in the canonical (NVT) or isothermal-isobaric ensemble (NPT) thermostating and barostating are required. Thermostats work by rescaling the velocities of the particles in the system so that the temperature remains constant. Barostats work by adjusting the volume of the box. For simulating non-isotropic phases, relaxing angle and edge lengths of the simulation box can be more appropriate [143]. The constant stress-isothermal ($N\sigma T$) ensemble can be implemented, which is similar to the NPT ensemble, however each element of the stress tensor can be controlled independently.

For simulating bulk systems, in order to not have interfacial effects at the boundaries of the box, periodic boundary conditions are used, so that particles leaving from one side of the box will come back from the other side.

Coarse grained molecular dynamics (CGMD) is a very popular simulation technique to study mesoscale systems. This is due to the fact that commercial codes available are highly parallelised, allowing for very large simulations to be carried out at length and time scales not accessible using stochastic techniques. However, there are certain disadvantages to MD simulations. MD relies on the fact that the system has to evolve into an equilibrium state. However, for many mesoscale systems, such as polymer chains, equilibration times can take a very long time. Moreover, for mixtures of long chains, exact determination of phase equilibria is challenging due to interfacial effects. To calculate the correct bulk thermodynamic properties for mixtures with phase separation, interfacial contributions have to be removed from the simulations. In order to do this, multiple simulations have to be run with different interfacial areas, and thermodynamic properties measured for each simulation. By plotting the thermodynamic property vs interfacial area and extrapolating the data to zero interfacial area, the correct value for that property could be calculated.

Monte Carlo

Monte Carlo (MC) is a stochastic technique based on Metropolis sampling [87]. The objective of this type of simulation is to generate an ensemble of microstates. The generation of the ensemble configurations is done by random perturbations to the system with a criterion to decide whether to accept the perturbation based on its

probability. In the NVT ensemble, the criterion is given by ratio of the Boltzmann factors of the new proposed state to the old state $\exp(-\beta\Delta U)$. If the new state has a higher probability, it is accepted, and if not a random number is generated and if the ratio of the Boltzmann factors is above the random number then it is accepted. Molecular dynamics and Monte Carlo techniques are complementary techniques. The advantage of MC to MD simulations is that they can easily treat different thermodynamic ensembles. Unlike MD, no thermostating is required. Moreover, MC moves can be very flexible. For example in the configuration bias Monte Carlo technique, chains can be deleted and grown in a totally different direction. This advanced sampling technique is advantageous in the study of polymers, as initial configurations can be equilibrated very efficiently. However, MC simulations cannot scale up to very large systems, as the codes cannot be as parallelised as easily as MD codes. Moreover, for dense systems translation and insertion moves become less efficient in MC simulations, even though advanced sampling techniques can be easily implemented, increasing the overall efficiency of the simulation.

Dissipative Particle Dynamics (DPD)

An alternative to MD or MC, *dissipative particle dynamics* (DPD) could be used as a mesoscale simulation method for phenomena that are observable at microseconds. An advantage of this method is that δt time-steps used can be in the order of nanoseconds and therefore large systems can be simulated very quickly [144–146]. This could be of great advantage for mesoscale simulations. The fundamental assumption of DPD is that the systems if made of ideal chains, where beads can overlap (2).

In a DPD simulation, the fluid is represented as a set of N point particles of mass m_i , position r_i , and velocity v_i ($i \in \{1, \dots, N\}$). Just like MD, the particles are assumed to be "fluid clusters" instead of individual atoms molecules. The equation of motion is also governed by Newton's laws of motion: [145]

$$m_i \frac{d^2}{dt^2} \mathbf{r}_i = \sum_{j \neq i} \mathbf{F}_{ij}^{DPD} = \sum_{j \neq i} (\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^{Diss} + \mathbf{F}_{ij}^{Rand}) \quad (3.79)$$

The particles in the system interact through three types of pairwise forces, namely conservative (F_{ij}^C), dissipative (F_{ij}^{Diss}), and random (F_{ij}^{Rand}) forces. Although the equation above looks similar to the Langevin equation for Brownian dynamics, it is different as the dissipative and frictional forces are pairwise [147]. This means that linear and angular momenta are conserved and therefore, hydrodynamics is conserved. Conserving hydrodynamic is particular advantage of dissipative particle dynamics.

For very large systems, where it is not realistic to represent an entire molecule by one spherical bead, harmonic potentials can be introduced to connect smaller particles together, as shown in Equation 3.80.

$$\mathbf{F}_{ij}^{Harm} = K(r_{ij} - r_{eq})\mathbf{e}_{ij} \quad (3.80)$$

Explicitly, the force terms are expressed as:

$$\mathbf{F}_{ij}^C = F_{ij}^C \mathbf{e}_{ij} \quad (3.81)$$

$$\mathbf{F}_{ij}^{Diss} = -\gamma\omega^D(r_{ij})(\mathbf{v}_{ij} \cdot \mathbf{e}_{ij})\mathbf{e}_{ij} \quad (3.82)$$

$$\mathbf{F}_{ij}^{Rand} = \sigma\omega^R(r_{ij})\xi_{ij}\mathbf{e}_{ij} \quad (3.83)$$

Where $\mathbf{e}_{ij} = \mathbf{r}_{ij}/r_{ij}$ is the unit vector, and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. ω^D and ω^R are weight functions, γ is the drag constant and along with the random force constant σ determine the magnitude of the dissipative and random forces respectively. $\xi_{ij} = \xi_{ji}$ are Gaussian random variables, with zero mean and unit variance [148]. It is important to mention that the values of ξ_{ij} are uncorrelated for different particle pairs and times:

$$\langle \xi_{ij}(t)\xi_{kl}(t') \rangle = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\delta(t - t') \quad (3.84)$$

Satisfying detailed balance, and ensuring Gibbsian ensemble equilibrium, requires:

$$\omega^D(r) = (\omega^R(r))^2 \text{ and } \sigma^2 = 2\gamma k_B T / m \quad (3.85)$$

Assuming the statements in Equation 3.85, Espanol and Warren [149] have shown that the system would sample the NVT ensemble and the instantaneous temperature

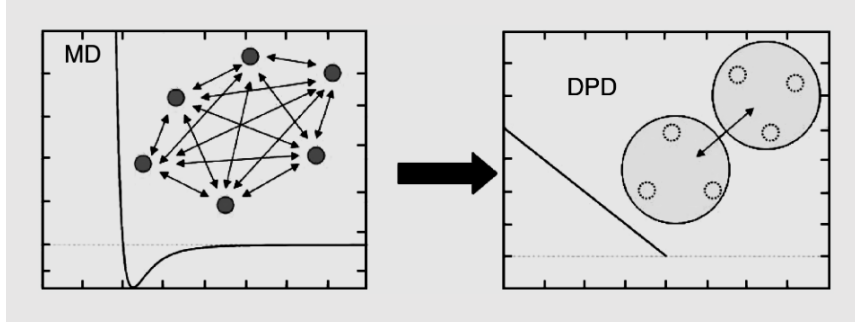


FIGURE 3.7: Comparison between the conservative potentials of MD and DPD methods, taken from [146]. The repulsion term in MD is much harder than DPD soft potential, preventing the use of large time steps to be used in the integrator

would be given by:

$$3k_B T = \left\langle \frac{\mathbf{p}_i^2}{m_i} \right\rangle \quad (3.86)$$

This renders DPD a thermostat. Finally, the weight functions ω^R and F_{ij}^C are given by:

$$\omega^R(r_{ij}) = \begin{cases} \left(1 - \frac{r_{ij}}{\sigma_{cut-off}}\right)^p & \text{for } r_{ij} \leq \sigma_{cut-off} \\ 0 & \text{for } r_{ij} > \sigma_{cut-off} \end{cases} \quad (3.87)$$

$$F_{ij}^C(r_{ij}) = \begin{cases} a_{ij} \left(1 - \frac{r_{ij}}{\sigma_{cut-off}}\right) & \text{for } r_{ij} \leq \sigma_{cut-off} \\ 0 & \text{for } r_{ij} > \sigma_{cut-off} \end{cases} \quad (3.88)$$

By comparing Equation 3.88 with Equation 3.9, it could be seen that a fundamental difference between DPD and CGMD is the difference between the conservative force terms. The DPD method has a linear soft force, whereas MD has a Mie type force. The argument used in using soft potentials is that as bead sizes become larger, at large time intervals, interparticle interactions become softer approaching the potentials used in DPD [146]. The potential is finite at zero separation distance, as these beads are made up of many small atoms and therefore the centre of mass of the beads can overlap. This soft potential means that much longer time steps (in the order of tens of picoseconds) can be used to simulate at the mesoscale level.

This potential however could also be disadvantageous as the conservative potential is not given by a physical model, unlike molecular dynamics simulations. DPD simulations ensure that hydrodynamic properties are preserved, however, as

Espanol and Warren have highlighted in a recent study, the DPD model as described here has a fundamental issue in that thermodynamic properties cannot ever be captured. The linear conservative forces of the model is based on the idea of simulation ideal chains. However, this means that the equation of state describing these systems is quadratic (not cubic) in volume [150]. This means that phenomena like vapour liquid equilibrium cannot be modelled with DPD [145]. Moreover, system size effects in DPD models are significant. Changing the number of particles in the system for the same given potentials does not produce the same results [150]. In terms of thermodynamic modelling of polymer solutions, DPD could only capture the UCST behaviour in the liquid phase (as explained in section 2.1.2). LCST behaviour cannot be captured, unless a correlation is added to model increasing repulsion at high temperature, which makes the DPD model a non-predictive approach to modelling polymer solutions [151, 152].

There are also problems with parametrising the intermolecular forces that still cannot be overcome. Frenkel and Smit have mentioned that ideal gas DPD systems have the correct structural properties, but are very viscous [153]. Moreover, so far ionic interactions have not been models with DPD, as the finite force at zero separation causes the superposition of oppositely charged beads. There can be alterations to a_{ij} to make it dependable on the local density, which can be useful in simulating liquid-vapour interfaces or wetting. All of these manipulations means that the parameters in DPD do not have a molecular, or a fundamental meaning and they are more matched to macroscopic properties to microscopic properties.

The clear advantages of DPD relative to CGMD are that much larger time steps can be used, and that hydrodynamics is also conserved. This has led to its widespread use in simulation community. However, as outlined, mesoscale methods are useful tools that are important can be used depending on one's need. For static properties, such as structures, and accurate thermodynamic properties, molecular dynamics is still the preferred method because of its underlying physical meaning at the atomistic level. However for a phenomenological study of very long polymer chains, naturally DPD models are better [153].

It is important to mention that the use of the DPD is strictly valid monomer sizes similar to that of segments of ideal chain, where there can be large amount of overlap

of the particles. Thus for an accurate representation of many liquid crystals that are less than 10 nm in size is it not a valid model.

Lattice Boltzmann Methods

There are many other techniques that could be categorised as meso-scale particle based methods. One of the most common techniques is the Lattice Boltzmann method, which discretises the Boltzmann equation and simplifies the system with only allowing particles to move in certain directions [154–156]. In lattice dynamics, statistical averaging of the behaviour of the molecules leads to a fluid which follows the Navier-Stokes equations of fluid dynamics. Hydrodynamics is conserved which is an advantage of this model and the discretisation allows for very fast simulations. Lattice Boltzmann is applied to large polymeric chains by treating the large solutes and polymers as coarse-grained molecular models and treating the solvent molecules using the Boltzmann equation. It has also been proved that Lattice Boltzmann models could be used to relax a system to its minimum free energy and be thermodynamically consistent [156]. However, the lattice models could introduce unrealistic dynamics into the system especially at fluid boundaries and for this reason off-lattice methods could be preferable.

3.6.2 Mesoscale Modelling Techniques: Field Theory Methods

In this section, field theoretic methods are described as an alternative to particle based methods, described above. An overview of the methodology is given and the pros and cons are explained. In general however, these methods are very complicated and the models have not been fully developed for many systems. This has so far limited a widespread implementation of these methods.

At the most basic level, a field theoretic model describes the free energy of a system in terms of phenomenological expressions [144]. For polymeric systems, the main parameters that are commonly used in describing a system are the degree of polymerisation, composition and segment-segment interaction, given as Flory χ parameter through the Flory-Huggins expression.

Phase formation occurs at extrema of the change of free energy with respect to order parameters: Global minimum is the most stable phase, local minima are metastable phases and maxima and saddle points are unstable phases. Thus the framework for self-consistent field theory is as following:

- Given some order parameters, or fields, chain statistics and polymer density are calculated
- Knowing the density, the order parameter or field $\omega(r)$ is self-consistently determined

Therefore, field theory could be a very fast method of modelling polymers. The assumptions for mean field treatment of polymers has been discussed previously in this thesis. The reader could refer to section 2.1.2.

Time Dependent Ginzburg-Landau Theory

This method has been one of the oldest methods of field theory, where the density is defined in terms of a free energy, $F(\phi)$.

Starting from the continuity equation for component i :

$$\frac{\partial \phi_i(\mathbf{r}, t)}{\partial t} = -\nabla \cdot j_i(\mathbf{r}, t) \quad (3.89)$$

Where $\phi_i(\mathbf{r}, t)$ is the density of the component, and $j_i(\mathbf{r}, t)$ is the mass flow into the system. This equation can be rewritten in terms of chemical potential, μ_i and a thermal mass current, $j_T(\mathbf{r}, t)$:

$$j_i(\mathbf{r}, t) = -\sum_j^{n-1} M_{ij} \nabla \mu_j + j_T(\mathbf{r}, t) \quad (3.90)$$

For incompressible binary systems, Equation 3.89 could be rewritten as:

$$\frac{\partial \phi_i(\mathbf{r}, t)}{\partial t} = \nabla \cdot (M \nabla \mu_j + j_T(\mathbf{r}, t)) = \nabla \cdot M \nabla \frac{\delta F[\phi]}{\delta \phi} + \eta(\mathbf{r}, t) \quad (3.91)$$

In this equation, chemical potential given in terms of the free energy functional, $F[\phi]$, and η is a Gaussian random noise. As can be seen from the above equation, there is a methodology where the free energy could be used to calculate the density, but

in order to achieve self-consistency, an expression for the free energy functional F in terms of density is required. Normally, for polymeric systems, this expression is given in terms of the Flory-Huggins free energy density $f_{FH}[\phi(r)]$, with an additional term accounting for the energy of forming an interface between the homogeneous micro-domains,

$$\frac{F[\phi_i(\mathbf{r})]}{k_B T} = \int d\mathbf{r} \left[\frac{f_{FH}[\phi(r)]}{k_B T} + \kappa(\phi) |\nabla \phi(\mathbf{r})|^2 \right] \quad (3.92)$$

Where the Flory-Huggins equation is given by,

$$\frac{f_{FH}[\phi(r)]}{k_B T} = \frac{\phi}{N_A} \ln \phi + \frac{1-\phi}{N_B} \ln(1-\phi) + \chi \phi(1-\phi) \quad (3.93)$$

TDGL methods as well as dynamical density functional theory (DDFT) methods are reliant on the format which has been explained above. The difference between TDGL and DDFT is that in TDGL, the free energy is usually given in Equation 3.93 is simplified to a truncated Taylor series (Landau Form), whereas DDFT does not simplify the equation and solves the path integral numerically. For a full review of DDFT methodology, refer to ref [157]. Additional terms can be added to account for hydrodynamics and viscoelastic behaviour, however as it could be seen, particle based methodology is much simpler and additional terms are not required to simulate materials. This makes implementation of particle based methods preferable to TDGL and DDFT methods. Another disadvantage of DDFT is that it is a mean field theory, and fluctuations are not observed [157].

These dynamic mean field methods have been successfully used to simulate spinodal decomposition in binary and ternary blends and block copolymers, both in bulk and near surfaces. This comes at a loss microscopic detail. However, mean field theories are in general flexible and additional terms can be added to study effects of phenomena such reactions and colloidal dispersions on the phase diagram of polymer. Particle based simulations cannot model reactions accurately.

Self-Consistent Field Theory (SCFT)

Another method of using field theory for complex fluids is self-consistent field theory [37]. It is by far the most advanced method to model very long homopolymer and copolymer melts. The methodology of SCFT is beyond the scope of this thesis, and the reader could render the last reference for an explanation. The theory describes the partition function of a single chain under an external field. This external field acting on the single chain is created by the medium surrounding the single chain. In reality, this medium is made up of many other chains. Thus the conformation of the single chain also affects the external field, as the chain is also acting on the external field. Thus to find the free energy minimum of the system, both the density and the external field need to be refined self-consistently. There is an overwhelming amount of literature on the application of SCFT on the self-assembly long block copolymers which can be observed experimentally.

Comments

Overall field theory methods have certain advantages of being very fast simulations, and may surpass particle based methods in predicting mesophases and morphologies of large scale systems. Moreover, field theory methods define the system in terms of its free energy, unlike particle based methods which calculate energies from mechanical properties (position and velocities). This might make it more theoretically robust. However, the main disadvantage of field theoretical methods is that they are based on the mean field assumptions of no local fluctuations in composition and incompressibility. These models use the Flory χ parameter, which as was described in detail in the previous chapter, is an effective energy term, which is state dependent. Moreover, field theories cannot be strictly used to model polymers in solution, given the local fluctuations in composition.

In this section the aim was to show that there are many techniques that can be used to model mesoscale materials. The key point is identifying which property it is that one needs. In this thesis, the aim is to develop thermodynamically accurate coarse-grained models that unlike most methods, can directly bridge mesoscale

phenomena to underlying molecular interactions. This would lead to a predictive approach to the phase behaviour of soft matter.

Chapter 4

SAFT- γ Mie Equation of State Modelling of Polymers

4.1 Introduction

Understanding the phase behaviour of polymeric systems is important for engineering applications, especially in the context of material and process design. Mixtures of polymers blends and solvents are known to exhibit a variety of different phases [41, 158]. Predicting thermodynamic properties of polymers helps engineers in accessing areas of the phase space where experimental data is scarce. One particular example is that of systems at high pressures, corresponding to polymerisation vessels and separation units containing mixtures of reactants, polymers and byproducts at different compositions [159]. Common applications of polymers in the fluid phase are in the paint and coating industries, and knowledge of interactions of polymers with solvents at different conditions can be used to find solvent blends that can enhance properties of paints [107]. Computer aided mixture/blend design (CAM^bD) methodologies [160] are based on designing optimal solvent mixtures predictably, provided that accurate thermodynamic models exist. Furthermore, knowledge of thermodynamic properties of polymers based on chemistry (di-, tri- or tetra-block copolymers) and structure (linear, branched, star, bottle-brush polymers) is also of importance, as it helps with the design of complex mesoscale particles with tunable properties. This can have useful applications for a whole range of technologies, from semiconductors [161], photovoltaics [162, 163] and advanced drug delivery processes in the pharmaceutical industry, where amphiphilic polymer vesicles can

transport API to targetted regions [164].

For conventional substances, there are many thermodynamic models that can accurately predict phase equilibrium of fluid mixtures. However, these models cannot be easily used for polymers in solution. The simple theory developed by Flory (FH theory) [165] can paint a qualitative picture of the phases of polymer mixtures. For some cases, it is possible to calculate the Flory χ parameter predictively using solubility parameters. However, χ is strongly dependent on the state of the system (temperature, density, composition, molecular weight), and thus the FH theory is not predictive. Moreover, FH theory does not predict the commonly observed LCST behaviour in polymer solutions as χ is inversely proportional to temperature. In terms of conventional thermodynamic models, cubic equations of state and activity based models have been applied to polymer solvent mixtures.

Sako et al. were one of the first to apply cubic EoS to polymers. Their eponymous model [166], called (Sako-Wu-Prausnitz) SWP, is based on the SRK cubic equation of state, with modifications to the excluded volume term. This model is shown to capture the correct phase behaviour of polyethylene hexane mixtures with a temperature dependent adjustable parameter for the cross interactions. Kontogeorgis et al. demonstrated in a study that unmodified cubics can be directly used to model polymer mixtures, with unphysical parameters [167]. New cubic EoS have been developed where the mathematical form of the EoS were not modified, but new mixing rules were proposed so that the excess free energy calculated via common activity models (UNIFAC) could be used to define the values of a and b in the cubic equation [168]. A problem with the use of activity models is that it limits the range of validity of the equation of state, as activity models work well for low pressures. Moreover, many cubic equations require variable adjustable parameters to capture the correct phase behaviour.

Activity models have also been used to model solvent activities in polymer solutions. Common models such as UNIFAC highly underestimate activities of solvents in polymers [85]. This can be improved by applying the concept of free volume, to scale activities of different solvents. These free volume type activity models, such as Entropic-FV [169, 170] and UNIFAC-FV [171], can qualitatively describe liquid-liquid equilibrium (LLE), and are valid for low pressures. Another disadvantage of

activity based models is that these models cannot model single phase, properties of single component polymers such as densities.

Lattice based equations of state form another class of models to study polymer phase equilibria. The advantage of a lattice based description is that polymers are modelled as chains of m segments with each segment sitting on a lattice site, therefore it is easy to derive close-form analytical expressions of the free energy. This is different to cubic EoS where the conformations of molecules are not considered. One of the most popular lattice models is the Sanchez-Lacombe equation of state [172]. It is founded upon the assumptions made in the FH theory, with the major exception that there are vacant sites on the lattice that make the liquid compressible. It is a highly versatile equation of state that can be applied to any molecule. Pure component parameters for polymers can be fitted to PVT data and binary and ternary mixtures can be modelled with high accuracy. Kiran et al. [173] used the Sanchez-Lacombe to study binary and ternary phase behaviour of polyethylene, n -pentane and CO_2 and it was shown that with molecular weight dependent adjustable parameters one could predict the correct UCST and LCST phase behaviour. There is an overwhelming amount of literature [174–176] on phase behaviour of polymers using the SL EoS, which is a testament to its success. However, for many systems, molecular weight dependent adjustable parameters are required to capture the correct critical points for LLE systems.

Finally, *statistical associating fluid theory* (SAFT) type equations of state are one of the most robust methods to model polymeric systems, as they are modelled using free energy perturbation theory. The SAFT model proposed by Huang and Radosz [108], perturbed chain SAFT (PC-SAFT) [113] and simplified PC-SAFT (sPC-SAFT) are the most popular EoS to model polymers. The advantage of the SAFT methodology comes from the fact that it is based on a highly accurate description of a system of molecules interacting with realistic dispersions. These molecules can be modelled as chains of any size. Especially for polymers, the chain contribution to the free energy accurately accounts for the structure of the molecules being modelled, be it the solvent molecule or the polymer. For most flavours of SAFT, pure component parameters are state independent, meaning that the full range of the phase diagram could be accessed without loss of accuracy due to the invalid parameters.

Gross and Sadowski developed PC-SAFT and applied it to binary and ternary mixtures of polyethylene, polypropylene and polystyrene in different solvents at a range of conditions [177]. It was demonstrated that a particular advantage of SAFT techniques to other models is that they can predict phases at high and low pressures. The system could accurately predict binary and even ternary phase behaviour of polymer, solvent and CO₂. Critical points of polydisperse systems could also be predicted. This was further extended to the study cloud point curves of random block copolymers [178]. von Solms et al. [179] simplified the dispersion term of the original PC-SAFT EoS so that parameter estimation could be done faster, with minimal loss of accuracy. sPC-SAFT was then used to develop a group contribution methodology to predict phase behaviour of a range of polymers [180]. Many polymers systems have since been modelled using PC-SAFT and its derivative. Discussing all the literature would be an exhaustive task for this thesis. For a comprehensive review of the systems studied, the reader could refer to ref [181] with an older review given in ref [85].

Even though PC-SAFT has been very successful in capturing the correct phase behaviour of polymeric systems, it suffers from representability at a molecular level. The reference system for the free energy perturbation is not of a hard sphere, but of a hard chain (hence the name perturbed chain). It can be seen that even though it is a very accurate EoS, the parameters cannot be interpreted as intermolecular interactions, but as interchain interactions. Therefore, the number of segments in a PC-SAFT polymer does not have to correspond the number of monomers in the real system, and σ and ϵ parameters interaction parameters do not represent a realistic size or a energy of an underlying intermolecular potential. An important question that comes from this is whether segment parameters used for polymers in PC-SAFT can be transferable to oligomers and smaller molecules. In general, this has not been discussed in great detail in literature as pure component parameters for polymers are fitted to density and experimental LLE or VLE data.

In this chapter, a new flavour of SAFT is used to model polymers. SAFT- γ Mie [27] is a flavour of SAFT where molecules are composed of monomers that interact with the Mie potential. A molecule can be composed of different functional groups

that are tangentially bonded to each other. A new approach is presented by estimating pure component monomer interaction parameters using small molecules containing the monomer functional group. This is done by exploiting the fact that SAFT- γ is a group to contribution equation of state, with molecules that can be composed of different functional groups. The properties of pure polymers are then predicted without any adjustments for a range of temperatures and pressures. In this way a robust set of parameters are found which can be used in small molecules, all the way to the largest of polymers. In mixtures, binary interaction parameters are then fitted if necessary.

SAFT- γ Mie EoS has been used to successfully model amines, n-alkane, alcohols, esters molecules with up to 30 carbons each molecule. Tables of fitted self and cross interaction parameters for many united-atom functional groups, such as CH_3 , CH_2 and aromatic aCH , exist. For the latest set of fitted parameters one could refer to ref [117]. Papaioannou et al. [27] predicted densities of LDPEs in n-pentane, as a function of temperature and pressure. It was also shown that the united atom group contribution methodology could qualitatively predict the UCST phase behaviour of polyethylene in n-pentane. It was also demonstrated that a predictive model for polyethylene was possible, based solely on parameters for polymers fitted to n-alkanes upto n-dodecane. A problem with the united-atom description using SAFT- γ Mie is that due to the small sizes of the functional groups, modelling them as tangentially bonded spheres is not strictly valid, and therefore an adjustable parameter, called the *shape factor* has to be applied to the dispersion term to account for the non-sphericity of the groups. This shape factor improves the transferability of the Mie potential parameters for smaller functional groups used in different molecules, however using a shape factor means that the potential parameters cannot be directly used in molecular simulations. By grouping many united atoms into one segment, interaction parameters with no shape factors can be used to calculate phase diagrams of common materials.

An advantage of this higher coarse-graining is that the parameters can directly be used in molecular simulations to capture exactly the same phase diagram. Lobanova et al. used higher coarse-graining to model ternary mixtures of n-alkanes (upto C_{15}), water and CO_2 with both the EoS and molecular simulations to clearly demonstrate

the validity of the intermolecular interactions used as dispersion terms in the EoS [182]. Rahman et al. [32] followed the same philosophy and estimated CG parameters for n-alkanes where each bead represents 3 united-atom carbons. Pure component VLEs were predicted for n-alkanes upto C₆₀, which for the highest chain length only qualitatively matched experimental results. The alkane models was then used to calculate single phase density of LDPE, which was comparable to experimental data with an absolute average deviation (AAD) of 0.8 percent. In this work, the phase behaviour of polyethylene mixtures was not modelled.

Given the success of SAFT models in modelling phase behaviour of polymers, as well as the very limited study of polymers using the recently developed SAFT- γ Mie EoS, the objective of this chapter is:

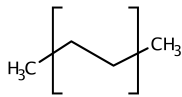
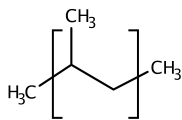
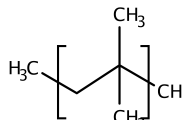
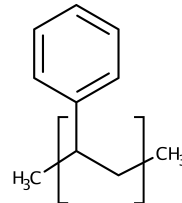
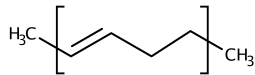
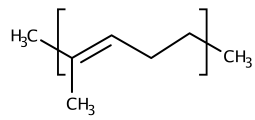
1. Developing a systematic method to find pure component parameters for polymers using SAFT- γ Mie EoS, from small molecules containing monomer units, so that the same parameters could be used to model small molecules all the way to large polymers,
2. Ensuring each monomer represents a chemically realistic functional group, so that the parameters could be used in molecular simulations,
3. Using parameters developed to model phase behaviour of polymer mixtures

4.2 Methodology

In this study, Mie interaction parameters (Equation 3.9) of six polymers were estimated using experimental data for short molecules. Details of each polymer, its corresponding monomer unit, the molecules used to fit the pure component interaction parameters and the coarse-grained mapping are presented in Table 4.1. Coarse-grained mapping is defined as the number of monomer units per one coarse-grained bead. Mapping ratios were chosen to maximise the number of monomers per bead, whilst ensuring the CG models are representable of real fluids.

In SAFT models, a higher mapping ratio corresponds to higher interaction energies and larger spheres. This can be seen in Figure 4.1, where the Mie interactions parameters are plotted against the mapping ratio for n-decane. These parameters were

TABLE 4.1: Polymers studied in this work

Polymer	Abbrev	Monomer	Molecules Used for Parameter Estimation	Mapping*
Polyethylene	PE		n-Hexane, n-Decane, n-Tetradecane, n-Octadecane	4:1
Polypropylene	PP		2,4-Dimethylhexane, 2,4-Dimethylheptane, 2,4-Dimethyloctane, 2,4-Dimethylnonane	2:1
Polyisobutylene	PIB		2,2,4,4-Tetramethylhexane 2,2,4,4-Tetramethylheptane	1:1
Polystyrene	PS		sec-Butylbenzene, 2-Phenylpentane, 2,4-Diphenylhexane	½:1, 1:1
1,4-cis-Polybutadiene	PBD		Hex-3-ene, Hep-3-ene, Oct-4-ene Dec-5-ene	1:1
Polyisoprene	PIP		3-Methyl-3-hexene, 3-Methyl-3-heptene, 4-Methyl-4-octene, 2,6-Dimethyl-2,6-decene	1:1

* Mapping is the number of monomers in one CG SAFT segment

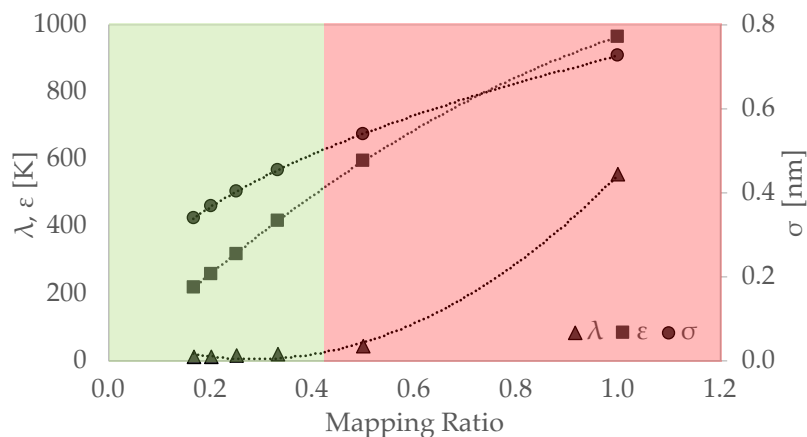


FIGURE 4.1: Mie interaction parameters estimated using VLE data vs mapping ratio for n-Decane. Green and red correspond to regions where parameters are feasible and infeasible in molecular simulations respectively. Lines are a guide to the eye.

estimated using saturation liquid density and vapour pressure. In this case all fitted parameters can reproduce the VLE curve, and a mapping ratio of one corresponds to one molecule of decane being represented by one CG sphere. Ostensibly having a higher mapping ratio is good for molecular simulations, since larger systems can be studied. However, as can be seen from Figure 4.1, increasing the mapping ratio can also lead to extremely high values for ϵ and λ_r . In this instance, a single sphere representation of n-decane has an $\epsilon \approx 970$ K. The melting point of a Lennard-Jones fluid is $T/\epsilon \approx 0.69$ [183] which for the n-decane sphere would correspond to 680 K. It could be seen that this model would be unrealistic to model n-decane at room temperature. Based on this heuristic approach, a constraint was set to limit the number of carbons per bead to around 4-6 carbons, whilst ensuring an integer number of monomers are mapped to one CG bead. The exception to this rule is polystyrene, due to the large size of its monomer. For polystyrene two cases were studied by mapping a monomer to two beads and to one bead. Overall, the molecular weights of each bead ranges from 50 to 100 g mol⁻¹, which is in agreement with molecular weights in PC-SAFT models.

For each polymer, saturation properties of the molecules mentioned in Table 4.1 were used to estimate the parameters of the polymer. Saturation properties are the

TABLE 4.2: Group parameters for the methyl and methylene functional groups (CH₃ and CH₂) taken from ref [117]

Functional Group	S_k [†]	λ_r	ϵ [K] [‡]	σ Å
CH ₃	0.5726	15.05	256.8	4.077
CH ₂	0.2293	19.87	473.4	4.880

[†] S_k is the shape factor, [‡] cross interaction dispersion parameter is $\epsilon_{ij} = 350.772$ K

vapour pressures and saturation liquid densities at different temperatures. An example of this methodology has already been given for polyethylene in section 3.3.1 and the minimisation procedure for parameter estimation explained in section 3.3.2. Parametrisation was done using a python version of the gSAFT software [184] called pySAFT. Moreover, all thermodynamic properties were calculated using this package.

All the molecules mentioned in the table are composed of two or three of the following groups:

- Monomer group,
- Two CH₃ groups, being at the ends of each molecule,
- CH₂ group,

For SAFT- γ Mie EoS, accurate CH₃ and CH₂ parameters exist that have been verified for a range of systems. The parameters are given in Table 4.2 and are taken directly from [117]. As mentioned before, the functional groups CH₃ and CH₂ are too small to be able to be modelled as spheres, and shape factors are used to model them. For some cases, binary interaction parameters between the monomer group and the other two groups were not fitted and Lorentz-Berthelot combining rules (section 3.3.1) were sufficient. However, for PS, PBD and PIP it was necessary to adjust the cross interaction parameters between the CH₃ group and the monomer to find good fits to vapour pressures and saturation liquid densities experimental data of the small molecules.

Once parameters for each monomer were estimated, a polymer was modelled as a chain of 1000 monomers. Liquid phase densities were calculated across a wide range of temperatures and pressures. At this high molecular weight, densities of polymers are no longer a function of their molecular weights, and densities could

be compared to those found in literature. The range of temperatures and pressures used were based on those provided by Rodgers [185]. Rodgers' study contains PVT data for a list of more than 56 polymers, where experimental densities were fitted to 6 different equations of state, with all equations of state having an average error of less than 0.1 percent for all pressures and temperatures up to 500 bar. Estimating interaction parameters of polymers by just fitting them to PVT data is also certainly possible with SAFT, however there is no guarantee whether the parameters can be used to model mixtures. The PVT calculations from SAFT were then compared to fitted parameters given in Rodgers for the Sanchez-Lacombe equation of state, from 1 to 500 bar.

The Sanchez-Lacombe equation for the density of a pure polymer melt is given by [186, 187]:

$$\tilde{\rho} = 1 - \exp[-(\tilde{\rho}^2 + \tilde{P})/\tilde{T} - \tilde{\rho}] \quad (4.1)$$

where $\tilde{\rho} = (\rho/\rho^*)$, $\tilde{P} = (P/P^*)$ and $\tilde{T} = (T/T^*)$ are the dimensionless mass density, pressure, and temperature, respectively, with values of ρ^* , P^* and T^* are variables that are different for different polymers and can be found in Rodgers [185].

Binary mixtures were then modelled using the polymers and solvents. All solvent models are homonuclear, as in all the beads in each solvent are of the same type. Solvent parameters were either fitted using VLE data (vapour pressures and saturation liquid densities), or were taken from ref [34]. Three types of phase diagrams were generated for this work, namely temperature vs composition (either volume or weight fraction), pressure vs composition or pressure vs temperature. Unless stated, for temperature composition diagrams, the pressure at each temperature is at the vapour pressure of the solvent, corresponding to real experimental set up. Finally unless stated, the cross interaction parameters are not adjusted using a constant adjusted parameter k_{ij} .

TABLE 4.3: PE monomer interaction parameters estimated using each molecule, N_{CG} refers to the number of CG monomers in the molecule.

$$M_{W, CG} = 56.108 \text{ g mol}^{-1}$$

Molecule	N_{CG}	N_{CH3}	λ_r	ϵ [K]	σ [Å]	$\Delta\rho$ %	ΔP_V %
n-Hexane	1	2	17.64	438.0	4.712	0.52	0.80
n-Decane	2	2	17.85	437.3	4.694	0.93	1.45
n-Tetradecane	3	2	18.54	442.2	4.680	1.14	1.83
n-Octadecane	4	2	18.64	441.69	4.670	1.51	3.54
PE			21.706	441.69	4.690		

TABLE 4.4: Molecules used to model binary mixtures of polyethylene, with self-interaction parameters and their cross interaction adjustment parameter with polyethylene, $k_{i, PE}$. m_{seg} is the number of CG monomers representing each molecule.

Molecule	m_{seg}	λ_r	ϵ [K]	σ [Å]	k_{ij}
Ethane	1	19.69	308.9	4.212	0
CO ₂ [†]	2	14.14	193.2	2.849	0.05, -0.109
Ethylene	1	20.23	284.5	4.152	0
Propane	1	23.17	395.8	4.809	0
n-Pentane	2	14.75	307.9	4.258	0
n-Hexane	2	18.01	371.1	4.517	0
n-Heptane	2	23.91	436.8	4.770	0
n-Octane	3	16.22	334.2	4.218	0
n-Nonane	3	18.31	374.3	4.383	0
n-Decane	3	21.18	417.4	4.535	0
n-Dodecane	1	23.32	472.2	4.907	0

[†] For mixtures with n-Decane, $k_{ij} = 0.05$ and for solubility of CO₂ in PE $k_{ij} = -.109$.

4.3 Results and Discussion

4.3.1 Polyethylene

As discussed previously, the mapping ratio of PE in this work is 4:1, with four CH₂ groups modelled as one CG monomer. Table 4.3 is a summary of the parameters estimated using four molecules that contain 1 to 4 CG monomers with two CH₃ terminal groups. Data was taken from NIST [188]. It can be seen that for σ and ε the difference between the smallest and the largest molecules are negligible (less than 1 percent), whereas the ratio between λ_r between n-Hexane and n-Octadecane is around 6 percent.

It is not possible to determine why increasing chain length leads to an increase in λ_r , i.e. CG beads are becoming harder, with the attractive region becoming smaller. Mejia and Müller [189] have studied the effect of λ_r on vapour pressures, and increasing the repulsive exponent corresponds to a lower vapour pressures. This could be one reason why the value of λ_r is increasing, as longer chain alkanes might have lower expected vapour pressures. However, experimentally, vapour pressures of longer n-alkanes can be difficult to measure. To find an optimal value of λ_r for larger oligomers and polyethylene, VLE of binary mixtures can be used instead of VLE of pure components.

Consequently, in this work values of σ and ε were chosen to be the average of the values determined via parameter estimation of the molecules mentioned in Table 4.3. However, $\lambda_{r, \text{polyethylene}}$ was determined using VLE of a binary mixture ethylene with a longer n-alkane, namely triacontane, C₃₀H₆₂. From previous works of [66, 177], the interaction parameters of triacontane and polyethylene are very similar, and using the value of λ_r obtained using VLE of the binary mixture of triacontane and ethylene can be used to model all polyethylene chains.

To fit λ_r for PE, triacontane (C₃₀H₆₂) was modelled with 7 CG monomers and 2 CH₃ groups. The VLE phase diagram of the binary mixture of triacontane and ethylene can be seen in Figure 4.3. The value of λ_r was adjusted to fit the model to experimental results. Again no adjustment parameters were used. Gross and Sadowski [177] have previously shown that in PC-SAFT the parameters for polyethylene can

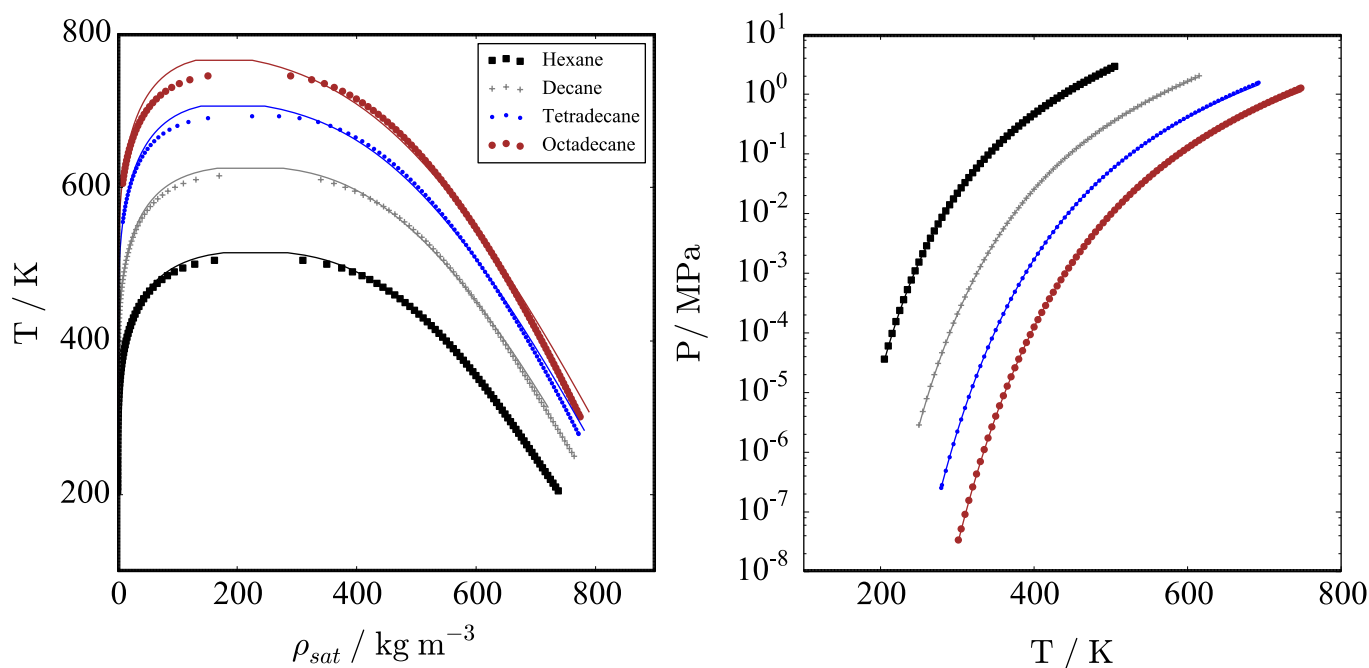


FIGURE 4.2: *Left* Temperature-density coexistence envelopes of n-Hexane to n-Octadecane, *Right* Corresponding vapour pressures, the description with SAFT- γ Mie model (continuous curves) is compared with data taken from NIST (symbols).

be used to model the VLE of triacontane with ethylene. Therefore, λ_r fitted for this mixture was used to model all polyethylene molecules.

Overall, four-to-one mapping has a better performance relative to alkane models previously studied, especially for the case of octadecane where Rahman et al. reported errors of 13% in vapour pressure and 3% in saturation liquid density [32]. This could be explained by the fact that in that study parameters were only fit to molecules up to dodecane and this trend in λ_r was not observed. In Figure 4.2, vapour-liquid coexistence densities and vapour pressures of pure components of the molecules used in the parameter estimation are presented. It can be clearly seen that all four models describe the phase envelopes accurately. The critical point is over predicted with increasing number of CG monomers, which for n-octadecane the difference to experimental data is 3.1 percent. A preliminary assessment of our models' ability to capture phase behaviour of binary mixtures of small alkanes with gases is presented in Figure 4.4, with the small alkane being n-decane and the gases being ethane and CO_2 . Ethane and CO_2 were modelled as one bead and two bead molecules respectively. For mixtures of n-decane and ethane, the cross interaction

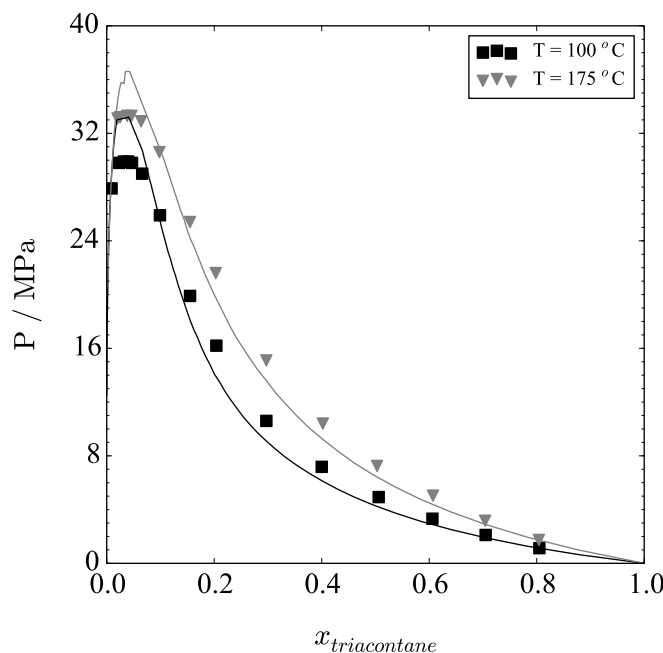


FIGURE 4.3: Isothermal pressure-composition of triacontane with ethylene at 100 °C and 175 °C. The value of λ_r for PE presented in Table 4.3 was estimated using this VLE data. Triacontane is modelled with 7 CG monomers and 2 CH₃ groups. Circles are experimental results taken from [190].

parameters were calculated using combining rules and with no adjustable parameters. It could be seen that apart from regions of higher pressures, SAFT- γ VLE description of n-decane-ethane corresponds to that of experimental results. For CO₂, it was not possible to capture the correct phase behaviour, and a k_{ij} was used to minimise the error between the model and experiments. $k_{ij} = 0.05$ was found to be the optimal value.

Moreover, for mixtures of small n-alkanes, namely n-hexane and n-decane, the excess speed of sound was predicted with comparison to experiments presented in Figure 4.5. The correspondence between the model and the experimental results shows the robustness of the CG parameters.

The PE parameters were then used to predict LLE of a small oligomer of polyethylene, namely n-hexacontane, C₆₀H₁₂₂ with propane. 14 CG beads and two terminal CH₃ groups were used in this model, which does not exactly correspond to n-hexacontane, but to C₅₈H₁₁₈. However, as can be seen from Figure 4.6, the phase behaviour is accurately predicted, with a slight over-prediction of the critical point. This slight difference can be due to both experimental error and polydispersity in the

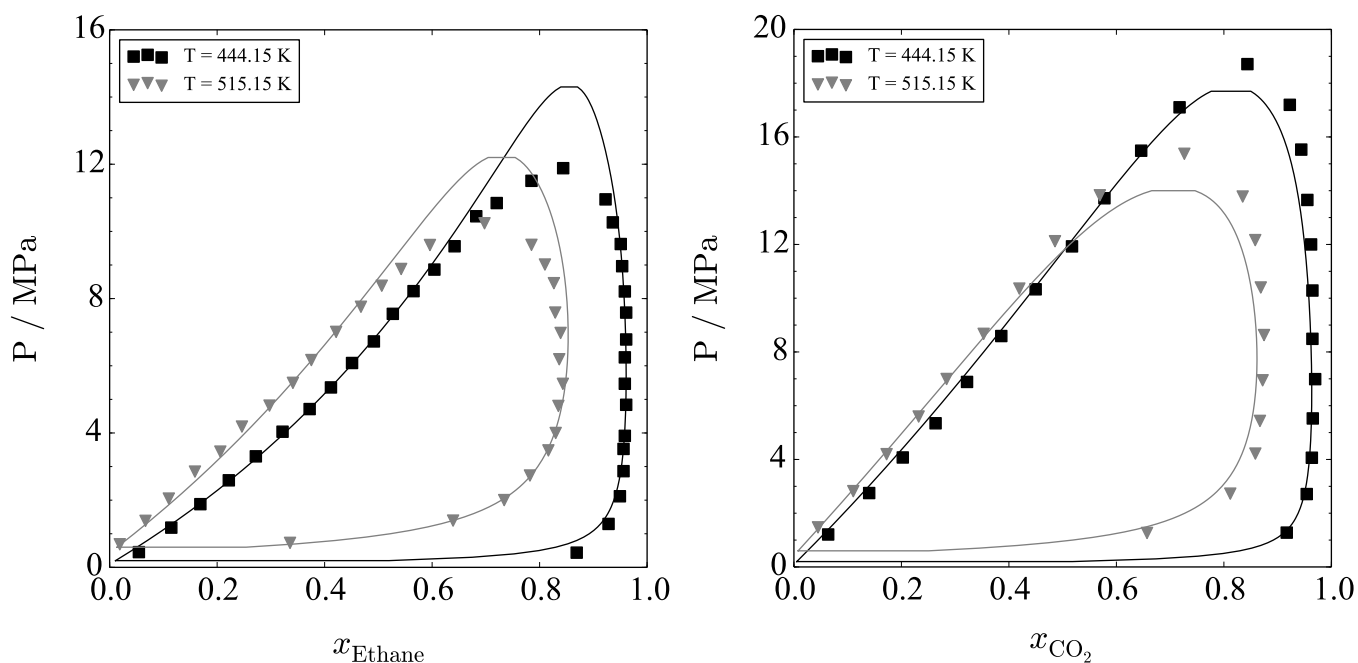


FIGURE 4.4: Isothermal pressure-composition of n-decane with **Left** ethane and **Right** CO₂ at 444.15 K and 515.15 K, for ethane no adjustable parameters were used, and for CO₂ $k_{ij} = 0.05$, symbols are experimental results taken from ref [86].

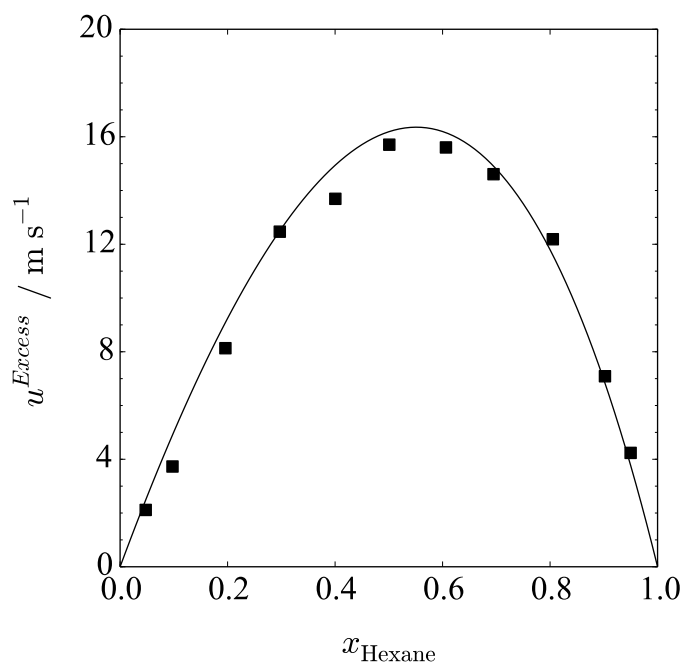


FIGURE 4.5: Prediction of the excess speed of sound of a binary mixture of n-hexane and n-decane (continuous curve), compared with experimental results [191] (symbols).

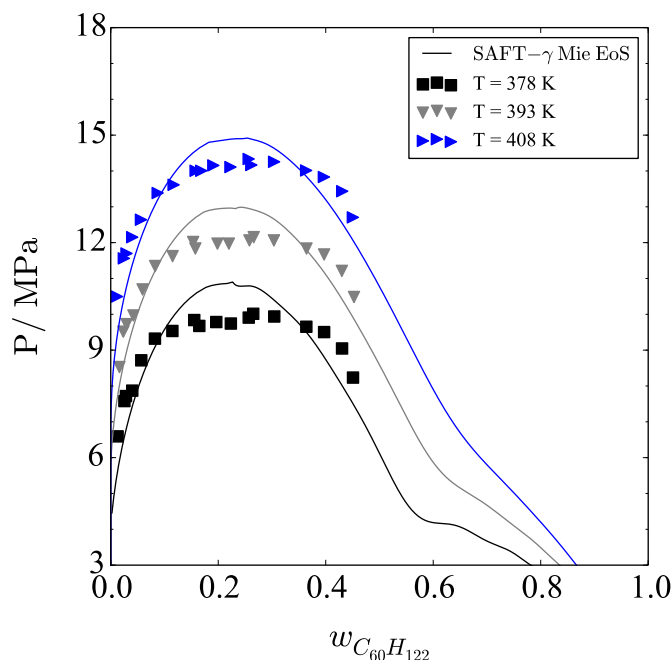


FIGURE 4.6: Liquid-liquid equilibrium of n-hexacontane ($C_{60}H_{122}$) and propane. Symbols are experimental data [192, 193] and the continuous curves correspond to the predictions of the model.

experimental set up. Modelling such a long alkane (M_W of 840 Da) with a representation of only 14 beads is very promising, especially in terms of molecular simulations.

Given the robust parameter developed and tested for small oligomers, density of polyethylene across a range of pressures and temperatures was calculated for a polymer of 1000 monomers. The results were compared to high density polyethylene (HDPE) PVT data, using Sanchez-Lacombe EoS with parameters fitted using experimental data by Rodgers [185]. Figure 4.7, is the comparison between the predictions in this work and SL fitted using PVT experimental data. Densities between our model and the SL EoS fit are very similar, with a larger difference observed at lower temperatures. There is a 1% error between the two data at the lower pressures. In contrast, at high pressures both models give the same densities. The AAD for the whole range is 0.5%.

Phase Behaviour of Polyethylene Solutions

Polyethylene is known to exhibit both LCST and UCST phase behaviour. Therefore, in this work a range of different systems was studied to assess the predictive nature of

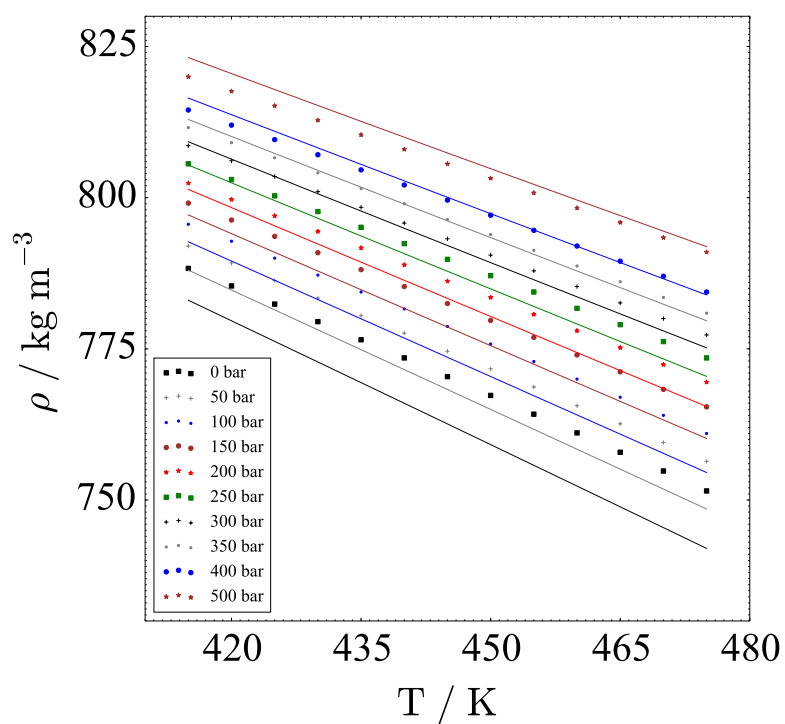


FIGURE 4.7: PVT of polyethylene, lines correspond to calculations using SAFT- γ Mie, and symbols correspond to SL EoS fitted using experimental PVT data from Rodgers [185]

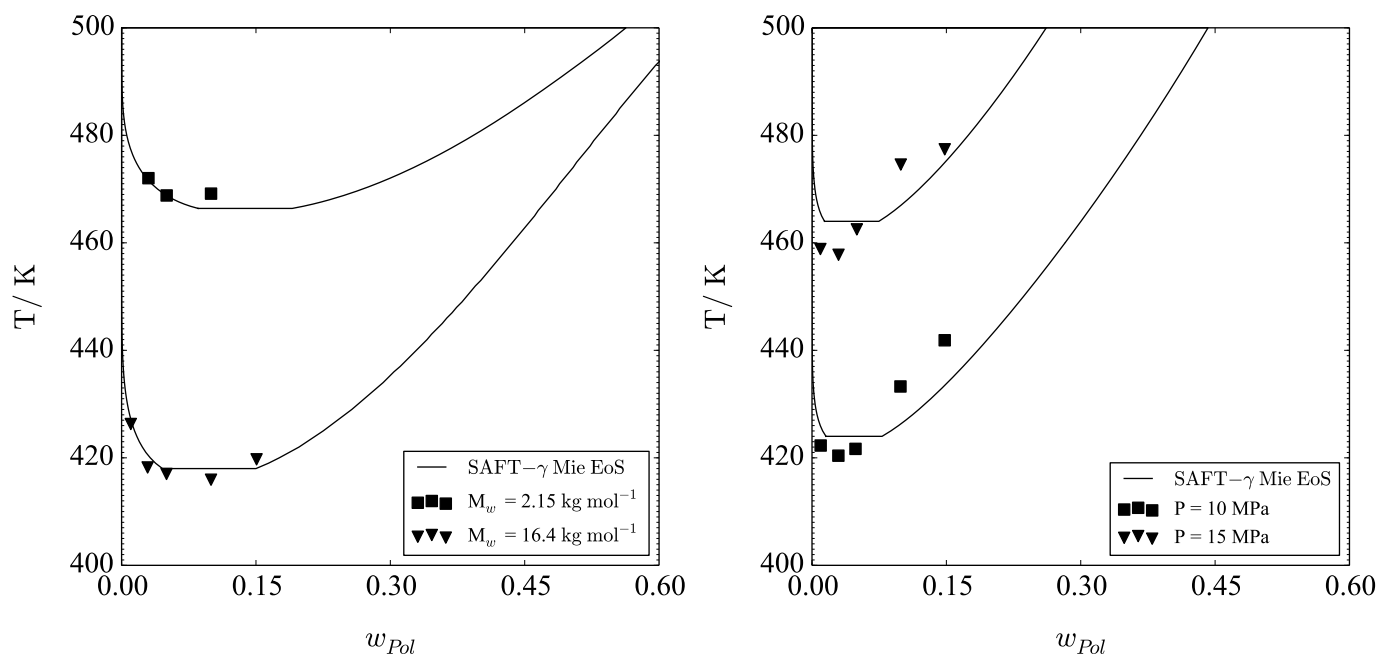


FIGURE 4.8: LCST phase behaviour of polyethylene in n-pentane. **Left** The effect of the M_W on the phase envelope, for a fixed pressure of 5 MPa. **Right** The effect of pressure on the phase envelope for a fixed M_W of 108 kg mol⁻¹ (Corresponding to 1982 CG beads). Model is fully predictive with no adjustable parameters, and symbols are taken from ref [194]

the model. The first two systems studied were that of PE in n-pentane, which has been previously studied by Paricaud et al. [66]. In that study, SAFT-VR Square-Well was used to parametrise small n-alkanes using VLE data and polyethylene parameters were correlated from those parameters.

It was found that their polyethylene model was robust, however the model could not predict the correct trends in the LCST phase behaviour when molecular weight was a variable at fixed temperature and pressure. Figure 4.8 shows the LCST phase behaviour of HDPE in n-pentane, with temperature, pressure and M_W as variables. First, the effect of molecular weight on the phase envelope was assessed, by keeping the pressure constant at 5 MPa. Two different molecular weights, 2.15 kDa and 16.4 kDa, were used which correspond to 39 and 292 CG beads respectively. The model is fully predictive capturing both the critical point and the shape of the phase envelope. In the second case, the M_W was kept constant and pressure was varied. Again the phase behaviour is predicted very accurately. Consequently, the UCST of 140 kDa PE in a range of alkanes was predicted. In this instance, the solvents

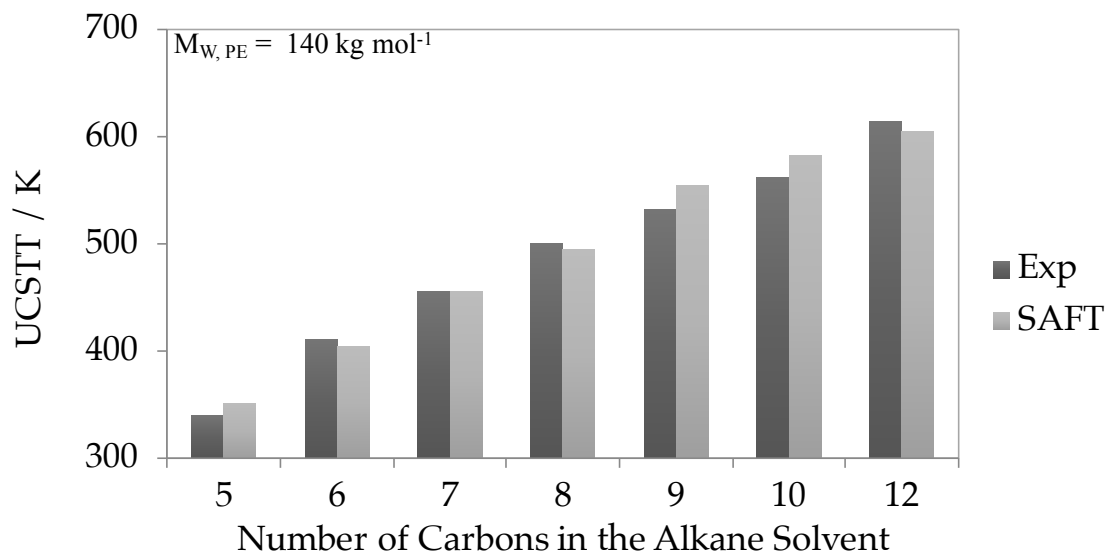


FIGURE 4.9: UCST temperatures of PE (140 kDa) in n-alkanes, compared with experimental data cited in ref [66], in this instance parameters for the n-alkanes were fitted to VLE data using from NIST

TABLE 4.5: Components representing a polydisperse system, as modelled by Gross and Sadowski [177]. For this three pseudo-component mixture, $M_N = 43$ kDa, $M_W = 112$ kDa and $M_Z = 231$ kDa

pseudo-component	M_N	Mass Fraction
1	2 767.6	0.035 096 52
2	83 769.0	0.868 629 42
3	468 830.0	0.096 274 06

were fitted using VLE data, and were all modelled as homonuclear chains, with parameters presented in Table 4.4. Again, this CG mapping is robust, and the upper critical solution temperatures are predicted without any adjustable parameters. The comparison between experimental results and our model can be seen in Figure 4.9.

Solubility of CO_2 in PE was calculated, as previously modelled with PC-SAFT in ref [177]. The comparison between the experimental data and SAFT- γ EoS is presented in Figure 4.10. Gross and Sadowski predicted the correct trend of CO_2 in PE, whereas here the solubility is only in qualitative agreement with experimental data found in ref [195]. However, it is interesting that the $k_{ij} = -0.109$ value used to fit to experimental data is less than the PC-SAFT value of $k_{ij} = 18\%$. The error between experimental results and our model is less than 1%.

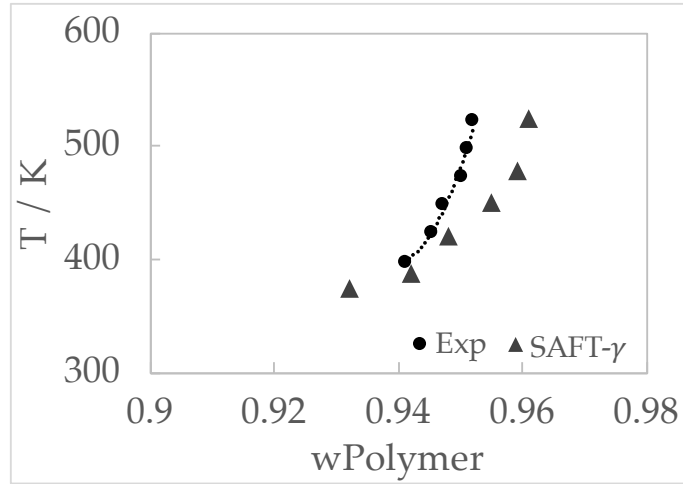


FIGURE 4.10: Solubility of CO₂ in PE at P = 90 bar, with experimental taken from ref [195]

Finally, to see if the model is robust enough to capture the effects of polydispersity predictively, a polydisperse PE-solvent mixture is modelled based on a method proposed by Gross and Sadowski [177]. Polydisperse systems can be modelled with a finite number of molecules that have the same molecular weight distributions as the experimental data. Having a finite number of pseudo-components with different chains allows one to qualitatively capture the phase behaviour of a polydisperse system with an equation of state. Gross and Sadowski modelled a polymer with $M_N = 43$ kDa, $M_W = 112$ kDa and $M_Z = 231$ kDa, using three pseudo-components. First, liquid-liquid equilibrium was calculated for the four component mixture using the EoS. In each phase, the weight fraction of polymer is given by $w_{Polymer} = 1 - w_{solvent}$. This is strictly not true thermodynamically, as there is more than one polymer component present in the mixture. However, phase equilibria of polydisperse systems are measured in this way experimentally, and modelling polydisperse systems using an EoS accurately could significantly help in designing process units.

The aforementioned polydisperse system used by Gross and Sadowski (PC-SAFT) is modelled here, with the molecular weight and the weight fractions of each pseudo-component of polyethylene given in Table 4.5. Figure 4.11 shows the results for the polydisperse mixture of polyethylene in ethylene. In this instance $k_{ij} = -0.002$ is

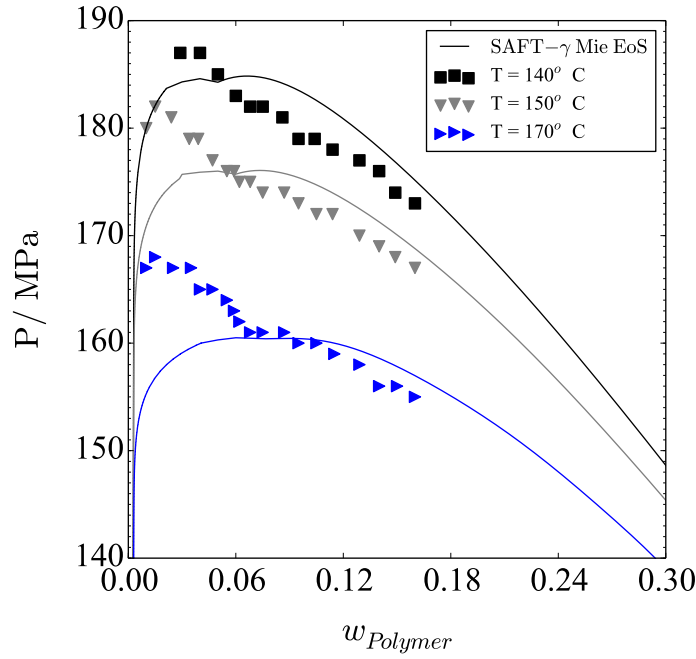


FIGURE 4.11: UCST phase behaviour of polydisperse PE in ethylene, with $M_N = 43$ kDa, $M_W = 112$ kDa and $M_Z = 231$ kDa. In this instance $k_{ij} = -0.002$, which is an extremely small adjustment. Symbols are experimental data taken from [196]

found to produce the experimental results. This is extremely small and almost negligible. In comparison, Gross and Sadowski used a k_{ij} of 0.0404 to capture the correct phase behaviour. The experimental data indicate a bimodal pressure-composition distribution, which is not observed with the models in this work. This bimodal distribution could be the effect of polydispersity [197], which is not accurately captured with the SAFT model. The PE model presented here qualitatively agrees with the polymer trends, with the shape of the phase envelopes being different at lower polymer compositions ($w_{polymer}$) and more consistent at higher polymer compositions. This is in contrast with the PC-SAFT model, where the phase envelope was only accurate at lower $w_{polymer}$.

It can therefore be seen that SAFT- γ Mie EoS can accurately, and predictably model polyethylene with minimum number of cross interaction adjustable parameters.

TABLE 4.6: PP CG monomer interaction parameters

Molecule	$M_{w, CG}$ [g mol ⁻¹]	λ_r	ε [K]	σ [Å]
PP	84.16	24.94	571.6	5.51

4.3.2 Polypropylene

SAFT- γ representation of polypropylene (PP) is one where two monomers of polypropylene ($\text{CH}_2\text{CH}(\text{CH}_3)$) are mapped onto one CG bead. Finding VLE data for molecules containing two monomers of polypropylene is difficult. Unfortunately, for this case study, the only type of alkanes used to fit the model contained only two monomers of polypropylene. Thus instead of finding trends in σ , λ and ε as a function of molecular weight, the parameters were fit using data of all molecules with equal weighting. Parameters used to model propylene are given in Table 4.6, and errors associated with using those parameters in modelling each molecule given Table 4.7. In this instance, the cross interaction parameter between PP CG bead and CH_2 was also adjusted to minimise the error between the model and experimental data. The interaction with CH_3 group was not adjusted. It could be seen that with increasing chain length, the errors in density do not increase. However, errors in vapour pressure increase with increasing chain length. The reason for this might be due to the interaction of CH_2 group with PP, however, given that the parameters in Table 4.6 were found to be the optimal ones, adjusting the cross interaction parameters would result in a higher error across all four models. Thus it was decided to stay with these parameters.

The coexistence phase diagrams are presented in Figure 4.12, and it is clear that the model parameters are robust enough to reproduce experimental data for these small chains, with deviations only seen for the vapour pressure of 1,2-dimethylnonane at lower temperatures.

To assess the validity of the parameters in modelling propylene, first the PVT of 1000 CG segments polypropylene is calculated for a range of pressures and temperatures, and compared to those calculated using SL parameters given in Rodgers [185]. The PVT calculations are presented in Figure 4.13, and in this instance, the results match the experimental data, with an average error of 0.1%. The polyethylene PVT

TABLE 4.7: PP CG monomer interaction parameters used in Table 4.6 are fitted using the following molecules, with N_{CG} defined the same way as in Table 4.1

Molecule	N_{CG}	$N_{CH_3}^+$	$N_{CH_2}^+$	$\Delta\rho$ %	ΔP_V %
2,4-Dimethylhexane	1	2	0	2.04	3.21
2,4-Dimethylheptane	1	2	1	2.96	2.76
2,4-Dimethyloctane	1	2	2	2.44	5.7
2,4-Dimethylnonane	1	2	3	2.92	8.7

[†] Polypropylene interaction parameter between monomer and CH_3 was not adjusted, however for CH_2 the cross interaction energy, ϵ_{ij} , was set to 470 K.

TABLE 4.8: Molecules used to model binary mixtures of polypropylene, with self-interaction parameters and their cross interaction adjustment parameter with polypropylene, $k_{i, PP}$. m_{seg} is the number of CG monomers representing each molecule.

Molecule	m_{seg}	λ_r	ϵ [K]	σ [Å]	k_{ij}
CO ₂	2	14.14	193.2	2.849	-0.166
Propane	1	23.17	395.8	4.809	-0.102
n-Pentane	2	14.75	307.9	4.258	-0.061

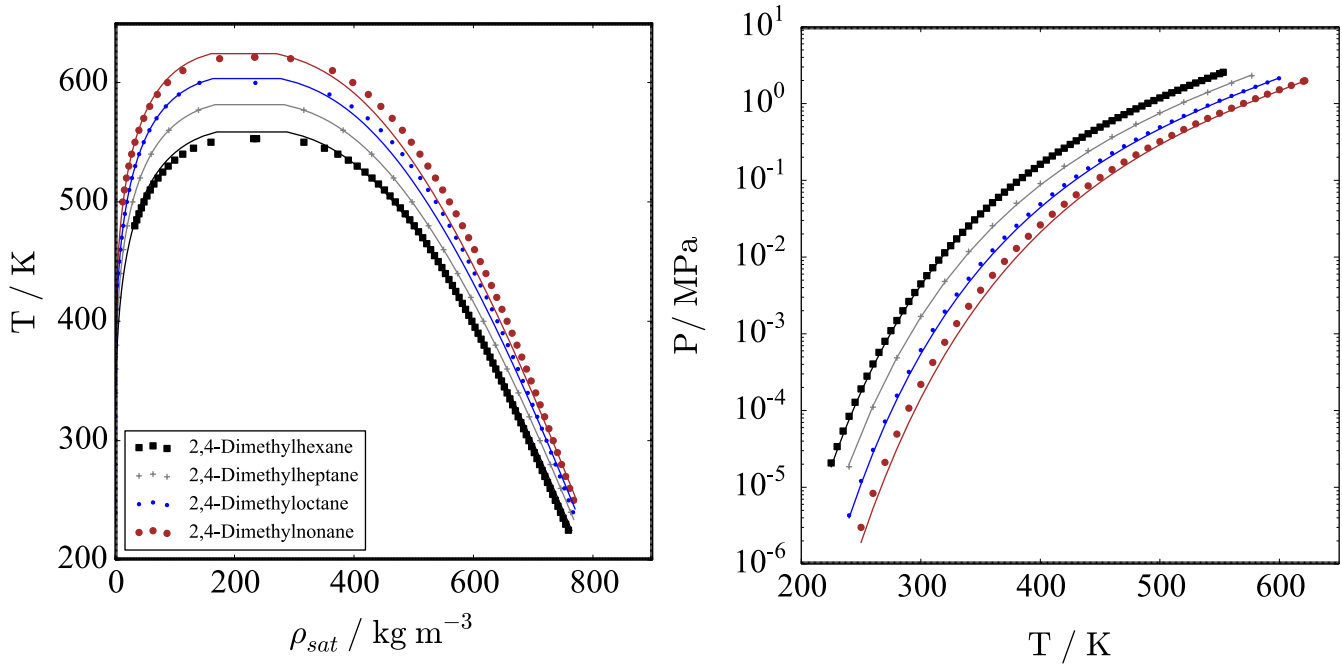


FIGURE 4.12: **Left** Temperature-density coexistence envelopes of 2,4-Dimethylhexane to 2,4-Dimethylnone, **Right** Corresponding vapour pressures, the description with SAFT- γ Mie model (continuous curves) is compared with data taken from NIST (symbols).

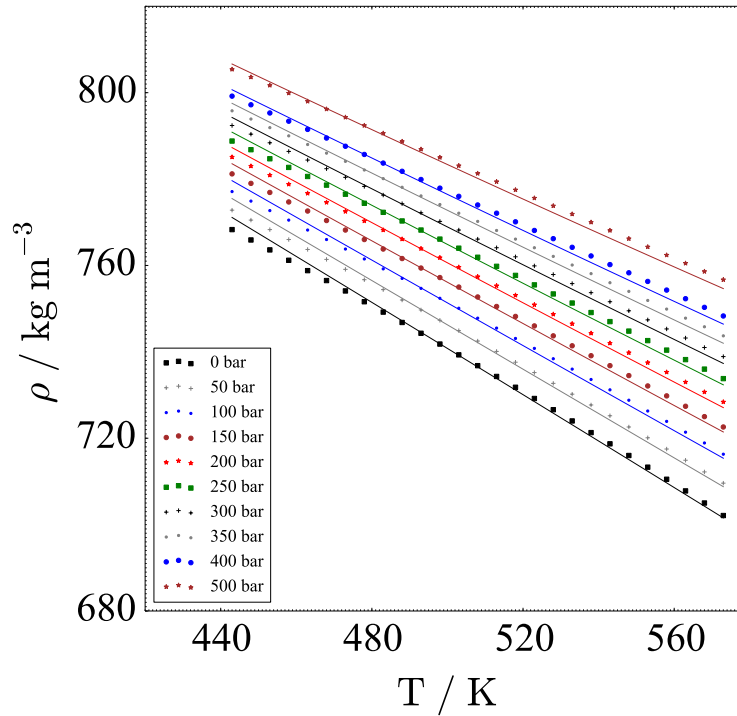


FIGURE 4.13: PVT of polypropylene, lines correspond to calculations using SAFT- γ Mie, and symbols correspond to SL EoS fitted to experimental PVT data from Rodgers [185]

calculations showed a more compressible fluid than that of the experimental data, but here the isothermal compressibility of the model prediction matches that of a real PP polymer. This is because of the level of course-graining done for PP, where the monomer is larger and therefore less compressible (refer to Figure 4.1). Overall, the PVT prediction is a good evidence that the parameter estimation was done robustly.

In following the same process as in the study of PE, the first binary mixture studied with polypropylene is that of PP-n-pentane mixtures. Here, a $M_W = 50.4$ kDa polypropylene ($M_W/M_N = 2.2$, $N_{CG} = 600$ beads) is modelled in n-pentane with the results presented in Figure 4.14. Again following the work of Gross and Sadowski, PP was modelled as a monodisperse polymer. Due to this assumption, unlike the case of polyethylene, calculations only agree in the value of the critical pressures, and the shape of the phase envelope is not similar to that of the experimental data. The difference in critical pressures between calculated and experimental data

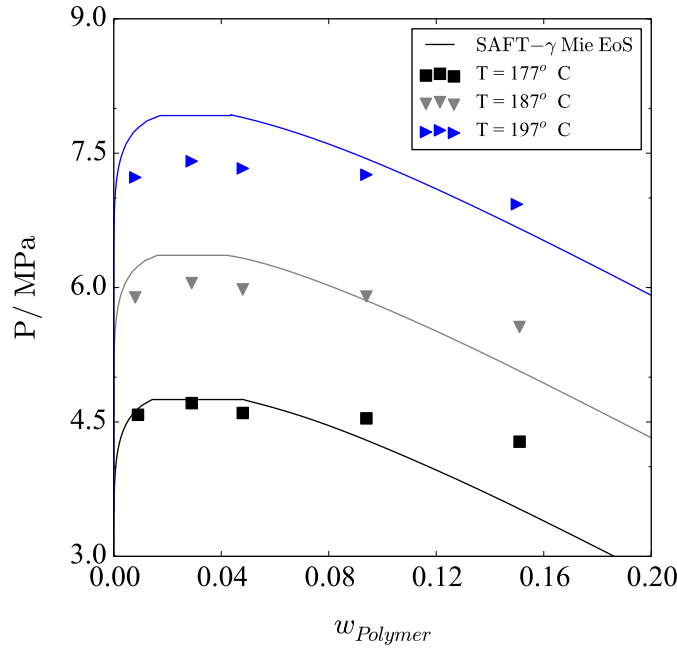


FIGURE 4.14: UCST phase behaviour of $M_W = 50.4$ kDa polypropylene ($M_W/M_N = 2.2$) in n-pentane. Phase diagram calculated assuming a monodisperse system. Symbols are taken from ref [198].
 $k_{ij} = -0.061$

is 3.1%. Another key difference between this model and that of polyethylene is that for PP-n-pentane mixture, a k_{ij} is needed to predict that phase diagram. This could be because in this model, a CG bead contains 6 carbons, and the scale of coarse-graining is higher. Although this is good for molecular simulations, this level of coarse-graining ultimately leads to averaging too many degrees of freedom in the coarse-graining process and therefore mixtures can only be modelled with binary interaction parameters. This discrepancy between the sizes of the polymer CG bead and that of the solvents could have connotations on the transferability of the parameters. It is therefore needed to test if a single state-independent binary interaction parameter could capture the entire phase diagram of polypropylene.

To assess the validity of using a single value of k_{ij} for all ranges of pressures and temperatures, the ternary PT phase diagram of polypropylene-CO₂-n-pentane was modelled using the same molecular weight polypropylene as that presented in Figure 4.14. To model this ternary mixture, first the cross interaction parameter, k_{ij} between n-pentane and CO₂ had to be estimated. This was done by using VLE data

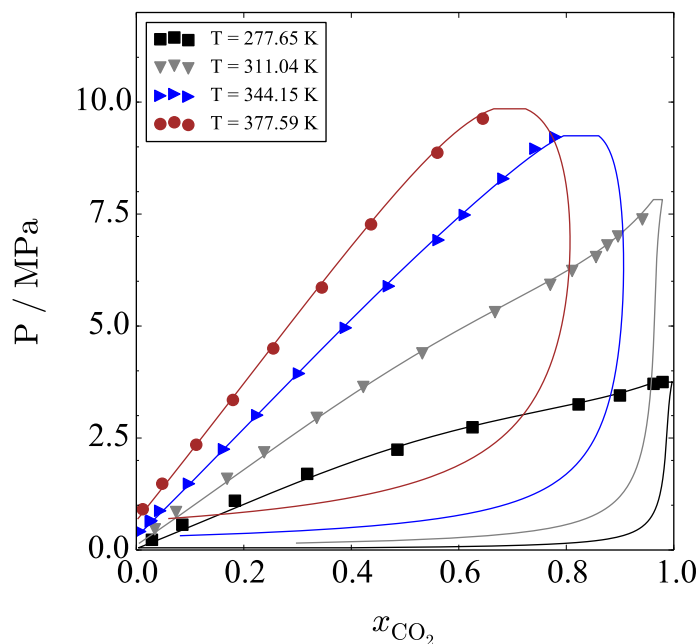


FIGURE 4.15: VLE of CO₂ and n-pentane mixture. Line represent our model and symbols are taken from ref [199]. $k_{ij} = -0.05684$.

found in ref [199], using the self-interaction parameters given in Table 4.8. VLE envelope of n-pentane-CO₂ is presented in Figure 4.15. It is clearly seen that our model parameters are robust and could accurately capture the VLE of simple molecules.

Given that the binary interaction parameter of PP is known with n-pentane and the binary interaction parameter of n-pentane and CO₂ was also calculated, it is now possible to model ternary phase diagrams of n-pentane-PP-CO₂. However, the final piece of the puzzle, i.e. the binary interaction parameter between CO₂ and PP, was yet to be determined. This was done by adjusting the cross interaction parameter in order to match the experimental ternary mixture data. The ternary PT diagram is presented in Figure 4.16. Two PT diagrams are presented at two different polymer compositions. The composition is defined as the global weight fraction of PP in a binary mixture of n-pentane-PP in the absence of CO₂. The k_{ij} parameters between PP and all solvents are given in Table 4.8. Again, the correspondence between the experimental data and the model gives further confidence that this approach is robust, with parameters being transferable across all temperatures and pressures. In reality only one point in the binary or ternary phase diagram is required to fit binary cross interaction parameters that are applicable everywhere in the phase space.

TABLE 4.9: Components representing a polydisperse propylene, as modelled by Gross and Sadowski [177]. For this three pseudo-component mixture, $M_N = 65.91$ kDa, $M_W = 290$ kDa

pseudo-component	M_N	Mass Fraction
1	35 761	0.508 437 58
2	504 684	0.479 290 585
3	2 438 723	0.012 271 832

It could be seen that although the PP parameters were found using molecules containing only one CG bead, the parametrisation approach is still valid.

Finally, following the same process as that of the polyethylene section, a polydisperse PP polymer is modelled with propane as the solvent. Again, the system studied by Gross and Sadowski is used to model the PP with $M_W = 290$ kDa and $M_W/M_N = 4.46$. The pseudo-components representing the polydisperse polymer mixture are described in Table 4.9. The comparison of experimental results with our model is shown in Figure 4.17. Again the cross interaction parameter had to be adjusted to capture the correct phase behaviour ($k_{ij} = -0.102$). In this case however, the shape of the phase envelope as well as the critical points are captured with quantitative accuracy.

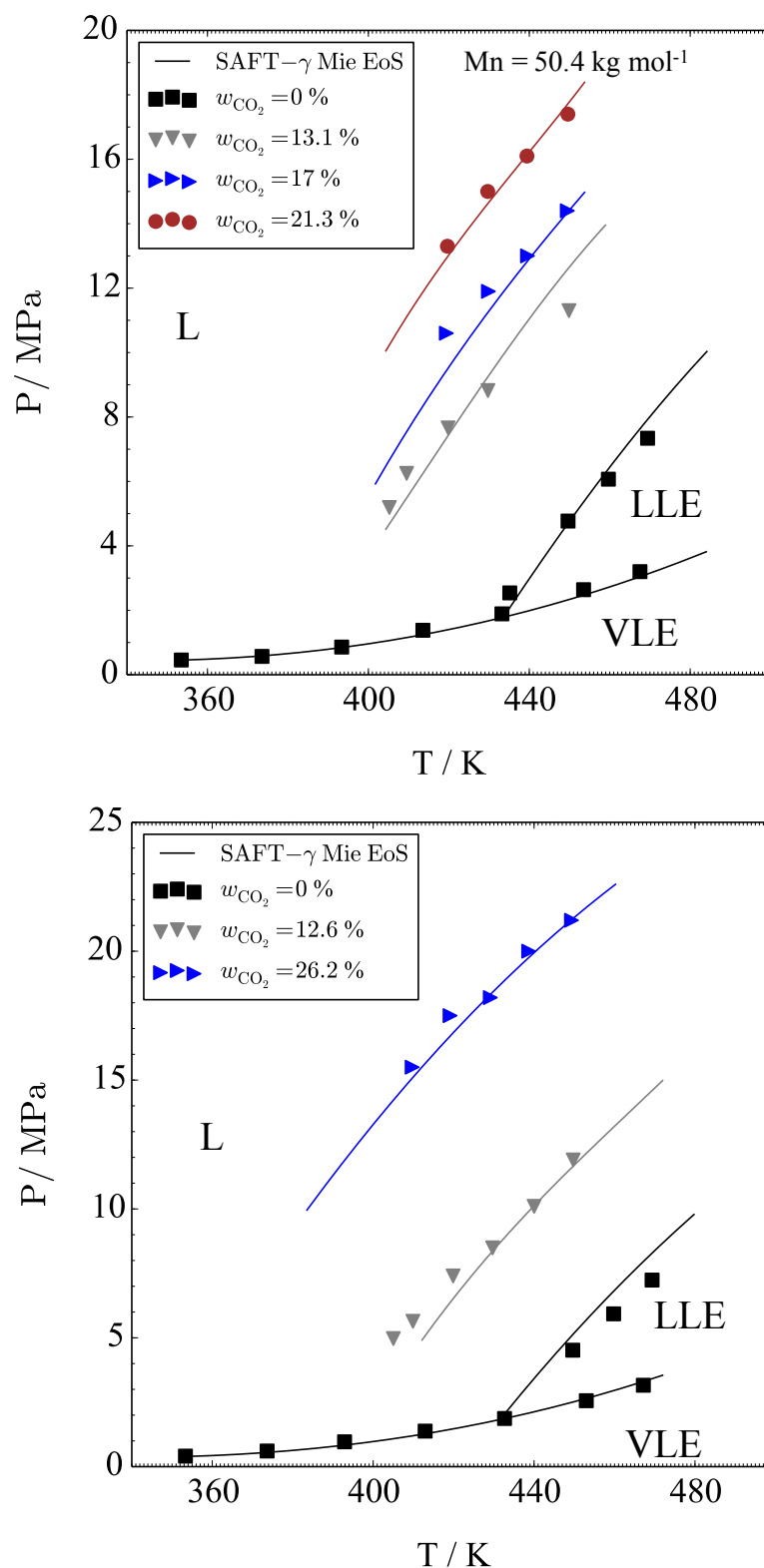


FIGURE 4.16: PT diagram of a ternary mixture of polypropylene, n-pentane and CO₂. In the absence of CO₂, the mass fraction of PP in n-pentane is $w_{\text{polymer}} = 0.03$ (Top) and $w_{\text{polymer}} = 0.097$ (Bottom). Black lines correspond to the coexistence lines of a binary mixture of n-pentane and PP. Coloured lines correspond to the LCST of the ternary mixture at different concentrations of CO₂. Binary interaction parameter of CO₂ PP was fit to the experimental data at the highest CO₂ concentration, $k_{ij} = -0.166$. Continuous lines correspond to SAFT- γ Mie model and symbols are data taken from ref [198].

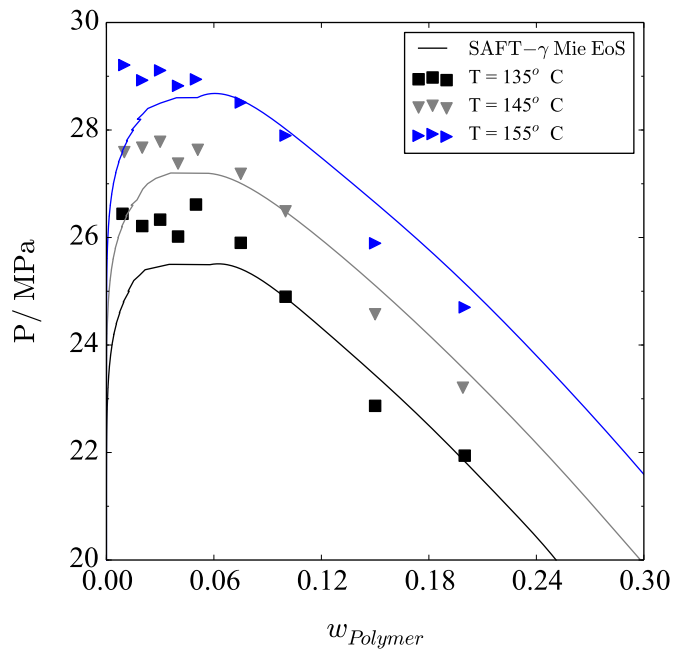


FIGURE 4.17: UCST behaviour of PP ($M_W = 290$ kDa, $M_W/M_N = 4.46$) in propane at high pressures. Lines represent our model, using 3 pseudo-components to model polydispersity. Symbols are taken from ref [200]. $k_{ij} = -0.102$.

TABLE 4.10: Polyisobutylene CG monomer interaction parameters

Molecule	$M_{W, CG} [g \text{ mol}^{-1}]$	λ_r	$\epsilon [K]$	$\sigma [\text{\AA}]$
PIB	56.108	10.23	291.4	4.52

TABLE 4.11: PIB CG monomer interaction parameters used in Table 4.10 are fitted using the following molecules, with N_{CG} defined the same way as in Table 4.1

Molecule	N_{CG}	$N_{CH_3}^\dagger$	$N_{CH_2}^\dagger$	$\Delta\rho \%$	$\Delta P_V \%$
2,2,4,4-Tetramethylhexane	2	2	0	2.10	4.94
2,2,4,4-Tetramethylheptane	2	2	1	2.54	4.71

[†] PIB interaction parameter between monomer and CH_3 and CH_2 was not adjusted.

4.3.3 Polyisobutylene

Modelling polyisobutylene using the same mapping as PP (2:1) is not realistic, as 8 carbons have to be coarse-grained into one bead (i.e. problem of high mapping ratios demonstrated previously in Figure 4.1 with ϵ being too deep). For isobutylene a mapping of 1 monomer to 1 CG bead was used. Just like the case of polyethylene, each CG bead represents four carbons. Again, PVT phase diagram of polybutadiene was predicted with the method explained before, with the comparison presented in Figure 4.19. The PVT results are predictions, and they are in quantitative agreement with the SL EoS fits. The PIB model in this work is slightly more compressible than the experimental data correlated with SL EoS. Overall, the AAD of the PVT is 0.5%.

The phase diagram of mixtures of this polymer was not investigated in great detail as the previous two polymers, as it has been shown that SAFT- γ Mie EoS does capture the correct phase behaviour of polyolefins. In this case, however, LCSTs of PIB ($M_W = 112$ kDa) were predicted for a range of solvents. The LCSTs were calculated without any binary adjustable parameters. The results can be seen in Figure 4.20. The solvents used are alkanes and benzene, with size, structure and chemistry of the solvents being variables. Remarkable agreement is observed, with the predictions being better than that of the SL EoS. For all cases studied, the AAD was 2.61%. The model correctly predicts that branched isomers of alkanes have a lower LCST than the linear ones, and that cyclo-alkanes are more miscible with PIB. Miscibility also increases with increasing molecular weight of the solvent. Finally, miscibility of benzene was also correctly predicted.

TABLE 4.12: Molecules used to model binary mixtures of polyisobutylene, with self-interaction parameters and their cross interaction adjustment parameter with PIB, $k_{i, \text{PIB}}$. m_{seg} is the number of CG monomers representing each molecule.

Molecule	m_{seg}	λ_r	ε [K]	σ [Å]	k_{ij}
n-Pentane	2	14.75	307.9	4.25	0
Cyclopentane	2	13.37	309.8	4.00	0
Isopentane	2	13.81	289.1	4.23	0
Hexane	2	18.01	371.2	4.52	0
2,2-Dimethylbutane	2	14.17	311.5	4.47	0
2,3-Dimethylbutane	2	14.83	328.1	4.46	0
Cyclohexane	2	13.3	338.7	4.24	0
Heptane	2	21.27	427.0	4.77	0
Octane	3	14.30	314.7	4.22	0
Benzene	2	13.43	346.7	3.98	0

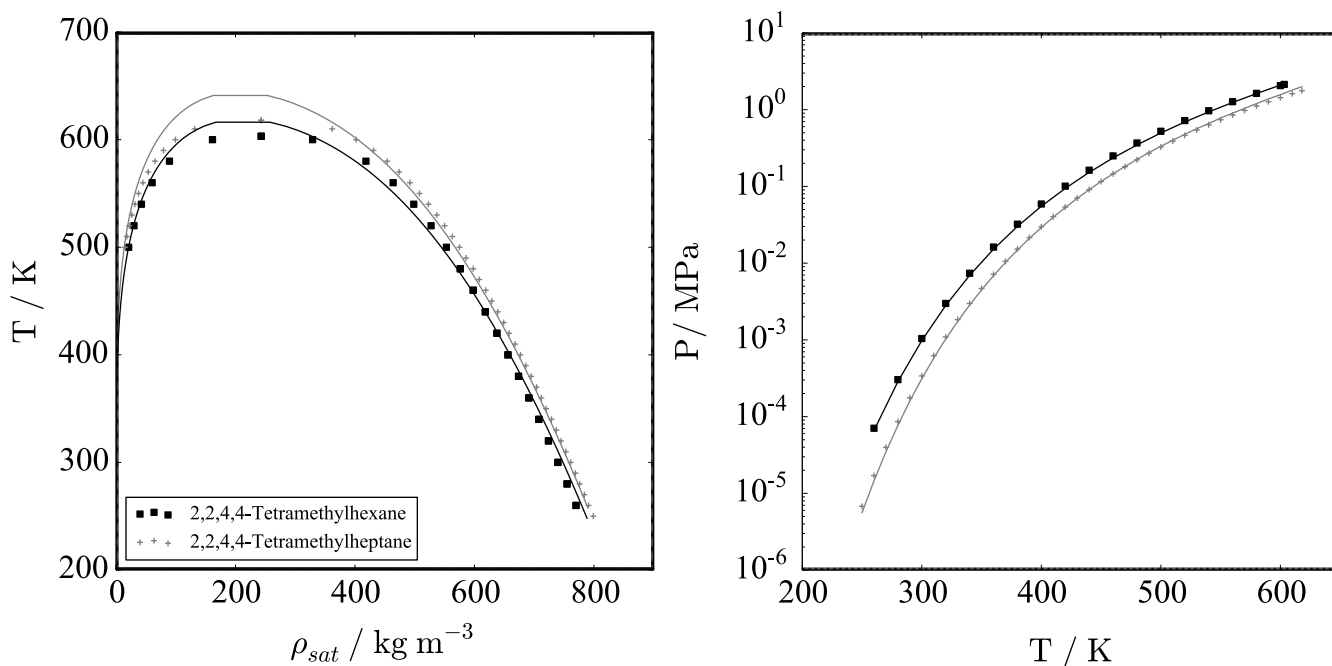


FIGURE 4.18: **Left** Temperature-density coexistence envelopes of 2,2,4,4-Tetramethylhexane and 2,2,4,4-Tetramethylheptane used to model polyisobutylene, **Right** Corresponding vapour pressures, the description with SAFT- γ Mie model (continuous curves) is compared with data taken from NIST (symbols).

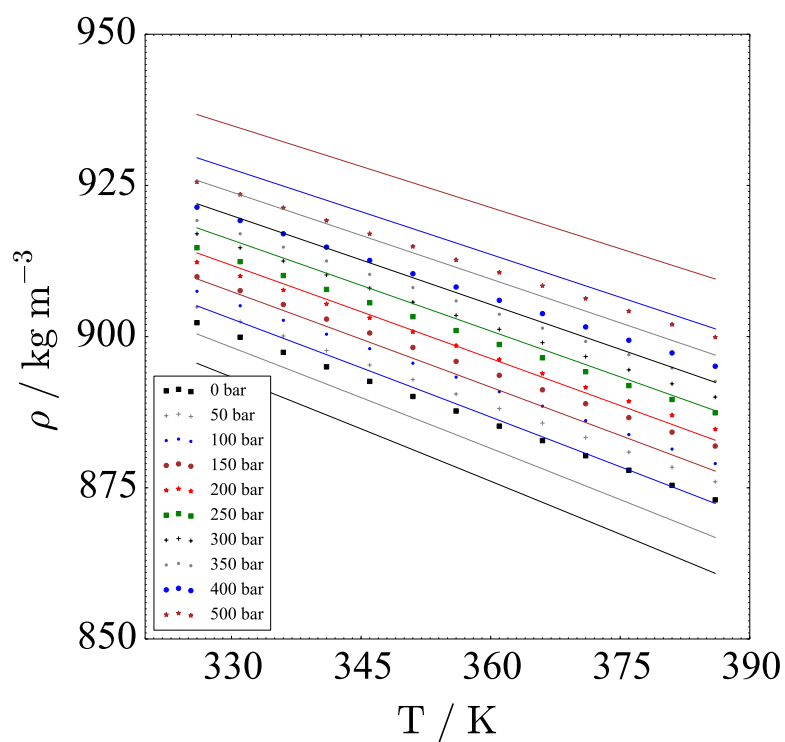


FIGURE 4.19: PVT of polyisobutylene, lines correspond to calculations using SAFT- γ Mie, and symbols correspond to SL EoS fitted to experimental PVT data from Rodgers [185]

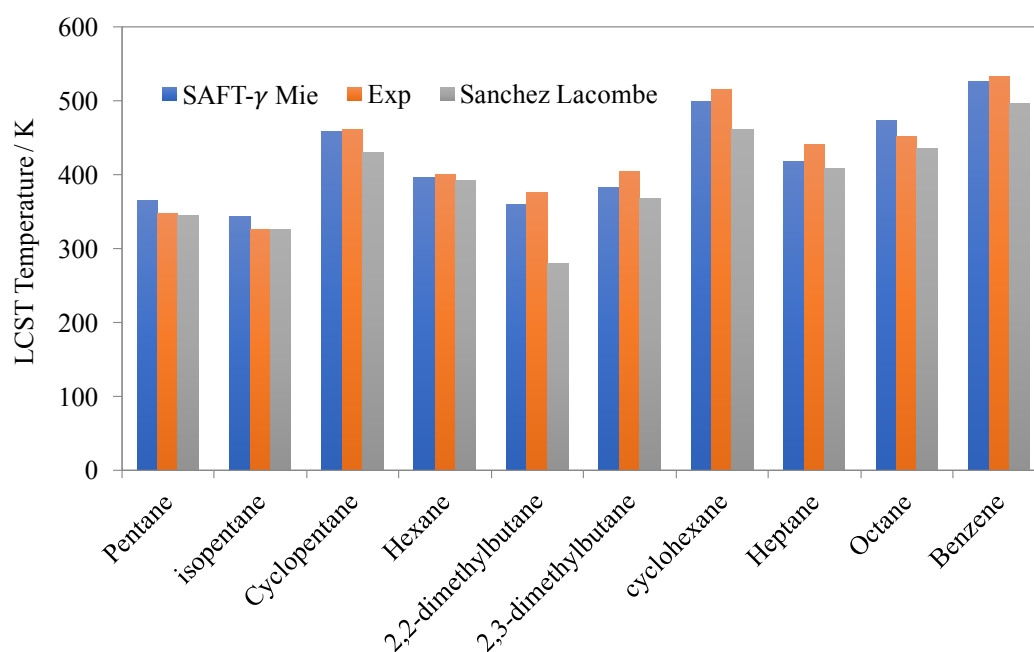


FIGURE 4.20: Prediction of the LCST of PIB in a range of solvents, with no adjustable parameters used. Experimental data and the calculations using the Sanchez-Lacombe EoS could be found in ref [201]

TABLE 4.13: 1,4-cis-Polybutadiene CG monomer interaction parameters

Molecule	$M_{W,CG}$ [g mol ⁻¹]	λ_r	ϵ [K]	σ [Å]
PBD	54.09	22.91	451.49	4.58

TABLE 4.14: PBD CG monomer interaction parameters used in Table 4.13 are fitted using the following molecules, with N_{CG} defined the same way as in Table 4.1

Molecule	N_{CG}	$N_{CH_3}^+$	$N_{CH_2}^+$	$\Delta\rho$ %	ΔP_V %
Hex-3-ene	1	2	0	1.9	9.2
Hept-3-ene	1	2	1	2.8	0.7
Oct-4-ene	1	2	2	2.0	13.2
Dec-5-ene	1	2	4	2.8	15.8

$$^\dagger \epsilon_{PBD,CH_3} = 364.3 \text{ K}, \epsilon_{PBD,CH_2} = 474.4 \text{ K}.$$

4.3.4 1,4-cis-Polybutadiene

Given the quality of this methodology in describing polyolefins, the same methodology of coarse-graining is applied to study polymers containing double bonded moieties. The simplest of these molecules is 1,4-cis-butadiene. A monomer of PBD contains 4 carbons, as can be seen in Table 4.1. Given this fact, a mapping ratio of 1:1 is used to have a robust CG representation. Coarse-graining with a mapping ratio of 4 carbons to 1 bead has already been shown to be predictive for polyethylene and polyisobutylene. Molecules presented in Table 4.14 were used to find accurate intermolecular interactions for PBD. The coexistence curves of these molecules are presented in Figure 4.21.

PVT of PBD is again calculated and compared as before, with the results presented in Figure 4.22. The AAD in density across the whole range of temperatures and pressures is 0.2%.

TABLE 4.15: Molecules used to model binary mixtures of PBD, with self-interaction parameters and their cross interaction adjustment parameter with the polymer, $k_{i,PBD}$. m_{seg} is the number of CG monomers representing each molecule.

Molecule	m_{seg}	λ_r	ϵ [K]	σ [Å]	k_{ij}
Hexane	2	18.01	371.2	4.52	-0.045
1,1,2-Trimethylpentane	2	18.59	405.9	4.92	-0.0045

[†] PIB interaction parameter between monomer and CH_3 and CH_2 was not adjusted.

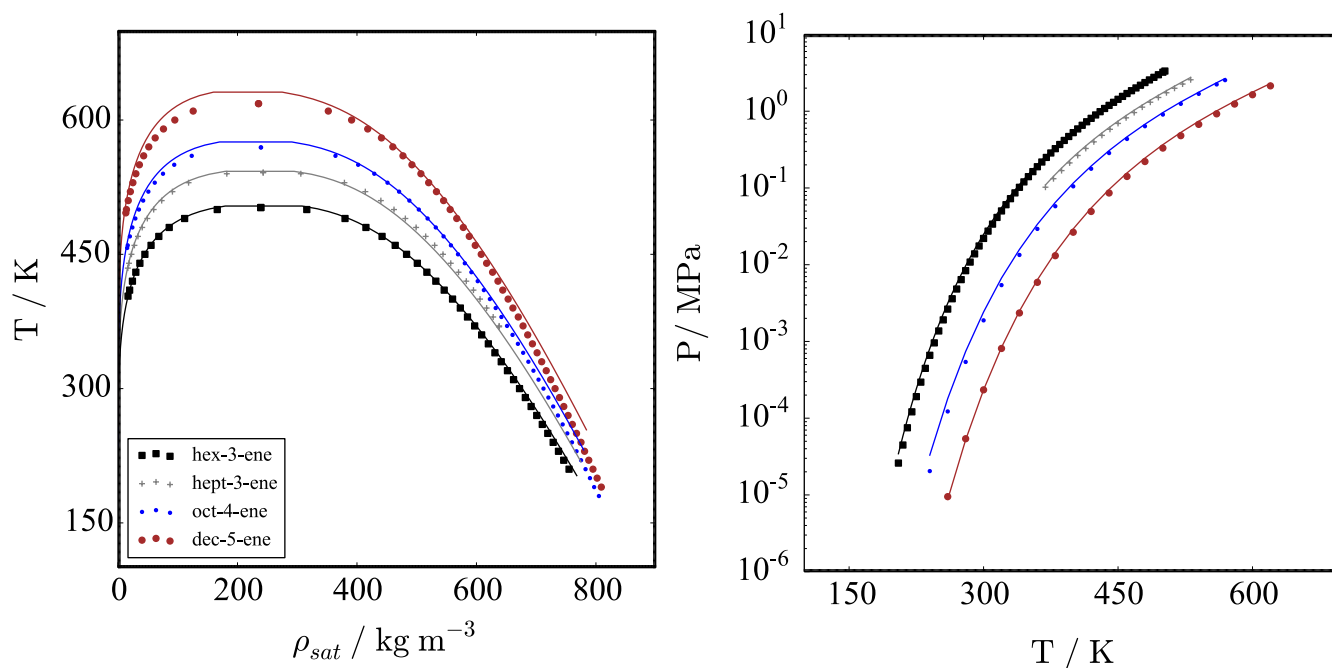


FIGURE 4.21: *Left* Temperature-density coexistence envelopes of Hexene to Decene used to model 1,4-cis-polybutadiene, *Right* Corresponding vapour pressures, the description with SAFT- γ Mie model (continuous curves) is compared with data taken from NIST (symbols).

Mixtures of polybutadiene in alkanes were also investigated, where experimental data was available. Two new types of phases are presented here: Type IV, where both UCST and LCST LLE regions are present in the system, as well as Type III, where the LCST and UCST regions join to form one LLE region, with two regions of miscibility at high and low polymer compositions at intermediate temperatures.

A mixture of PBD in n-Hexane was first studied. For this case, only type IV phase behaviour was observed, with both LCST and UCST regions clearly visible. According to experimental data [202], the mixture becomes only slightly less miscible with increasing molecular weight. Using the model developed for PBD, the correct phase behaviour could not be calculated predictively, and a binary interaction parameter was used, with $k_{ij} = -0.045$. With this adjustment, it was possible to capture the correct phase diagram of PBD n-hexane mixture. Due to the very high M_W modelled in this case, there is a lot of uncertainty in values near the critical region, hence the flat lines.

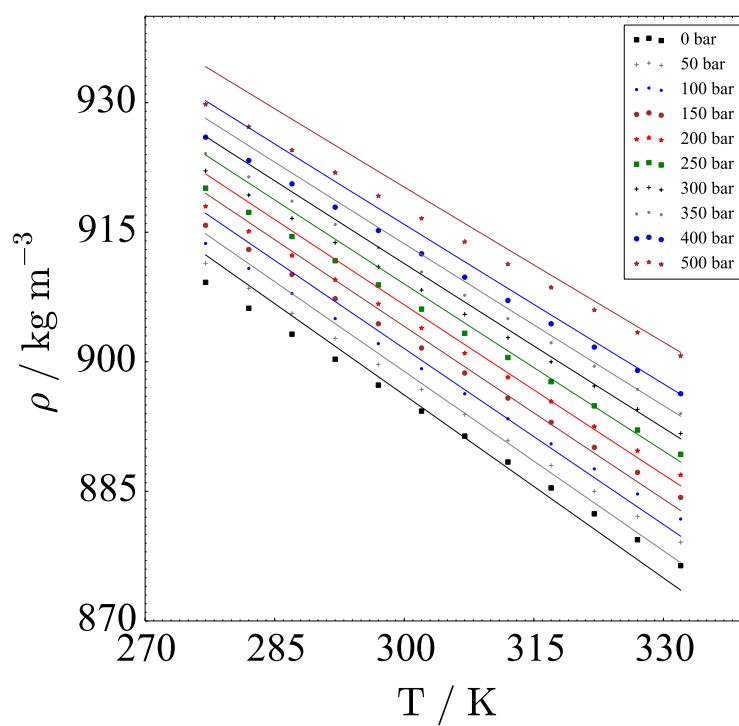


FIGURE 4.22: PVT of 1,4-cis-butadiene, lines correspond to calculations using SAFT- γ Mie, and symbols correspond to SL EoS fitted to experimental PVT data from Rodgers [185]

A much more interesting case was also studied with mixtures of PBD and 1,1,2-trimethylpentane, an isomer of n-octane. For this system, two types of phase behaviour (type III and type IV) have been observed experimentally. At lower molecular weights, there are two clear regions of LLE, and by increasing molecular weight type III phase behaviour is observed. Our model could capture this behaviour, with an extremely small adjustment in the binary interaction parameter, using a $k_{ij} = -0.0045$. This is the first time in this work where Type III phase behaviour (the hour glass shape) is presented. Both set of results are presented in Figure 4.23. It could be seen from the aforementioned Figure that the shape of the phase envelopes only qualitatively match with experimental data. It is however interesting to notice that for PBD in n-hexane, the LCST and UCST regions are insensitive to the molecular weights of the polymer up to 400 kg mol^{-1} , whereas for branched alkanes, as previously discussed for polyisobutylene, mixtures become more immiscible at much lower molecular weights. It is this greater immiscibility that leads to the coalescence of the two regions at higher molecular weights.

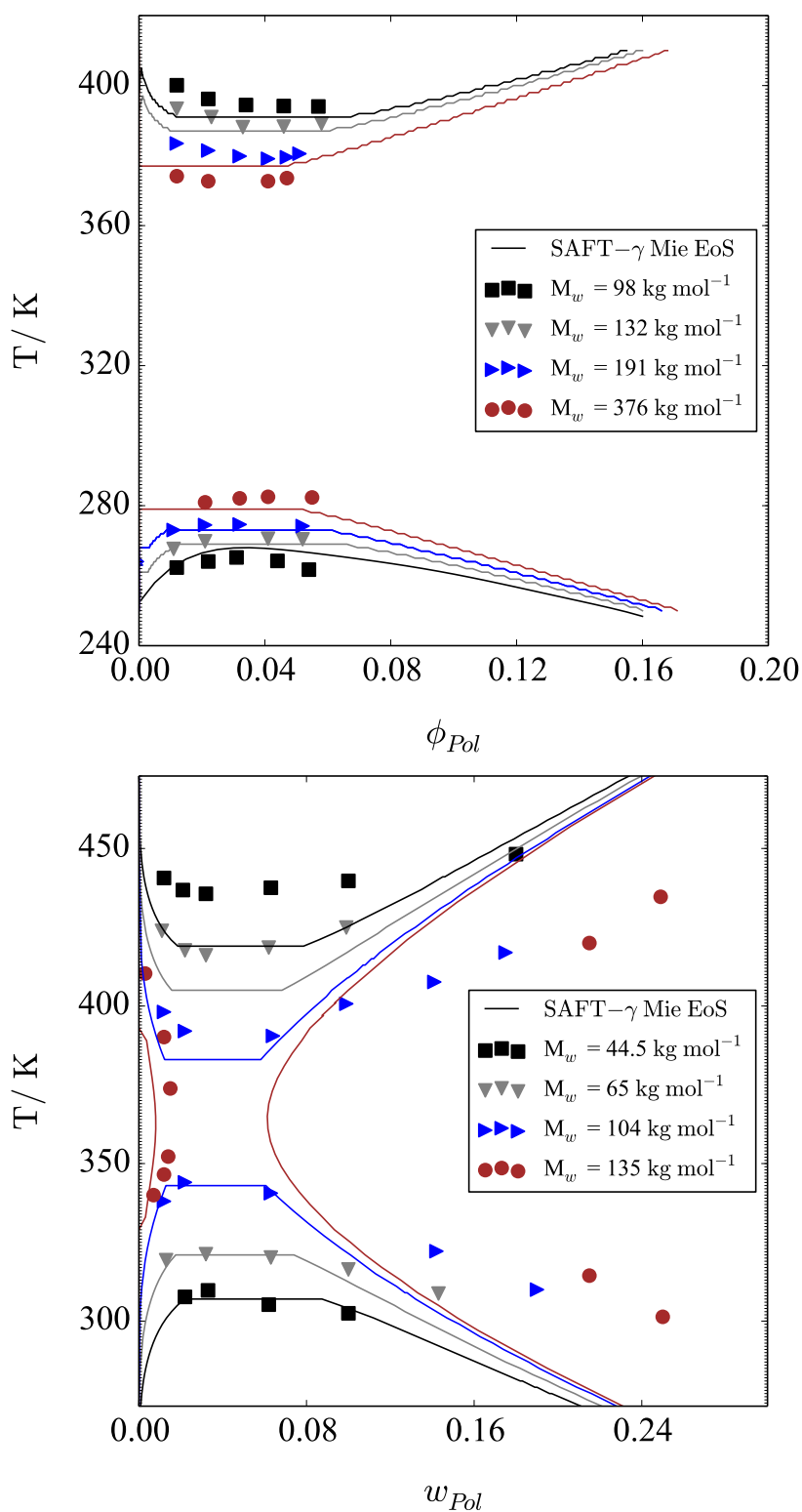


FIGURE 4.23: Temperature-polymer composition phase diagram of a binary mixture of PBD in *Top* n-Hexane ($k_{ij} = -0.045$), and *Bottom* 1,1,2-Trimethylpentane ($k_{ij} = -0.0045$). symbols correspond to experimental data taken from ref [202]

TABLE 4.16: Polyisoprene CG monomer interaction parameters

Molecule	$M_{W,CG}$ [g mol ⁻¹]	λ_r	ϵ [K]	σ [Å]
PIP	68.12	23.39	514.28	4.98

TABLE 4.17: PIP CG monomer interaction parameters used in Table 4.16 are fitted using the following molecules, with N_{CG} defined the same way as in Table 4.1

Molecule	N_{CG}	$N_{CH_3}^+$	$N_{CH_2}^+$	$\Delta\rho$ %	ΔP_V %
3-Methylhex-3-ene	1	2	0	2.4	3.5
3-Methylhept-3-ene	1	2	1	1.7	9.2
4-Methyloct-4-ene	1	2	2	2.3	7.3
2,6-Dimethyl-2,4-decene	2	2	0	5.24	10.5

$$^+ \epsilon_{PIP,CH_3} = 357.9 \text{ K}, \epsilon_{PIP,CH_2} = 490.6 \text{ K}.$$

4.3.5 Polyisoprene

Just like PBD, polyisoprene (PIP) was modelled with a mapping ratio of 1:1. This corresponds to 5 carbon atoms per bead. In this work, the phase diagram of polyisoprene (PIP) in different solvents was not studied. However, polyisoprene is commonly used in block copolymers with polystyrene and therefore, a robust parameter set was needed to model polyisoprene, as the parameters will be used in simulations in the next chapter. Moreover, later in this chapter, PIP will be used to model polymer blends. Self-interaction parameters of PIP are given in Table 4.16. Molecules used in the parameter estimation given in Table 4.17, with the VLE plots given in Figure 4.24. The model underpredicts the densities of 2,6-dimethyl-2,6-decadiene by about 5%, however it is to note that the experimental uncertainty for this molecule is 5.5%. If the density is really underestimated for larger molecules, the density of the polymer has to be underestimated too. However, the PVT of polyisoprene in this case is captured correctly, shown in Figure 4.25.

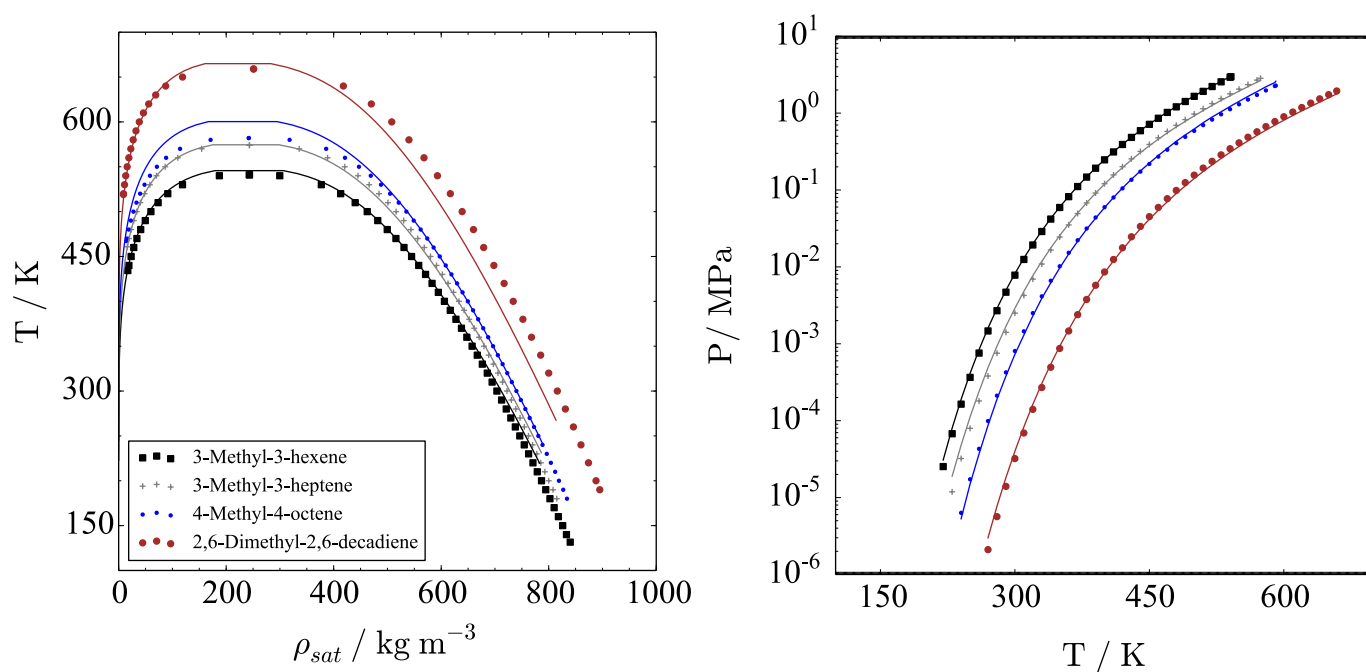


FIGURE 4.24: *Left* Temperature-density coexistence envelopes of branched alkenes to model polyisoprene, *Right* Corresponding vapour pressures, the description with SAFT- γ Mie model (continuous curves) is compared with data taken from NIST (symbols).

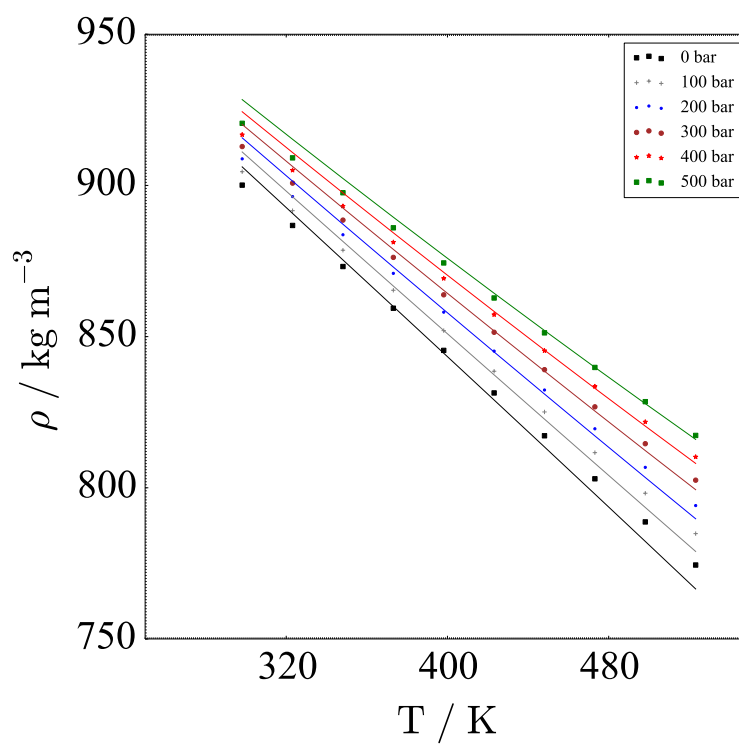


FIGURE 4.25: PVT of polyisoprene, lines correspond to calculations using SAFT- γ Mie, and symbols correspond to SL EoS fitted to experimental PVT data from Rodgers [185]

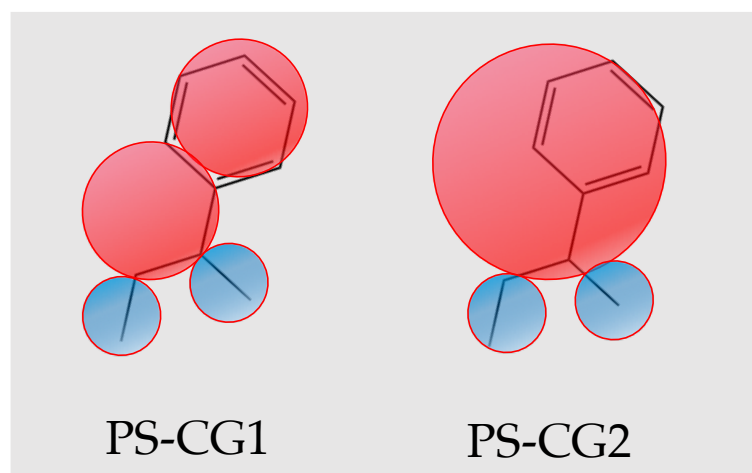


FIGURE 4.26: Two models of PS proposed in this work

4.3.6 Polystyrene

Finally, the last polymer to be modelled is polystyrene. A realistic description of polystyrene, using a bead for one monomer is quite challenging, as one monomer contains 8 carbons. This means that although a monomer could in theory be fitted to one sphere, this comes at a cost of reduced accuracy. In this work, two approaches were used to model polystyrene, with two models used seen in Figure 4.26. First case, called PS-CG1, is one where the philosophy of 4 carbons to 1 CG beads is used. This has been used for PE, PIB and PBD in this work and the results suggest that at this level of coarse-graining phase equilibria can be accurately calculated either predictably, or with the help of a state-independent k_{ij} . Another representation of PS would be a 1:1 mapping. In this case, the whole monomer is represented by a CG bead. This model is called PS-CG2.

The first point of comparison is comparing the VLEs of small molecules containing PS-CG1 and PS-CG2 monomers. Table 4.19 is the table of molecules used in parameter estimation, with the corresponding VLE curves presented in Figure 4.27. Relative to the previous polymers modelled here, both models are remarkably difficult to fit accurately to experimental data, especially in terms of density. This is potentially because the CH_3 group parameters used here were not estimated by using molecules containing phenyl groups and the use of this CH_3 group is not applicable to studying alkanes with phenyl side chains. An important variable in this

TABLE 4.18: Polystyrene CG monomer interaction parameters, for the two models proposed

Molecule	$M_{W, CG} [g \text{ mol}^{-1}]$	λ_r	$\epsilon [K]$	$\sigma [\text{\AA}]$
PS-CG1	52.08	10.67	284.6	4.16
PS-CG2	104.15	21.07	538.0	5.43

is the shape factor of both CH_3 and the PS monomers, which accounts for the non-sphericity of functional groups. In the presence of PS monomers, CH_3 might have a different shape factor. Moreover, so far in this study, none of the molecules used in parameter estimation have had a side chain as large as the phenyl side chain of PS. This difference in size between CH_3 groups requires terms such as shape factors to be used to account for non-ideal interactions in the system. In this work, models have to be tangentially bonded spheres that interact only via Mie potentials, without additional adjustment terms, so that they could directly be used in molecular simulations. Therefore, the effect of shape factor was not investigated, and it is definitely something that needs to be addressed in the future.

Small molecules were used to fit the self-interaction parameters of PS, as well as the cross-interaction with the CH_3 group. The optimal set of results are those presented in Table 4.18. For these parameters, the cross interaction energy between the CH_3 group and the monomer was found to be extremely large, as reported in Table 4.19. In terms of the VLEs, PS-CG2 performs worse than PS-CG1 in modelling sec-butylbenzene and 2-phenylpentane, but it does considerably better in modelling 2,5-diphenylhexane. A difference between these two sets of molecules is that the latter contains two polystyrene monomers, whereas sec-butylbenzene and 2-phenylpentane only contain one PS monomer. Sec-butylbenzene is demonstrated in Figure 4.26. Overall, calculations of the VLE curves are not satisfactory.

Both PS-CG1 and PS-CG2 were used in calculating the density of PS polymer. This is shown in Figure 4.28. PS-CG2, which captures the density of diphenylhexane better than PS-CG1, again does better in calculating the density of polystyrene. PS-CG1 is not accurate in measuring the density of PS, with an AAD of 0.9% across all temperatures and pressures. For the case of the lowest pressures, the average error between experimental results and the PS-CG1 model is 1.5%, which is considerably

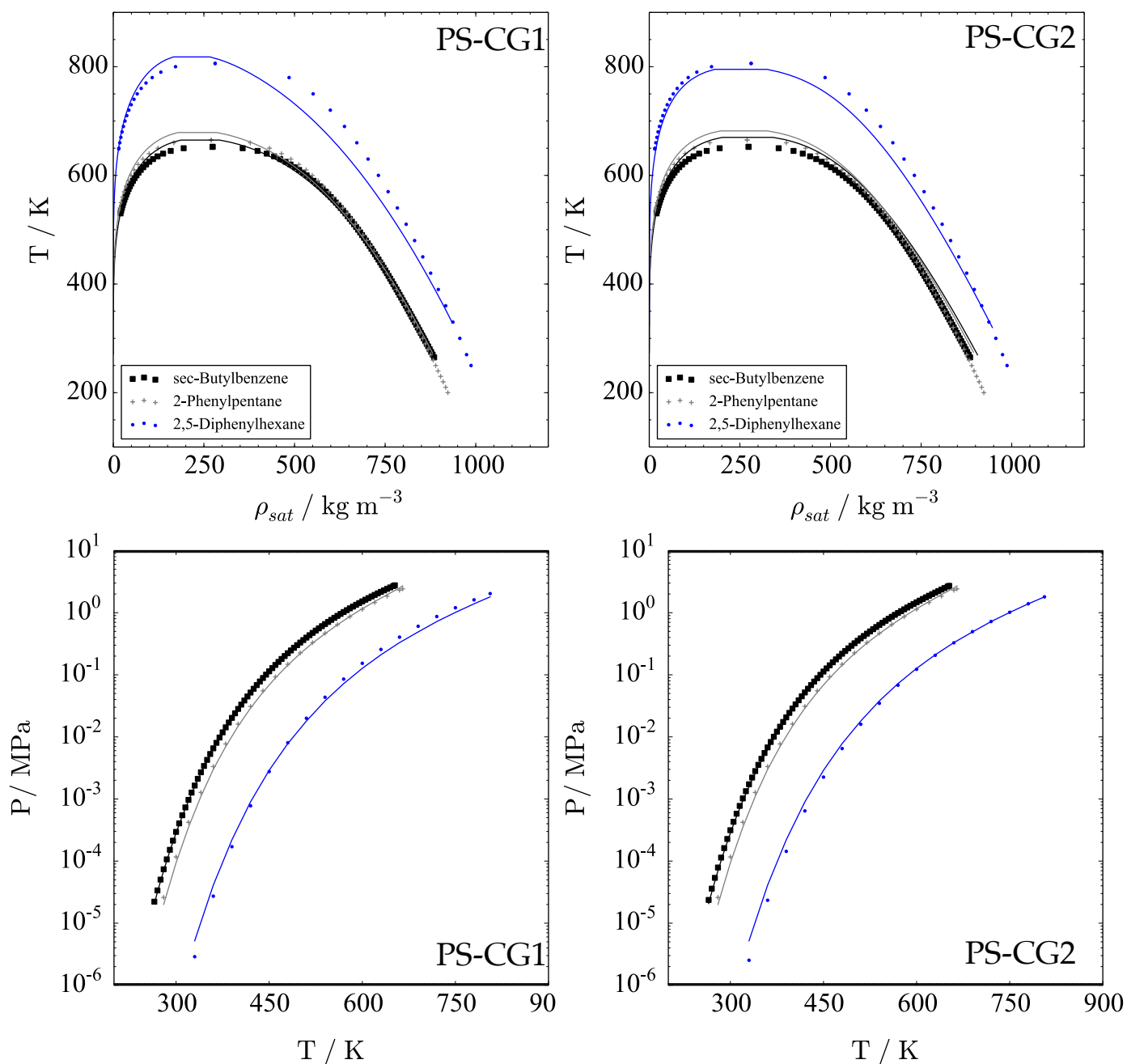


FIGURE 4.27: *Top* Temperature-density coexistence envelopes of alkanes with phenyl side chains used to model PS, *Bottom* Corresponding vapour pressures, the description with SAFT- γ Mie model (continuous curves) is compared with data taken from NIST (symbols).

TABLE 4.19: CG monomer interaction parameters used in Table 4.18 are fitted using the following molecules, with N_{CG} defined the same way as in Table 4.1

Molecule	N_{CG}	$N_{CH_3}^+$	$N_{CH_2}^+$	$\Delta\rho$ %	ΔP_V %
sec-Butylbenzene (PS-CG1)	2	2	0	1.7	6.5
sec-Butylbenzene (PS-CG2)	1	2	0	4.4	8.5
2-Phenylpentane (PS-CG1)	2	2	1	3.0	5.6
2-Phenylpentane (PS-CG2)	1	2	1	5.6	10.2
2,5-Diphenylhexane (PS-CG1)	4	2	0	6.5	15.1
2,5-Diphenylhexane (PS-CG2)	2	2	0	3.4	11.0

[†] $\varepsilon_{PS-CG1, CH_3} = 357.9$ K and $\varepsilon_{PS-CG2, CH_3} = 530$ K, no adjustment parameters used for CH_2 -PS.

poor in comparison with all polymers previously modelled. PS-CG2, however, predicts the density of polystyrene with an AAD of 0.5%. In this sense, it could be seen that PS-CG2 outperforms PS-CG1.

The classic phase diagram of polystyrene-solvent mixtures is the one presented by Schultz and Flory in 1952 [64]. For both models in this work, the phase diagram of PS-cyclohexane at different molecular weights was calculated. The results are shown in Figure 4.29. Both models can predict critical temperatures accurately. Remarkable agreement, however, is only observed for the PS-CG2 model, where the shape of the PS-cyclohexane diagram is perfectly captured. This is in contrast with the PS-CG1 model, which can only predict the critical temperatures accurately. What is more interesting is that PS-CG1 requires only a small amount of adjustment.

PS-cyclohexane and PS-methylcyclohexane mixtures are known to exhibit type III phase behaviour, with both UCST and LCST phases observed for a given mixture. In our case, both models are known to predict the existence of these LLE regions. For the sake of not repeating the same Figures twice for each model, for these two solvents only PS-CG1 model is presented. However, the cross interaction parameters for both models are given in Table 4.20. The results can be seen in Figure 4.30. For the case of PS in cyclohexane, the effect of Molecular weight on miscibility is demonstrated with the model capturing the correct critical behaviour, with both LCST and UCST being calculated. In the case of PS-methylcyclohexane mixtures, the effect of pressure on the critical point of fixed M_W polystyrene is studied. In this case $M_W = 405$ kg mol⁻¹.

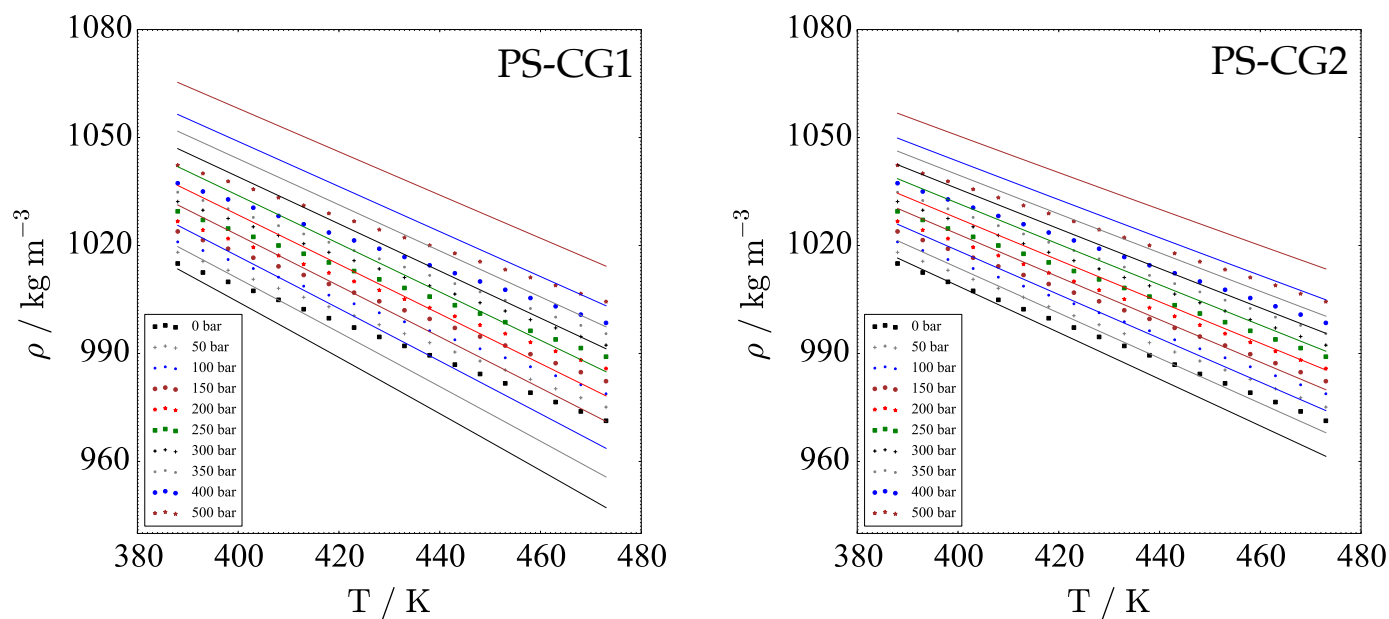


FIGURE 4.28: PVT of polyisoprene, lines correspond to calculations using SAFT- γ Mie, and symbols correspond to SL EoS fitted to experimental PVT data from Rodgers [185]

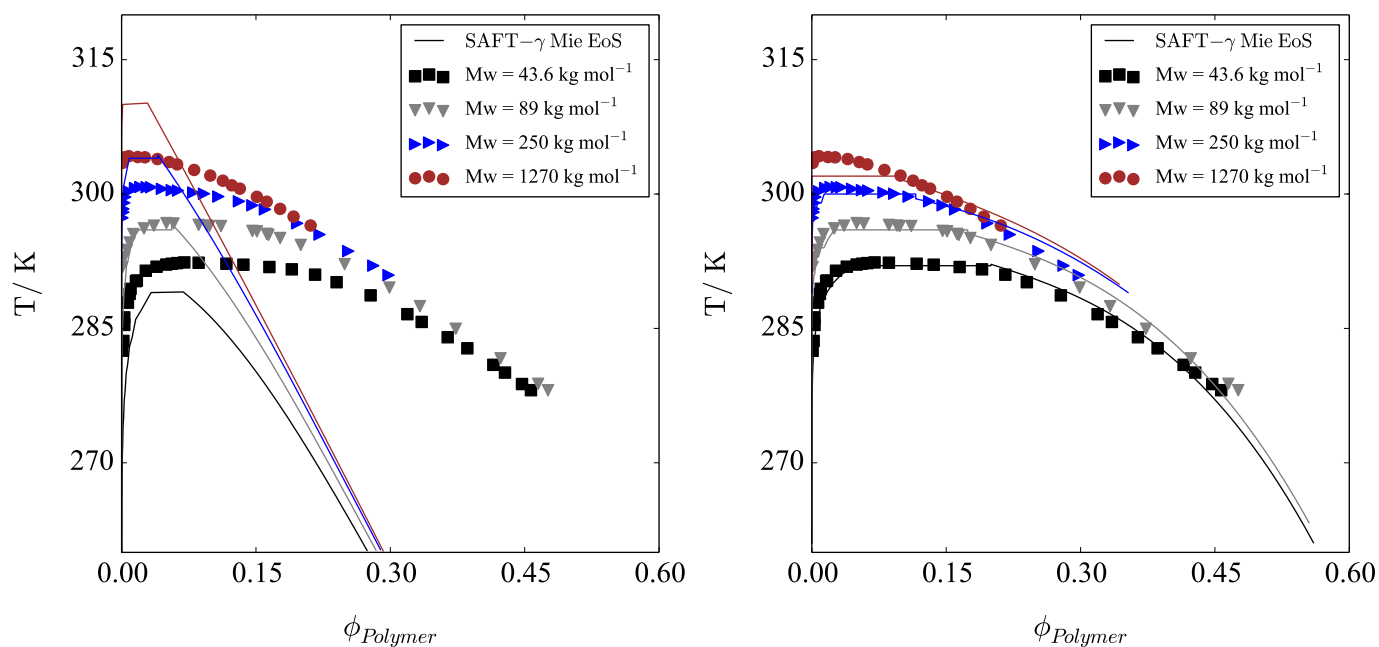


FIGURE 4.29: Temperature-composition graph of polystyrene in cyclohexane, with *Left* PS-CG1 model and *Right* PS-CG2 model. Symbols are experimental data from ref [64]. For PS-CG1 $k_{ij} = 0.0155$ and for PS-CG2 $k_{ij} = -0.0020$

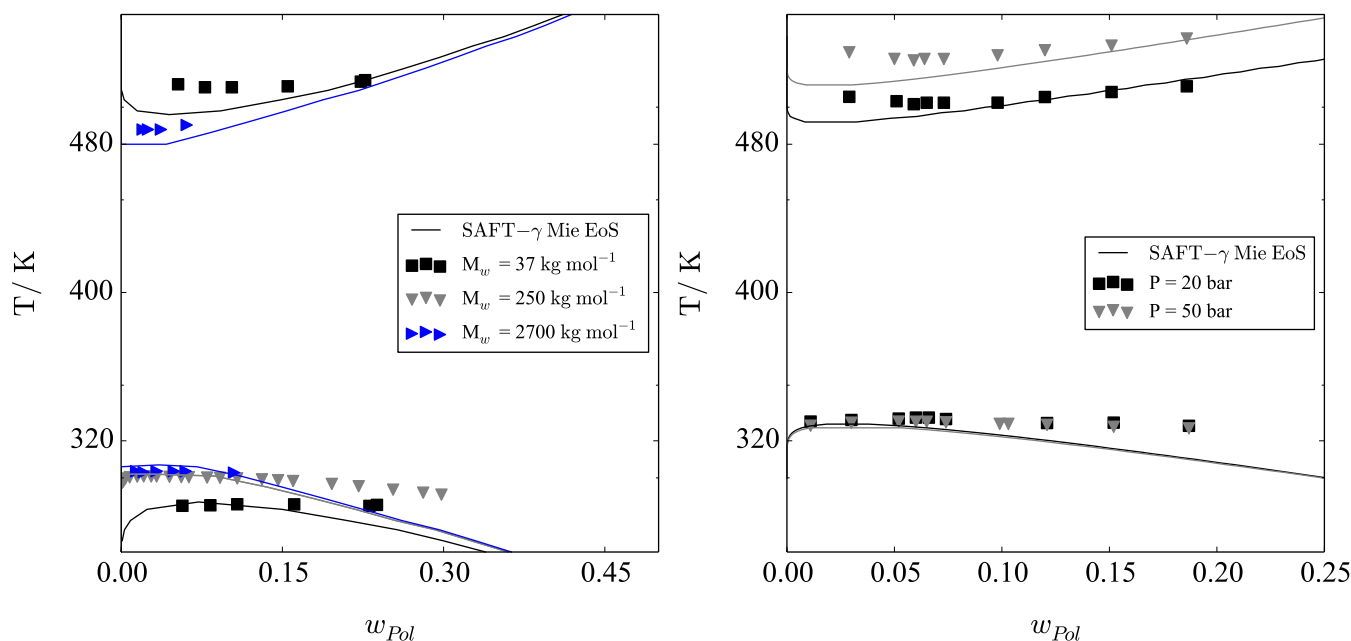


FIGURE 4.30: Phase behaviour of polystyrene in *Left* cyclohexane and *Right* methylcyclohexane mixtures. In *Left* the molecular weight was the variable, and in *Right* $M_w = 405 \text{ kg mol}^{-1}$ and pressure was varied. both PS-CG1 and PS-CG2 can produce these phase diagrams. Results are only shown for the PS-CG1 model, with binary interaction parameters given in Table 4.20. Symbols are experimental results. For cyclohexane, data are from [203], and for methylcyclohexane data are taken from ref [204].

For both models, a k_{ij} was required to calculate the correct critical regions. The value of k_{ij} was very small ($< 2\%$). For polystyrene in cyclohexane, molecular weight does not significantly change the critical temperatures. However, pressure improves the miscibility of polystyrene and cyclic alkanes at higher temperature, pushing the LCST higher, with the UCST region unaltered. The predictions of the model matches that of the experimental data. Neither model performs particularly better when it comes to modelling LCST-UCST phase behaviour.

Given that type IV phase behaviour can be observed with PS-cyclohexane mixtures, the PS parameters were then used in modelling mixtures with a range of solvents. Firstly, mixtures of PS and n-alkanes were modelled using both PS-CG1 and PS-CG2. High M_w polystyrene does not dissolve in alkanes. However, at low molecular weights (less than 10 kDa), there is a region of miscibility that can be observed experimentally. Below a certain polymer molecular weights, PS-alkane mixtures exhibit both LCST and UCST behaviours. Again like the case of PBD and

TABLE 4.20: Molecules used to model binary mixtures of polystyrene, with self-interaction parameters and their PS cross interaction adjustment parameter, $k_{i, PS}$. m_{seg} is the number of CG monomers representing each molecule.

Molecule	m_{seg}	λ_r	ϵ [K]	σ [Å]	PS-CG1 k_{ij}	PS-CG2 k_{ij}
Cyclohexane	2	13.3	338.7	4.24	0.0155	-0.0020
n-Hexane	2	18.01	371.1	4.517	0.0113	0.0114
Heptane	2	21.27	427.0	4.77	0.007	0.017
Octane	3	14.30	314.7	4.22	0.0148	0.005
Methylcyclohexane	2	14.68	372.3	4.50	0.0161	0.005
Acetone [‡]	2	17.43	286.002	3.60	-0.007	
CO ₂ [‡]	2	14.14	193.2	2.849	0.055	-0.062

[‡] Acetone is not modelled with only dispersions, and it is modelled as an associating molecule with parameters previously published in ref [205].

trimethylpentane, increasing the molecular weight leads to more immiscibility and the two regions coalesce. This is clearly demonstrated in Figure 4.31. For the case of PS in n-hexane, the onset of coalescing occurs around a M_W of 4.8 kDa, whereas in n-Octane, this occurs around 10.3 kDa. Again, the SAFT- γ methodology is robust in calculating the critical temperatures, with the correct phase diagrams of low M_W PS in n-alkanes correctly captured.

In this chapter, all solvents used so far to investigate polymer phase behaviour have been non-polar and non-associating. This is to ensure that when the use of Mie potentials in describing the interactions is valid. For these systems, the parameters can be used in molecular simulations to study phase behaviour of polymers in solution, capturing both LCST and UCST temperatures.

However, to test the limit of the model, a mixture of PS in a polar solvent (acetone) is also modelled. Kouskoumvekaki et al. [203] had previously studied polystyrene in cyclohexane and acetone using PC-SAFT. No set of parameters could estimate both the LLE of PS-acetone and PS-cyclohexane. The result calculated in this work is presented in Figure 4.32. An accurate phase diagram of the mixture was only calculated for PS-CG1, with $k_{ij} = -0.007$. The parameters for acetone were taken from elsewhere [205], without any fitting. The PS-CG1 could predict the correct phase diagram with a k_{ij} of only -0.7%.

Finally, to test the transferability of the parameters at different conditions, a

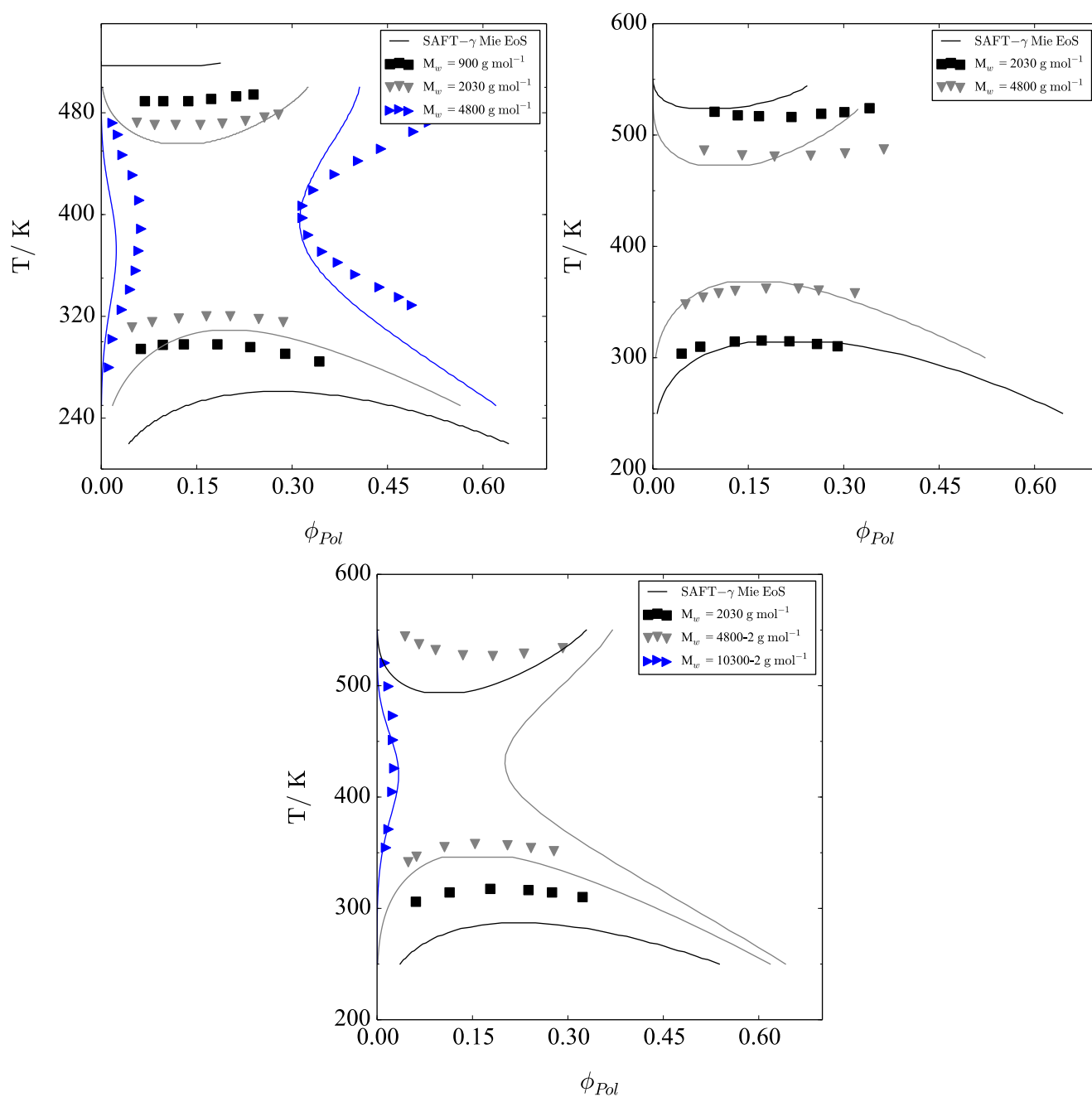


FIGURE 4.31: Phase behaviour of polystyrene and n-alkane mixtures, both PS-CG1 and PS-CG2 can produce these phase diagrams. Results are only shown for the PS-CG1 model, with binary interaction parameters given in Table 4.20. **Top Left** PS in n-Hexane, **Top Right** in n-Heptane and **Bottom** in n-Octane. Symbols are experimental results taken from ref [206].

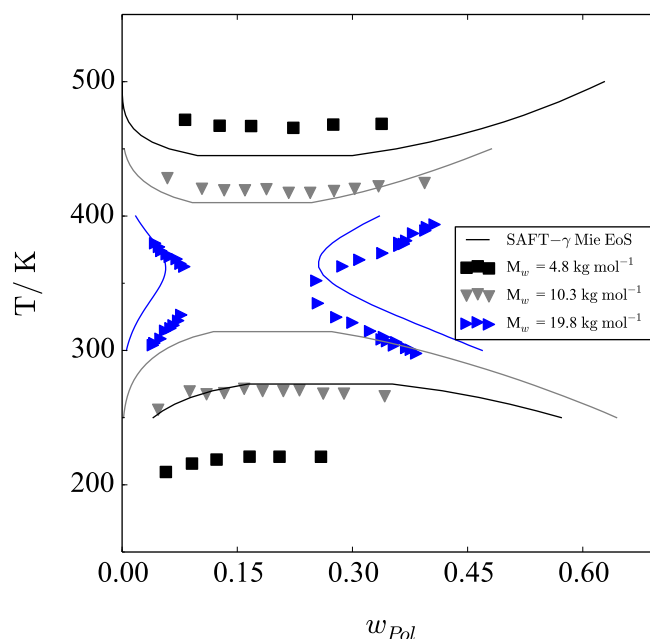


FIGURE 4.32: Phase behaviour of polystyrene and acetone mixtures, Symbols are experimental results taken from ref [203]

ternary mixture of polystyrene-cyclohexane- CO_2 ($M_{W, PS} = 101.4$ kDa) was modelled, again based on the work of Gross and Sadowski. The cross interaction parameter of CO_2 and cyclohexane were estimated using bubble pressure experimental data. The results are shown in Figure 4.33. Apart from the highest temperature, the isothermal VLE curves can be accurately fitted to experimental data. The data for the bubble pressure at 473.15 K was taken from ref [207], and other points taken from refs [208, 209]. The former reference is from 1960s, with the latter references being more recent. The cross interaction parameters were fitted using data for the range 313-423 K found in the latter two sources. The AAD in this case is 1.2 percent.

Knowing the binary interaction parameter between PS-cyclohexane, and cyclohexane- CO_2 , the ternary mixture PT diagram could be calculated. The binary interaction parameter between PS and CO_2 was fitted using the ternary data, by minimising the errors between experiments and the EoS. Figure 4.34 shows the results as calculated by the EoS. In this instance, the ternary phase diagram could only be calculated accurately using the PS-CG1 model. Both models can capture the the correct PT phase diagram for a binary mixture of PS-cyclohexane (in the absence of CO_2). However,

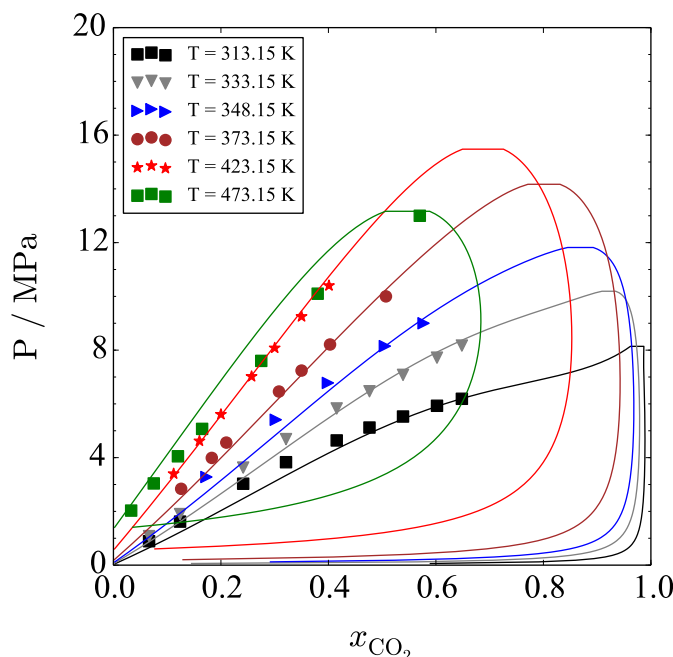


FIGURE 4.33: Pressure-composition diagram of the VLE of CO₂-cyclohexane binary mixture. The binary interaction parameter $k_{ij} = 0.067$. Symbols are experimental data taken from refs [207–209]

when CO₂ was added, only PS-CG1 model was able to reproduce the experimental results. It was not possible to model the ternary mixture with the PS-CG2 model. This is due to the level of coarse-graining of the polystyrene model. PS-CG2 contains 8 carbons per bead, whereas the CO₂ model used in this work is represented by 2 beads. This discrepancy between the two sizes makes it difficult to model ternary mixtures of CO₂-PS-Cyclohexane with PS-CG2 model.

Overall, it could be seen that apart from ternary mixtures containing CO₂, both PS models could calculate the critical temperatures and the phase behaviour of the mixtures investigated here. PS-CG2 is more robust in capturing the shape of the phase envelopes, with PS-CG1 being much more transferable across all temperatures and pressures. PS-CG1 is also the less accurate model in the calculation of polymer PVTs for all the polymer models studied. Providing a reliable and robust set of parameters for polystyrene is much more difficult than other simpler molecules modelled here.

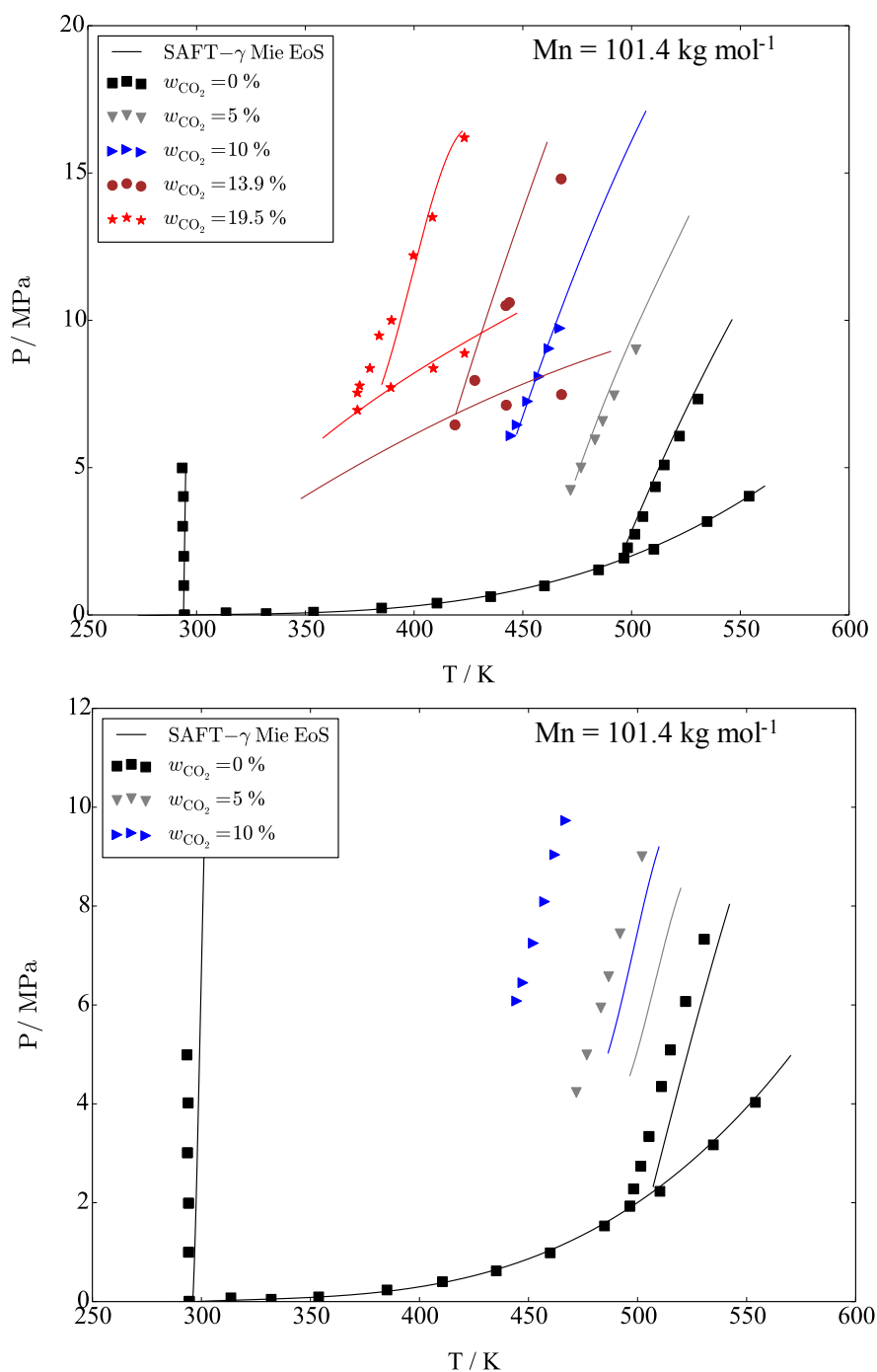


FIGURE 4.34: PT diagram of a ternary mixture of polystyrene, and CO_2 . In the absence of CO_2 , the mass fraction of PP in n-pentane is $w_{\text{polymer}} = 0.1$. **Top** is the ternary phase diagram using PS-CG1 model to represent PS and **Bottom** is the corresponding phase diagram using PS-CG2. Black lines correspond to the coexistence lines of a binary mixture of cyclohexane and PS. Coloured lines correspond to the LCST of the ternary mixture at different concentrations of CO_2 . Binary interaction parameter of polymer with CO_2 was fit to the experimental data at 5 wt%, with cross interaction parameters given in Table 4.20, CO_2 -cyclohexane $k_{ij} = 0.067$. Continuous lines correspond to SAFT- γ Mie model and symbols are data taken from ref [113, 210, 211].

TABLE 4.21: Polystyrene CG monomer interaction parameters, for the two models proposed

Polymer 1	Polymer 2	k_{ij}
PBD	PIP	-0.00110
PS-CG1	PBD	-0.02521
PS-CG2	PBD	-0.03387
PS-CG1	PIP	-0.04171
PS-CG2	PIP	0.0029

4.3.7 Polymer Blends

So far in this study the parameters have been using in modelling pure components and polymer-solvent mixtures. It is important to assess the transferability of the model parameters to modelling of polymer blends. This would be particularly important in modelling block-copolymers. Three polymer blends are modelled in this work, namely PBD-PIP, PS-PBD and PS-PIP. Table 4.21 given the binary interaction parameters used to model polymer blends.

The first system studied here is that of PBD-PIP blends. Polyisoprene and polybutadiene blends exhibit LCST behaviour [212]. The results of EoS modelling and experimental data for a blend of 81 kDa polyisoprene with 55 kDa polybutadiene are presented in Figure 4.35. The correct LCST could be calculated using a $k_{ij} = -0.0011$. This adjustment is extremely small and the phase envelope is extremely sensitive to the blend binary interaction parameter. For example for the case of no adjustment, full phase separation was observed. It is interesting that the model predicts the correct type of phase behaviour (i.e. Type V phase behaviour with an LCST LLE region). This correct phase behaviour is pure prediction.

Many cases of polymer blends also exhibit UCST phase behaviour. A common blend in modelling such systems is that of PS-PBD and PS-PIP blends. To test if the model could predict the correct UCST type of phase behaviour in the aforementioned blends, both PS models were used to see whether they could both produce accurate results. Figure 4.36 shows the phase diagram of low M_W PS-PBD blends. The cross interaction parameter was fitted to the case with lower molecular weight PS. IT can be seen that, just like the previous phase behaviour of the two PS models studied in this work, both models can calculate the correct critical temperatures

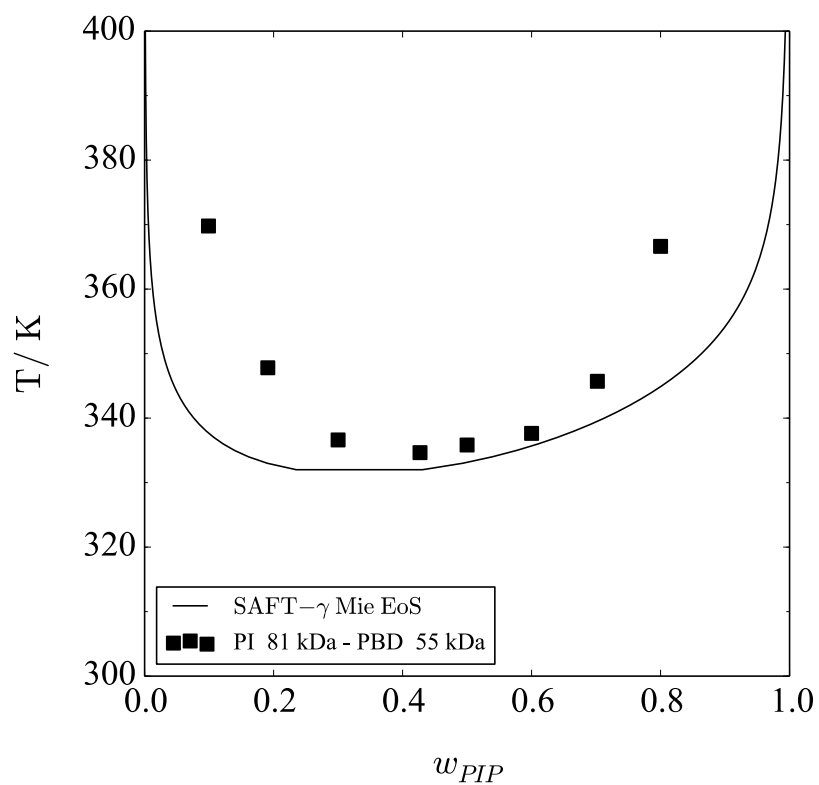


FIGURE 4.35: Phase behaviour of polymer blend of PIP ($M_W = 81$ kDa) and PBD ($M_W = 55$ kDa). The binary interaction parameter $k_{ij} = -0.001102$. Symbols are experimental data taken from ref [212]

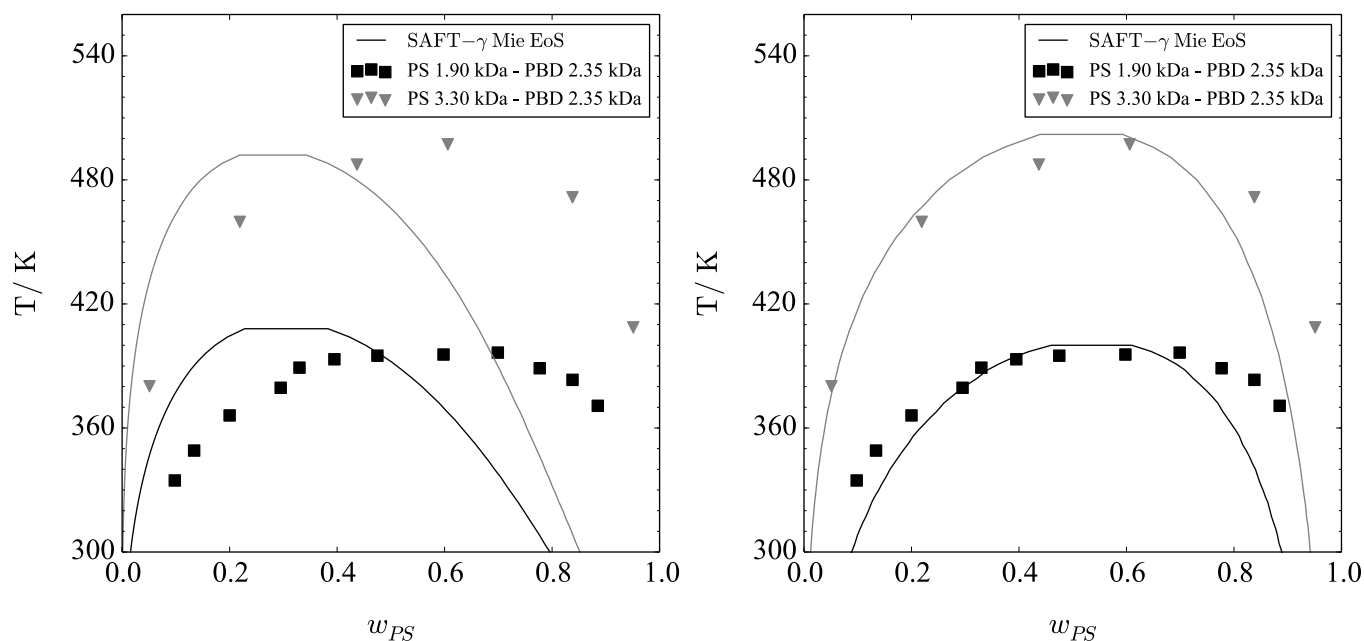


FIGURE 4.36: UCST phase behaviour of PS-PBD blends, with two different PS models used. The polystyrene model used in *Left* PS-CG1 and *Right* PS-CG2. The binary interaction parameters are given in Table 4.21. Symbols are experimental data taken from ref [213].

with varying molecular weights, however, the shape of PS-CG1 does not correspond to the experimentally observed phase envelope. However, it is still remarkable that the parameters can correctly predict a UCST phase behaviour, without fitting pure component parameters to blend data.

However, for the case of PS-PIP mixtures, PS-CG1 is not compatible with modelling the blend at all. This can be seen in Figure 4.37. Like the PS-PBD blend The cross interaction parameter was fitted to the data with the lower molecular weight PS. Increasing the M_W of PS leads to a massive overestimation of the UCST. However, PS-CG2 can accurately model the phase behaviour of the blend of low M_W PS-PIP blends.

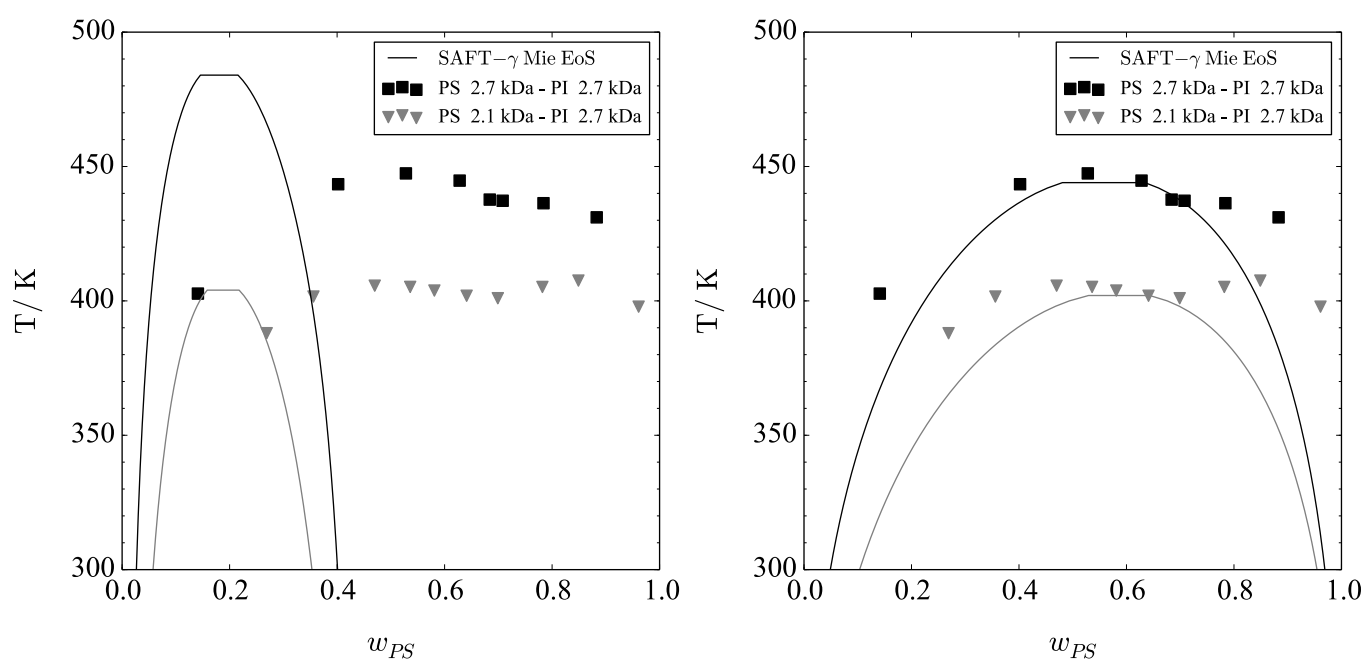


FIGURE 4.37: UCST phase behaviour of PS-PIP blends, with two different PS models used. The polystyrene model used in *Left* PS-CG1 and *Right* PS-CG2. The binary interaction parameters are given in Table 4.21. Symbols are experimental data taken from ref [197].

4.4 Conclusions

In this chapter, polymer models were developed using SAFT- γ Mie Equation of state for 6 types of polymer. Self-interaction parameters were estimated using VLE data of small molecules containing monomer functional groups. The coarse-grained framework used in this study was based on consolidating an integer number of monomers into one CG spherical bead, so that the aforementioned self-interaction parameters given by Mie potential, could be a realistic representations of monomer units, so that these parameters could be used in molecular simulations to study phase behaviour of polymers with thermodynamically accurate models. It was shown that for PE, PP, PBD and PI it is possible to accurately model these polymers with the parameters developed in this work. However, the case of polystyrene is much more difficult. Two models of PS are presented here, PS-CG1 and PS-CG2, which correspond to two different representation of the PS monomer. PS-CG2 could model UCST and LCST of alkanes, producing the correct shape of the phase diagrams. However it failed in modelling ternary mixtures of cyclohexane and CO₂. On the other hand, PS-CG1 could capture the correct critical temperatures and pressures, however the shape of the phase diagrams were wrong.

Modelling polymers with SAFT- γ Mie is as good as other flavours of SAFT. In this thesis, the aim is not to compare the models with other SAFT models, but to develop reliable intermolecular interaction parameters for molecular simulations. Although PC-SAFT is commonly used in modelling polymers, the use of SAFT- γ Mie can be a viable alternative. The key difference between the two models is that the reference fluid here is that of a hard sphere, however, in PC-SAFT the reference fluid is that of a hard chain. The parameters in our models can be used directly in molecular simulations as will be shown in the next chapter.

Chapter 5

SAFT- γ Mie Coarse-Grained Simulations of Polymer Solutions

5.1 Introduction

Polymers are the quintessential multiscale materials in that their structural and dynamic properties span many length and time scales. With advances in computing power and simulation techniques, there has been major progress in simulations of polymeric materials. Abundant literature exists atomistic or united atom representation simulations of homopolymer melts [214–220]. Structural properties such as radii of gyration and end to end distances, dynamic properties such as self-diffusion of polymers or the end-to-end relaxation times, Rouse and entanglement regimes, polydispersity, cross-linked networks and elastic properties have all been accurately studied using this scale of modelling. An issue with atomistic simulations is that they are limited to the smallest of systems, as computational expense scales exponentially with system sizes.

It becomes much more challenging to simulate longer polymers using all atom representations as the relaxation times could be very long, rendering modelling at this scale redundant. Moreover, for cases where one is no longer concerned with modelling homopolymer melts, such as phase equilibria of polymers in solutions, system sizes required to observe phase separation are so large that, given current computing capacities, it is an insurmountable challenge to use atomistic simulations to study these systems.

Particle based coarse-graining (CG) is a viable alternative to atomistic simulations for large systems. There are two main philosophies of coarse-graining, namely structural coarse-graining (bottom-up) or thermodynamic coarse-graining (top-down) that can be used to group atoms together to form super-atoms [22]. By reducing the degrees of freedom of the system, much less computational expense is required to calculate properties. The vast majority of literature on coarse-graining of polymers belongs to the former philosophy. Bottom up approaches involve mapping the underlying atomistic potentials into larger coarse-grained beads with the aim of conserving local structures. This coarse-grained potential can then be used to relax a large system. Once the large system is equilibrated, the final configuration can be reverse-mapped to the atomistic-detailed representation to study the relaxed system in more detail. The most common type of structure matching is achieved using the iterative Boltzmann inversion (IBI) technique, which tries to develop the CG potential by minimising the difference of the coarse-grained structure with the underlying atomistic one iteratively. A coarse-grained simulation is run, and the radial distribution function of the particles, as well as the angular and bonded distribution functions measured. These are compared to the underlying atomistic simulation of the same system, and the potential parameters are updated to minimise the difference between the two scales. Simulations are repeated until the difference between the local structures are minimised. There is an overwhelming amount of literature using this technique, with common polymers being modelled with accurate representation of their local structures. [130, 133, 221–226] The implementation of IBI can be done as part of a bigger optimisation technique taking into account structural properties at different state points [227]. Also, the shape of the CG particles can be very versatile, as it has been shown that this technique could be applied to ellipsoidal, non-spherical (anisotropic) CG monomers too [228].

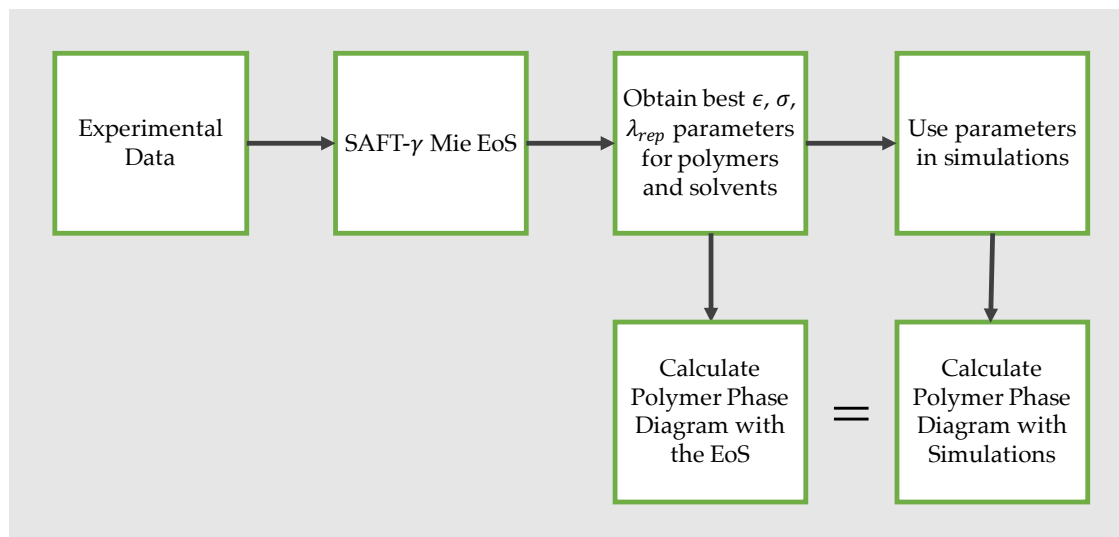
Accurate representation of the local structures intuitively makes IBI a robust methodology to study polymeric systems at larger scales. However, a major problem with this technique is that the potentials developed are state dependent. The interaction potentials are dependent on density, pressure, temperature, composition and molecular weight of the components studied. [120, 124] Structure based coarse-graining is very applicable when investigating properties of homopolymers melts in

a narrow range of temperatures and pressures, as the parameters are independent on the degree of polymerisation [134]. However, application of this technique to study mixtures of polymers (blends or in solvents) is much more challenging [229]. Few studies exist on coarse-grained modelling of polymers mixtures using IBI method. Sun and Fallor were one of the first to investigate a blend of polystyrene and polyisoprene [229] at a fixed temperature and pressure, and they could observe miscibility and immiscibility of these polymer blends as a function of the chain lengths. In that study it was highlighted that the potential parameters were state-dependent and that parameters need to be fitted for different states. Another seminal paper to study solutions was that of ref [124], which was a study on CG modelling of polyisoprene and cyclohexane. It was demonstrated that no set of potential parameters were adequate to capture the local structure at both high and low concentrations. Two sets of potentials had to be developed for the polymer, for the concentrated regime and dilute regime. In another study, Peters and Kremer [120] highlighted a challenge in modelling dilute solutions of polymers using IBI, which is that the solute-solute radial distribution functions converge very slowly, requiring very long atomistic simulations to have enough statistics that account for this. The vast majority of the studies on polymer solutions with structure matching [120, 124, 224, 230–232] only attempt to capture the correct local structures of the monomers in solution at a particular temperature and pressure. A systematic study of polymers in solution, especially liquid-liquid equilibria of requires parametrising the potentials at each concentration, temperature and pressure. Many sets of simulations at different state points will need to be run to fit interaction parameters, which makes this process a very laborious task.

Thermodynamic, or top-down, approaches, aim to improve this issue by fitting potential parameters to macroscopic properties. Hydration energies, interfacial tensions, densities and pressures could all be used to fit potential parameters. This however, comes at a cost of reduced accuracy in the structural properties of the polymers. Again, like the case of bottom up approaches, top-down approaches have been used to model homopolymer melts of common polymers, capturing the correct densities and conformations (radius of gyration). The MARTINI forcefield has been applied to the study of polystyrene, polyethylene oxide, pluronics and polyolefins

[139, 140, 233, 234] with transferable potentials that could match the correct conformations in solvents. In all these studies conformations of polymers and densities are comparable to those of the bottom-up approaches. However, in most of these studies, liquid-liquid equilibria of polymers and solvents are only studied in narrow temperature and pressure ranges.

To our best knowledge, upper critical and lower critical phase behaviour of polymers mixtures are very rarely modelled using the top-down and bottom-up approaches mentioned above. The vast majority of studies of lower critical and upper critical phase behaviour have been phenomenological studies, using model systems instead of real molecules. Sheng et al. [69] accurately modelled the VLE of pure component chains formed of Lennard-Jones spherical monomers using Gibbs ensemble Monte Carlo (GEMC) simulations. It was shown that this methodology is robust in calculations of the phase diagrams. The use of this methodology was extended to simulations of polymer mixtures. The first GEMC simulations which modelled both LCST and UCST behaviour in polymer-solvent mixtures without any adjustment parameters were carried out by Gromov et al. [235] in 1998. In this study, mixtures of Lennard-Jones chains and spheres represented polymers and solvents respectively. LCST miscibility was observed at high pressures, whilst increasing the molecular weight led to UCST phase behaviour. The key result of this work was that LJ models could be used to model phase behaviour of polymer mixtures. However, real systems were not simulated in the aforementioned work. Wijmans et al. [152] used dissipative particle dynamics (DPD) potentials (i.e. soft overlapping spheres) with GEMC to model phase separation in polymer-solvent mixtures. It was shown that with DPD, it is possible to capture UCST phase behaviour of polymer solutions. DPD simulations were used to find a closed form expression for the LLE phase envelope as a function of the volume fraction and the chain length of the polymers. It was shown that this correlation could accurately model the UCST phase behaviour of polystyrene in methylcyclohexane, provided that the parameters of the correlations were fit to experimental data. In this study, only temperature induced phase separation was studied, and the phase envelope could only be estimated for UCST type phase separation. Vliet et al. extended the previous work to apply DPD potentials to study pressure induced phase separation of polymer-solvents. [151] However,

FIGURE 5.1: SAFT- γ Mie CG method.

to achieve this, the intra and interspecies repulsion parameters were modified for each state point, clearly highlighting a non-predictive approach to pressure induced phase separation.

For all the systems discussed above (both top-down and bottom-up techniques) it is still challenging to study phase equilibria of real polymers in solutions and blends with quantitative accuracy, especially when investigating the critical points of immiscibility. These techniques have been successful in studying homopolymer melts accurately, but it is difficult to obtain cross interaction parameters that are independent of all temperatures and pressures using these simulation techniques. [229] Accurate cross interaction parameters are necessary if one wants to quantitatively model polymer phase behaviour.

SAFT- γ Mie is an accurate EoS that can address this particular issue. The EoS describes polymers as tangentially bonded spheres that interact with other spheres using Mie potentials. The use of Mie potential parameters as input variables to the EoS makes the EoS a forcefield development toolkit. By minimising the error between the calculations of the EoS and experimental data, one could obtain non-bonded forcefields for molecular simulations. The process can be better understood by referring to Figure 5.1.

In this thesis, it has been demonstrated for the first time that the EoS can accurately describe polymer phase behaviour. Moreover, in the study of polymer mixtures, the EoS can also be used to find cross interaction parameters for polymer-solvent and polymer-polymer mixtures.

There has been only one study on polymer solvent mixtures using potentials obtained using SAFT- γ Mie methodology [236] to develop a polystyrene model. In that work the potential parameters were not directly fitted using the EoS, and polymers were assembled like lego pieces: a polystyrene molecule was modelled as an alkane backbone with a side chain composed of toluene molecules. The parameters for alkanes and toluene were previously developed. Although this study showed promising results in terms of modelling polymers with SAFT- γ Mie EoS, the process of obtaining interaction parameters was not robust. It was not possible to determine the extent to which the polystyrene presented in that study represented a real polystyrene molecule as described by the EoS. Moreover, the cross interaction parameters were not fitted with the EoS and they were adjusted using simulations. Finally, the effect of intramolecular potentials was not investigated, and the polymer was modelled as a freely rotating chain. The development of the potential parameters could definitely be improved.

In this chapter, SAFT- γ Mie Forcefield is obtained using the non-bonded potential parameters calculated in the previous chapter. For easier accessibility, the parameters of polymers used in the simulations are presented in Table 5.1. Bonded interaction parameters are obtained using all atom simulations of oligomers. Density and conformational properties of the polymers are then presented.

This is followed by the simulations of mixtures of polymers in solvents and blends, which is the main highlight of this chapter. Simulations are run with the same interaction parameters as given in the previous chapter, to assess the viability of the EoS in parametrising accurate forcefield parameters for polymers. It will be shown that the potential parameters are robust, with accurate correspondence between the EoS and molecular simulations. Potential parameters, both inter and intraspecies, are state-independent. Phases II to V seen in Figure 2.7 can be reproduced with this methodology, with an additional and novel phase behaviour, that is pressure induced phase separation, also presented.

It can therefore be seen that this new methodology is a viable alternative to commonly used approaches for modelling polymer solutions.

5.2 Methodology

5.2.1 Potential Parameters

The basic framework for developing forcefields using SAFT- γ Mie has already been presented in section 3.4.2. Here the methodology is further explained. In general the potential used in coarse-grained molecular simulations is composed of two contributions:

$$U^{Potential} = U^{Intermolecular} + U^{Intramolecular} \quad (5.1)$$

$U^{Intermolecular}$ is the non-bonded interactions developed by SAFT- γ Mie EoS, and $U^{Intramolecular}$ is the potential describing how CG beads are connected to each other in the polymer chain.

Intermolecular Potential Parameters

Polymers in this work are modelled as tangentially bonded spheres that interact with the Mie potential [28]:

$$u^{Mie}(r) = C\epsilon \left[\left(\frac{\sigma}{r} \right)^{\lambda_r} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (5.2)$$

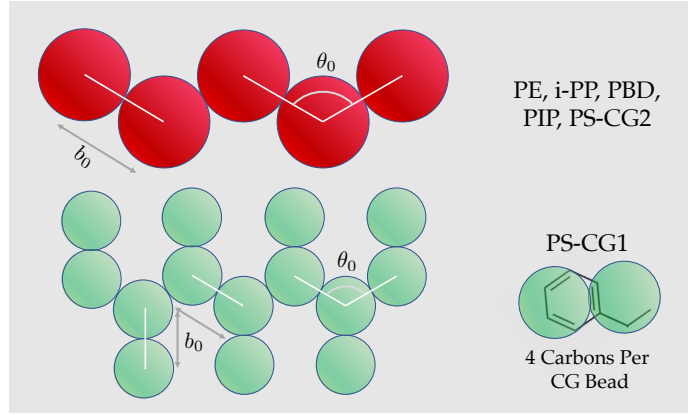
$$C = \left(\frac{\lambda_r}{\lambda_r - 6} \right) \left(\frac{\lambda_r}{6} \right)^{6/(\lambda_r - 6)} \quad (5.3)$$

The non-bonded potential parameters have already been parametrised in the previous chapter for 6 polymer models that will be used in this study, with the methodology explained in Figure 5.1. The polymers and their self-interaction parameters are given in Table 5.1.

Cross interactions between different groups are calculated using mixing rules, as explained in section 3.3.1. A state-independent k_{ij} is used to model the cross

TABLE 5.1: Polymers studied in this work, with parameters estimated in the previous chapter

Polymer	$M_{W, CG \text{ Monomer}}$	Mapping	λ_r	ϵ [K]	σ Å
Polyethylene (PE)	56.11	4	21.706	441.69	4.69
Polypropylene (PP)	84.16	2	24.94	571.6	5.51
1,4-cis-Polybutadiene (PBD)	54.09	1	22.91	451.49	4.59
Polyisoprene (PIP)	68.12	1	23.39	514.28	4.98
Polystyrene (PS-CG1)	52.08	1/2	10.67	284.6	4.16
Polystyrene (PS-CG2)	104.15	1	21.07	538.0	5.43

FIGURE 5.2: CG representation of the polymers used in this study. Apart from PS-CG1 which is modelled as a branched polymer, all other polymers were modelled as linear chains. The parameters for θ and b_0 are given in Table 5.3.

interaction energy between two different species:

$$\epsilon_{ij} = (1 - k_{ij}) \frac{(\sigma_{ii}^3 \sigma_{jj}^3)^{1/2}}{\sigma_{ij}^3} \sqrt{\epsilon_{ii} \epsilon_{jj}} \quad (5.4)$$

For the different polymer systems presented in this work, the value of k_{ij} was calculated in the previous chapter, and will be reported in the results section as appropriate.

Intramolecular Potential Parameters

As previously discussed, SAFT- γ is based on the thermodynamic perturbation theory (TPT1) of Wertheim. The derivations of the contributions to the free energy for the chain term assume a freely-jointed chain. This is not necessarily valid at the levels of coarse-graining presented in this work. For the freely joined chain assumption

to be valid, each coarse-grained bead should be at a scale of Kuhn lengths. However, for some cases, such as the case of polystyrene, the Kuhn length is 5 to 10 monomers. Therefore, angle potentials need to be fitted so that the underlying local structures are captured by this model. It is important to note that SAFT- γ Mie is a top-down model and therefore it is not necessarily possible to accurately capture the local structure of the chains. Thus, if the angle bending potential did not give the correct melt conformations, the potential parameters were modified to capture the correct radius of gyration.

Moreover, in TPT1 theory no assumptions are made about the connectivity of the monomers in a polymer, with the exception that monomers cannot form rings. Within all SAFT EoS frameworks, the phase behaviour of a star polymer and a linear polymer with the same number of monomers would be the same. The PS-CG1 polymer model, where each polystyrene monomer is represented by two CG beads, can be modelled as a polymer composed of a backbone with side chains. This is visually explained in Figure 5.2.

In this work, harmonic potentials are used to model angle and bond stretching, by first calculating probability distributions of bonded and angular distributions from underlying atomistic simulations. The probability distributions, $P(x)$, were fitted by weighted Gaussian distributions [32, 118]:

$$P(x) = \frac{w(x)}{\sqrt{2\pi}s^2} e^{-(x-\mu)^2/2s^2} \quad (5.5)$$

Here x is the intramolecular variable for which the probability distribution is calculated. In this work it is either the distance ($x = b$) between two neighbouring CG segments or the angle ($x = \theta$) between three neighbouring CG segments. The mean distance or angle between the segments is given as μ ($\mu = b_0$ or θ_0 in Figure 5.2) and s is the standard deviation of the Gaussian distribution. A weighting function $w(x)$ is used to account for the asymmetry of the distributions. $w(r) = b^2$ and $w(\theta) = \sin(\theta)$ were used as the weight functions for bond stretching and angular bending respectively. The harmonic potentials are then given as below:

$$u_{Bond} = \frac{1}{2}k_b(b - b_0)^2 \approx k_B T \ln P(b) \quad (5.6)$$

$$u_{Angle} = \frac{1}{2}k_{\theta}(\theta - \theta_0)^2 \approx k_B T \ln P(\theta) \quad (5.7)$$

Here, k_b and k_{θ} are measures of the stiffness of the harmonic potentials. In this work, given the constraints of the theory, $b_0 = \sigma$. However, k_b , k_{θ} and θ_0 were fitted using atomistic simulations.

Fully atomistic simulations were run using the OPLS-AA (all atom) forcefield [237], which is very accurate for modelling alkanes, alkenes and aromatics. Atomistic simulations were run at $T = 400$ K and $P = 1$ bar for oligomers containing 8 monomers for all molecules presented in Table 5.1, except polyisoprene, which was modelled using the same bonded potentials as polybutadiene. This could definitely be improved in the future. Also the harmonic potentials for PS-CG1 model was only fitted for the backbone of the polymer, as shown in Figure 5.2. Finally, dihedral potentials were not fitted, which could be investigated in the future.

Once the intramolecular potential parameters were calculated with OPLS-AA forcefield, simulations of polymer melts were run to calculate the radius of gyration polymers in good solvent conditions. This was then compared to other literature, and k_{θ} was modified to fit the experimental, or atomistic simulation calculations of the polymers, if necessary.

5.2.2 Molecular Simulations

In this study, only molecular dynamics simulations were run to simulate polymers, using GROMACS/4.5.5, GROMACS/4.6.5 [238, 239] and GROMACS/5.1 [240] packages. Given previous simulations studies using SAFT- γ forcefields typically use time-steps (Δt) of 0.01 ps [236, 241], the same value was used in this work. The leapfrog algorithm was used for the numerical integration of the equation of motion. Either NVT or NPT ensemble simulations were used to model systems at constant volume and temperature or at constant pressure and temperature respectively. Nosé-Hoover thermostat [242, 243], and Parrinello-Rahman barostat [244, 245] were used to correctly obtain the canonical or isobaric-isothermal distributions. In all simulations in this work, a cut-off of 2 nm was used with no tail corrections.

Using molecular dynamics to model polymeric mixtures means that very large

system sizes need to be simulated to take into account interfacial boundaries between two immiscible fluids. GEMC circumvents this problem by having two boxes composed of each of the separate phases, with no interfacial boundaries. GEMC has been used to study chains systems of up to 100 beads. In this work chains of up to 600 beads are used to model phase behaviour of very large polymers in solvents. GEMC could be very slow for long chains as insertions and deletions are required to move a chain from one box to the other. This problem is exacerbated for highly dense systems. Thus direct coexistence simulations using MD was preferred given that highly parallelised packages are available. Most simulations were run up to 2 μs , and for the largest polymers simulations of up to 10 μs were run as computing capacity was available. 1 μs corresponds to 100 million time steps using $\Delta t = 0.01 ps$.

Simulations were performed using either Imperial College's HPC facilities or Thomas Cluster of UCL HPC facilities.

Homopolymer Melts

Once the intramolecular potential parameters were fitted using atomistic simulation, systems containing polymer melts composed of 500 CG monomer units were simulated for a range of temperatures and pressure to compare the densities to the predictions of the EoS.

Moreover, the conformation of the polymer melt was also studied by measuring radius of gyration and end to end distances of polymers in pure melt. If the radius of gyration was not correctly calculated, the value of k_θ was re-adjusted in the simulations in order to obtain the correct conformational properties in melt. Top-down approaches do not necessarily have to have the correct local structural properties as they are fitted to macroscopic properties, but it is important that the models have the correct R_g And R_E in melt and solution.

Radii of gyration and end to end distances were calculated using Equations 2.4 and 2.3 respectively.

TABLE 5.2: Intramolecular potential parameters fitted to OPLS-AA simulations of oligomers composed of 8 monomers at $T = 400$ K and $P = 1$ bar. b_0 refers to bonding distance between to CG beads obtained from atomistic simulations.

Polymer	k_θ (kJ mol ⁻¹ rad ⁻²)	θ_0 (degrees)	k_b (kJ mol ⁻¹ nm ⁻²)	b_0 (nm)
PE	21.67	179.97	2900.20	0.4768
PP	3.94	174.00	2356.30	0.4899
PBD	14.63	159.30	2366.10	0.4122
PS-CG1 [†]	12.07	118.21	2743.43	0.3066
PS-CG2	24.21	74.77	747.31	0.5501

[†] Only angle potential for the backbone of PS-CG1 was fitted to experimental data, with no other angle potentials for the side chains.

Phase Behaviour of Polymer Mixtures

It is quite challenging to accurately measure coexistence compositions of mixtures of polymers with solvents and in blends. The interfacial region of the polymers mixtures are not planar and polymers could have different instantaneous conformations. This means that it is not usually possible to differentiate bulk and interfacial regions in simulations. In order to indicate whether phase separation has occurred in the simulation box, a novel method first proposed by Gelb and Müller [246] was utilised and applied to our simulations boxes. In this method, local compositions are measured for small regions in the simulation box, and the phase separation is inferred by studying the distribution of the local compositions of the polymer in solution. The small regions are cubes of side length of ≈ 1.5 nm. The method is visually explained in Figure 5.3. This method might not give exact coexistence compositions due to the interfacial effects in the simulations, however, it is used as a tool to qualitatively observe the onset of immiscibility.

5.3 Results and Discussion

5.3.1 Bonded and Angle Potentials

Intramolecular potential parameters obtained from atomistic simulations are presented in Table 5.2. It is difficult to compare these values to those found in literature, as the mappings used in this work are not similar to those found elsewhere. IBI

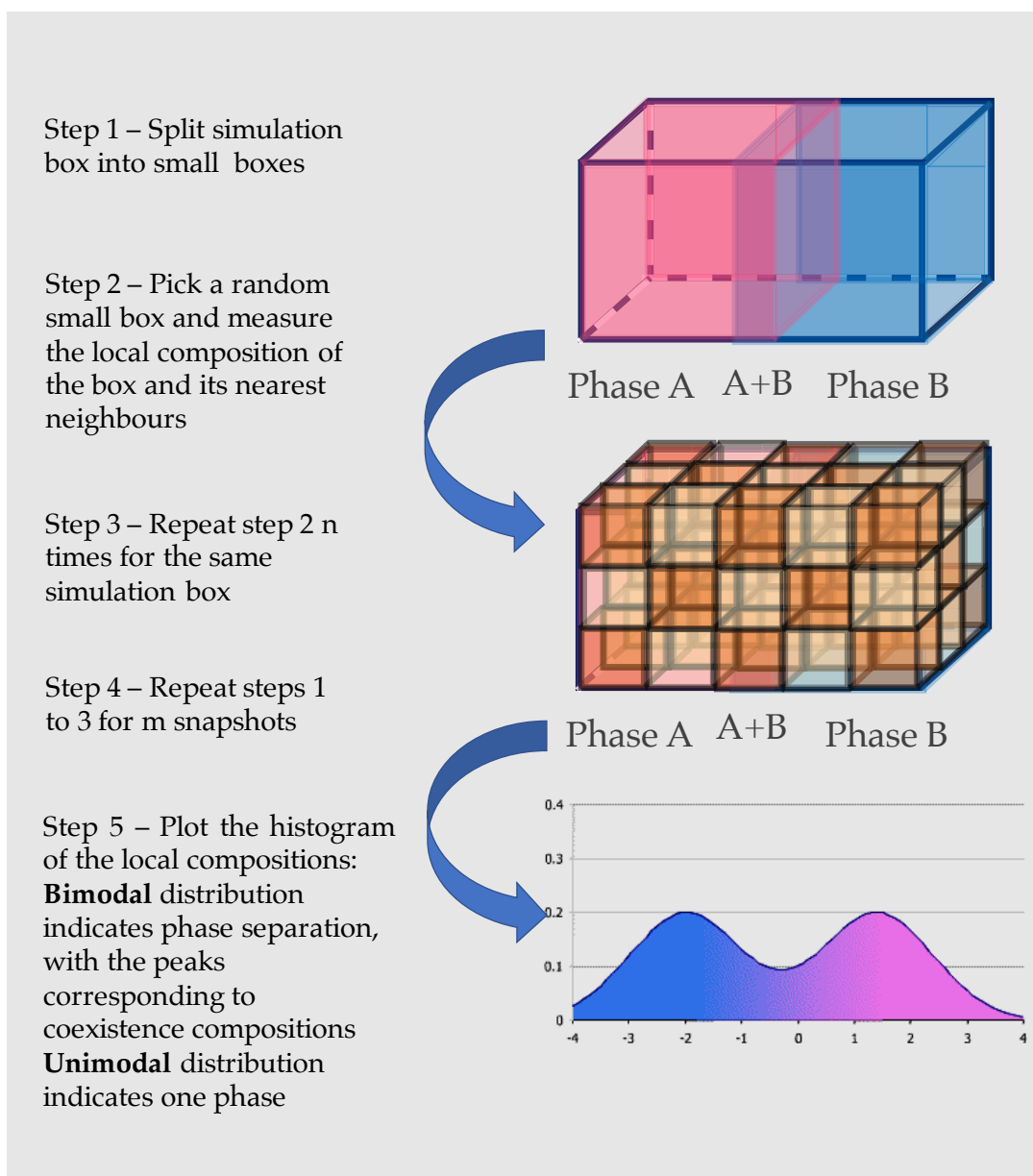


FIGURE 5.3: The method of Gelb and Müller [246] used in this work to observe phase separation in polymer mixtures.

methods use tabulated potentials and therefore the only points of comparison are with top-down models.

The only example found in literature that was similar to any of our polymer models was the polyethylene model in the work of Panizon et al. [139] In that study, polyethylene was modelled using a 4 to 1 mapping. The angle and bond stretching potential parameters calculated in that work are very similar to those presented here. In their work $k_b = 2000 \text{ kJ mol}^{-1} \text{ nm}^{-2}$ with $b_0 = 0.46 \text{ nm}$. In this work $k_b = 2900 \text{ kJ mol}^{-1}$ with $b_0 = 0.477 \text{ nm}$. More similarity is in the angle bending potentials, with the same angle of 180 degrees being used in both models, with $k_\theta = 25 \text{ kJ mol}^{-1} \text{ rad}^{-2}$ used in their study, compared with $21.67 \text{ kJ mol}^{-1} \text{ rad}^{-2}$ used here. This demonstrates that the intramolecular potential parameter estimation method implemented here (Equations 5.5-5.7) is robust.

For PS-CG1, following the methodology of Jiménez-Serratos et al. [236], only the backbone of the chain was fitted with an angular potential. This could certainly be improved in the future.

Figure 5.4 shows the comparison between bonded and angular distribution simulations from atomistic simulations and the corresponding coarse-grained simulations for polyethylene and polypropylene. In SAFT- γ methodology, the bond distance has to be equal to the value of σ in the chains, and therefore only the value of σ is shown using vertical lines for the bonded distances. However, for the angular potentials, the distribution of the angles from both CG simulations and the OPLS-AA simulations are presented. The angular distributions are very similar for all cases. However, for polyethylene, k_θ was significantly lowered (to a value $8.67 \text{ kJ mol}^{-1} \text{ rad}^{-2}$) to match the correct radius of gyration for PE. This has the effect of shifting the distribution to smaller angles. The angular distribution of i-PP follows that of the OPLS-AA distributions for angles of 120-180 degrees. However, below these angles there is another peak around 60 degrees. The cause of this was not investigated and this definitely needs further investigation.

In terms of the bond lengths, it could be seen that the average bond length for SAFT- γ Mie and OPLS-AA mapping are very similar for the case of PE. For polypropylene, however, the average bond length given by SAFT- γ Mie EoS is around ten percent higher than that given by OPLS-AA mapping.

TABLE 5.3: Intramolecular potential parameters used in this work.
For PE and PBD, k_θ was adjusted to match experimental radius of gyration.

Polymer	k_θ (kJ mol ⁻¹ rad ⁻²)	$\theta_{0, SAFT}$ (degrees)	k_b (kJ mol ⁻¹ nm ⁻²)	$b_{0, SAFT}$ (nm)
PE [†]	8.67	179.97	2900.20	0.469
PP	3.94	174.00	2356.30	0.551
PBD [†]	5.63	159.30	2366.10	0.459
PS-CG1	12.07	118.21	2743.43	0.416
PS-CG2	24.21	74.77	747.31	0.543
PIP [‡]	5.63	159.3	2366.10	0.498

[†] For this two systems k_θ was modified from the values given Table 5.2 to fit the correct radius of gyration and end to end distances.

[‡] For PIP, k_{bond} , k_θ and θ_0 was modelled using the same parameters as PBD. R_g and R_E were not calculated for PIP.

The same comparison between OPLS-AA and SAFT- γ intramolecular potential parameters for PBD, PS-CG1 and PS-CG2 models can be seen in Figure 5.5. Here, angle and bond distance distributions for all three models are very similar for all three models investigated, with the exception of the bond distance in the backbone of the PS-CG1 model. The backbone of polystyrene is much smaller than what the EoS is calculating. This is an artifact of the EoS. It is important to mention that the PS-CG1 model used here is very similar to the model of Jiménez-Serratos et al. in terms of σ , and since in that model it was possible to calculate the correct radius of gyration it was decided to further study this model as well.

The intramolecular parameters used in this study are all presented in Table 5.3.

5.3.2 Homopolymer Melts

With intermolecular potential parameters given in Table 5.1 and intramolecular potential parameters given in Table 5.3, densities of chains of 500 beads were calculated by simulation, and compared with calculations of the EoS.

Once this was done, conformational of pure melts were investigated, by measuring end-to-end distance, R_E and the radius of gyration R_g of polymer melts at 450 K and 1 bar.

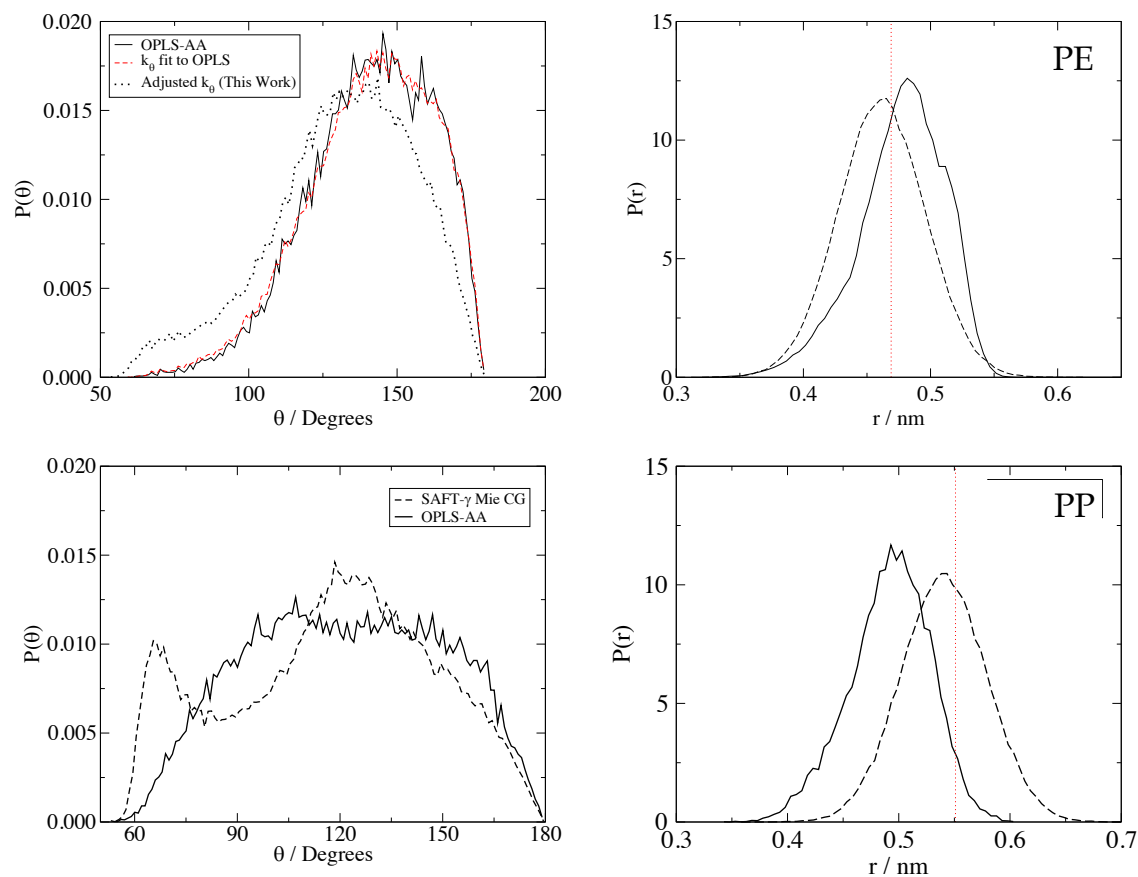


FIGURE 5.4: Angles and bonded distribution of *Top* PE and *Bottom* i-PP, mapped from OPLS-AA simulations at $T = 400$ K and $P = 1$ bar. Solid lines represent results atomistic simulations, dashed lines correspond to SAFT- γ Mie CG FF with θ_0 , k_θ , and k_b given in Table 5.3. The dashed vertical line corresponds to the value of σ given by the theory and used as the intramolecular bonding distance.

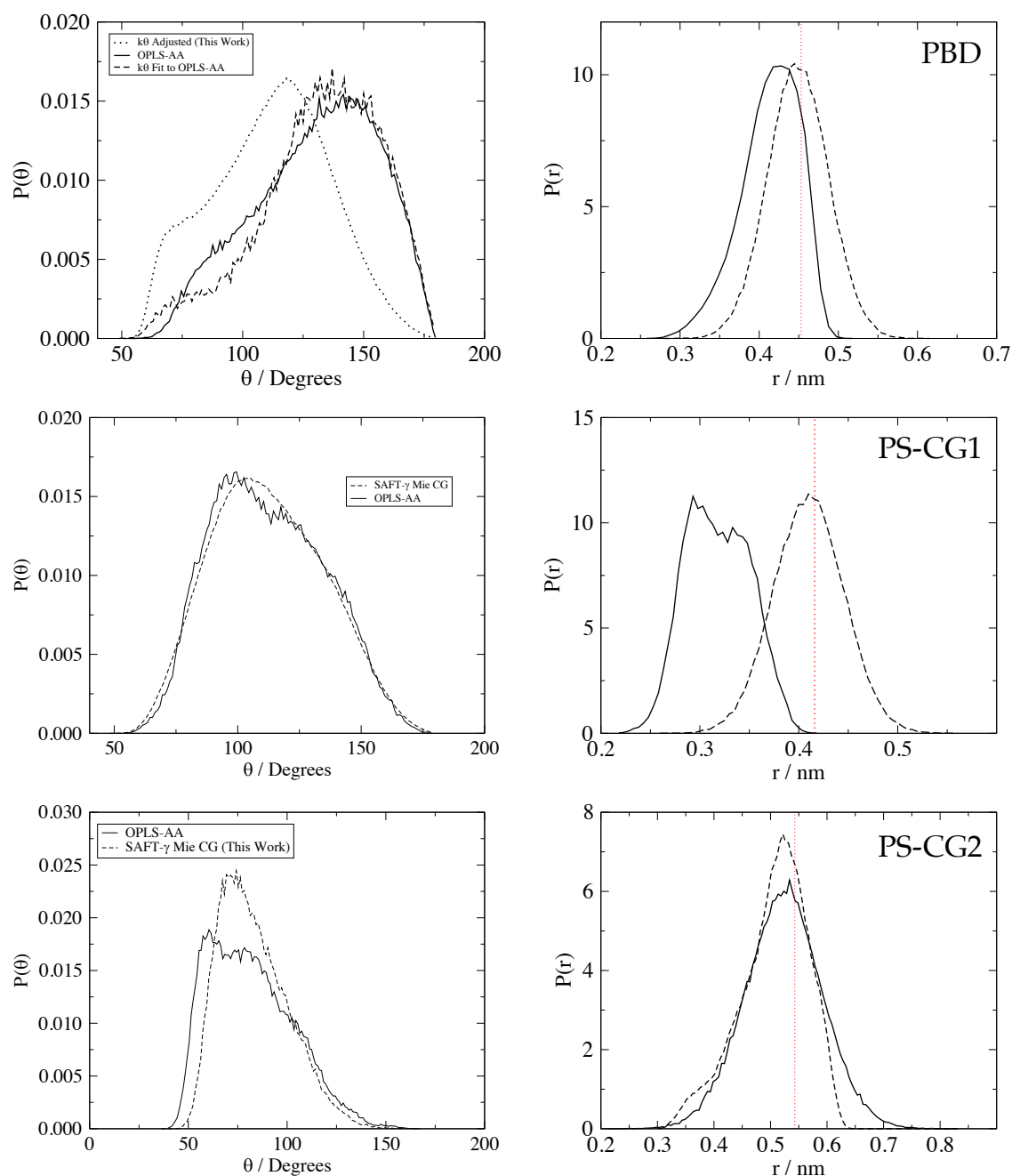


FIGURE 5.5: Angles and bonded distribution of CG *Top* PBD, *Middle* PS-CG1 and *Bottom* PS-CG2, mapped from OPLS-AA simulations at $T = 400$ K and $P = 1$ bar. Solid lines represent results atomistic simulations, dashed lines correspond to SAFT- γ Mie CG FF with θ_0 , k_θ , and k_b given in Table 5.3. The dashed vertical line corresponds to the value of σ given by the theory and used as the intramolecular bonding distance.

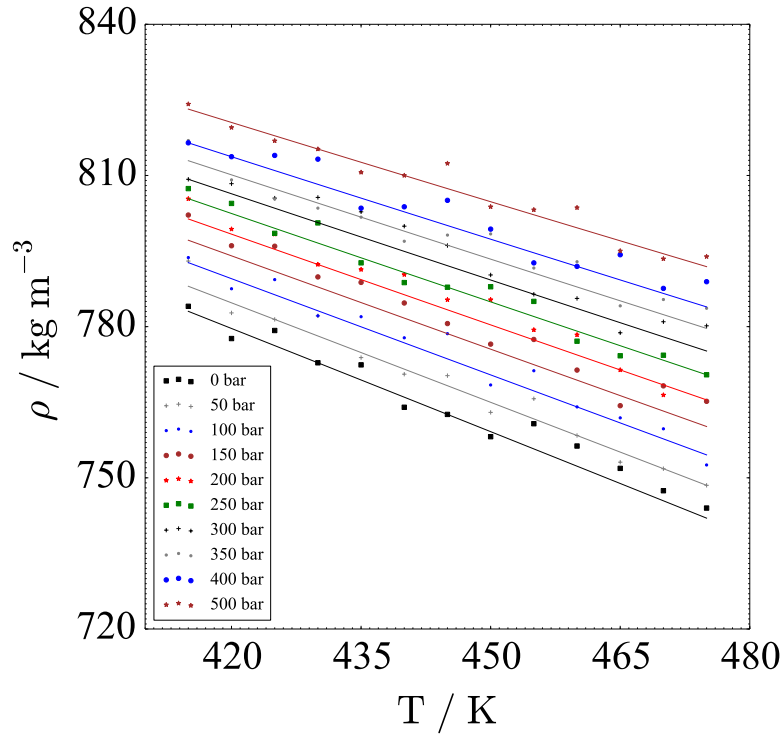


FIGURE 5.6: PVT data of 500 monomer units of PE in melt at different temperatures and pressures. Lines correspond to the calculations of the EoS and symbols are simulations in this work.

Polyethylene

PVT data of PE melt is presented in Figure 5.6. The results are very similar for both simulations and the EoS with an AAD of less than 0.2%. This shows the robustness of forcefield parametrisation using the equation of state.

Radius of gyration and end-to-end distances of PE melts were calculated for chains up to 160 CG beads. In order to test that the system is well equilibrated, the end-to-end autocorrelation function for each chain length was calculated, using the following equation:

$$C(t) = \frac{\langle \mathbf{R}_{EE}(0) \cdot \mathbf{R}_{EE}(t) \rangle}{\langle \mathbf{R}_{EE}^2 \rangle} \quad (5.8)$$

where $\mathbf{R}_{EE}$ is the end-to-end vector. Figure 5.7 shows that profiles of the autocorrelation functions and it could be seen that after a certain time, the autocorrelation

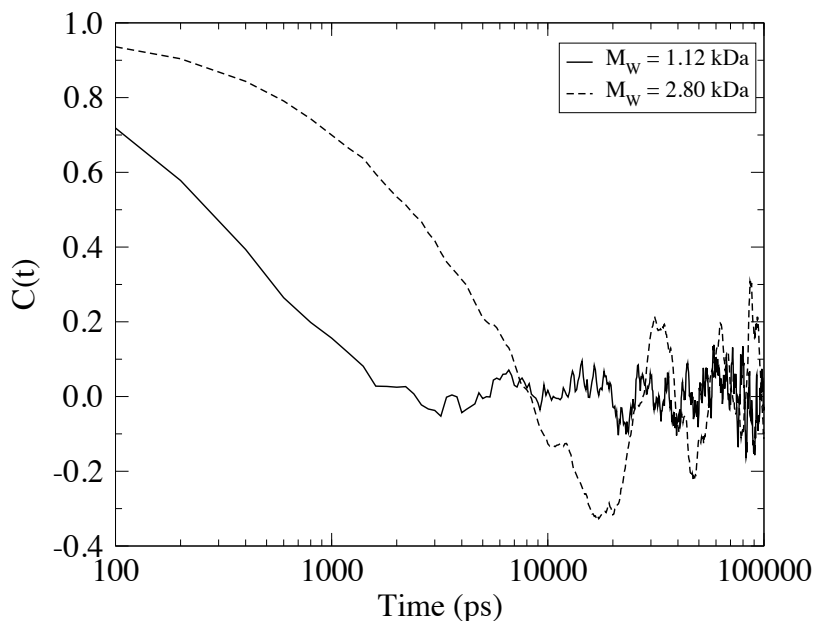


FIGURE 5.7: End-to-end autocorrelation for PE chains with $N = 20$ and 50 beads.

function collapses to the value of 0. The time it takes for the end-to-end distances to become uncorrelated is called the relaxation time. Simulations were run longer than the relaxation time of the polymers to ensure an equilibrated system. As can be seen from the aforementioned Figure, the longer the chain length, the longer the end-to-end relaxation times. This is also observed in other models.

R_g and R_E of polyethylene are presented in Figure 5.8 and compared with an array of different simulation studies found in literature. Here, the value of k_θ was modified to capture the correct behaviour. Using k_θ as given in Table 5.2 led to overpredictions of R_g by around 30%. It is very surprising that this was not observed in the work of Parizon et al., as the bond and angle potentials used in their study were very similar to those found in this study. More than 10 independent simulations were run in this work with different starting configurations for a chain of 50 monomers long, and the average overprediction of R_g was 32%. Reducing the value k_θ reduced the value of R_g . k_θ was reduced by a factor of three, and as can be seen in Figure 5.8, R_g and R_E were found to be in quantitative agreement with atomistic simulations of Mavrantzas et al. [215] and Foteinopoulou et al. [247]. In those models, highly efficient monte carlo algorithms were used to relax the melts very quickly,

with the former calculating the R_g of very long polymers. To verify that the model was capturing the correct conformations, the characteristic ratio of the polymer was calculated:

$$C_\infty = \lim_{N \rightarrow \infty} \frac{R_E^2}{(N-1)b^2} \quad (5.9)$$

Where b is the backbone carbon-carbon bond length, N is the degree of polymerisation and R_E the end-to-end distance.

Tzounis et al. [248] have reported a characteristic ratio of 8.2 for long linear polyethylenes. In this work, the longest monomer of $N = 640$ was used to calculate the characteristic ratio, where N is the number of carbon atoms in the polyethylene. The end to end distance was 11.3 ± 0.32 nm. Assuming a carbon-carbon bond length of 0.154 nm in alkanes, the characteristic ratio of 8.41 was calculated, which is in agreement with the results of Tzounis et al. [248]

Isothermal compressibility was also compared with other studies in literatures. Isothermal compressibility, κ , was calculated using the following equation in an NPT ensemble:

$$\kappa = -\frac{1}{\langle V \rangle} \left(\frac{\partial \langle V \rangle}{\partial P} \right)_T = -\frac{1}{k_B T \langle V \rangle} (\langle V^2 \rangle - \langle V \rangle^2) \quad (5.10)$$

Foteinopoulou et al. [247] reported isothermal compressibility of an atomistic polyethylene model (C1000) with a value $1.92 (\pm 0.4) \times 10^{-3} \text{ MPa}^{-1}$. In this work $\kappa = 1.96 \times 10^{-3} \text{ MPa}^{-1}$, which is again in quantitative agreement. It could be seen that the parametrisation of this polyethylene model is very robust, with a range of properties that have matched with literature available.

Polypropylene

PVT data for polypropylene is presented in Figure 5.9. Again like the case of polyethylene, the PVT data match almost exactly with the calculated results of the EoS. What is more interesting is that this PP model could predict the correct radius of gyration without any adjustments to its angle potentials fitted from OPLS-AA. This is surprising given that the sizes of the beads are much larger than that of the underlying OPLS-AA model (Figure 5.4). This could be explained by the bimodal distribution

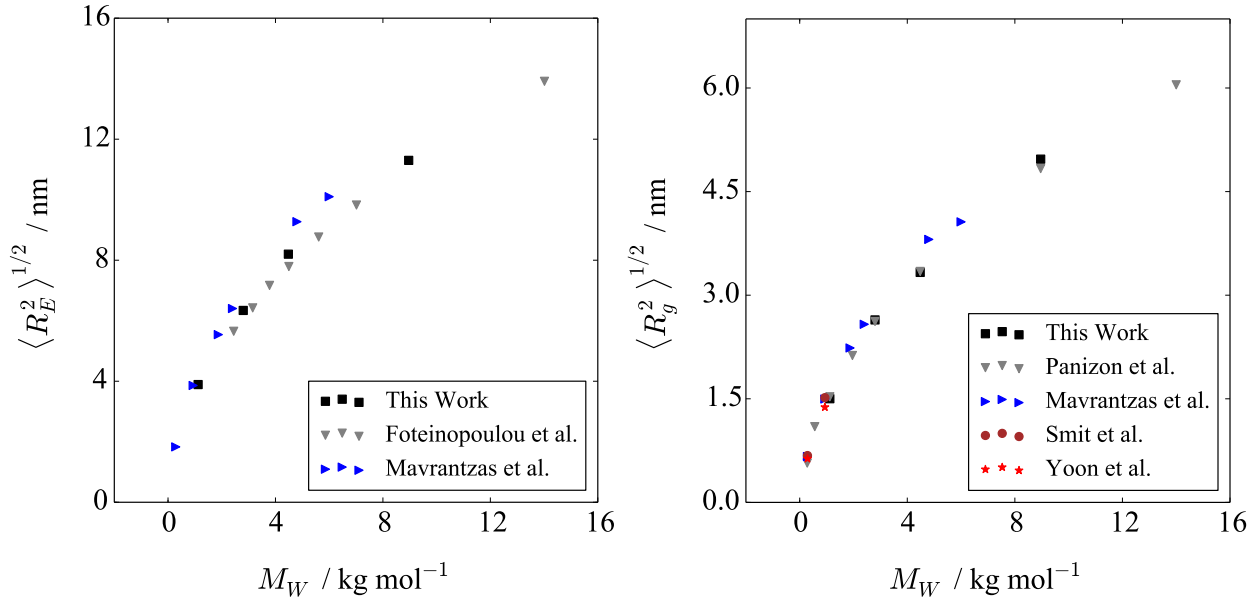


FIGURE 5.8: Radius of gyration, R_g , and End-to-End distance, R_E , of linear PE as compared with simulations of Panizon et al. [139], Mavrantzas et al. [215], Foteinopoulou et al. [247], Smit et al. [249] and Yoon et al. [250]

of the angles in the CG model, where a peak around 60 degrees is observed, leading to more compact conformations in the CG model relative to atomistic models.

Again to validate the conformation of i-PP in melt, the characteristic ratio was calculated for the longest chain studied and compared with the work of Tzounis et al. [248] The largest PP chain studied in this work had 150 CG beads, corresponding to 600 carbons in the backbone of the polymer (with 900 carbons in total). The characteristic ratio was calculated to be 6.41, which is in quantitative agreement with $C_\infty = 6.2$ as calculated by Tzounis. Again here the carbon-carbon backbone bond length was assumed to be 0.154 nm.

Isothermal compressibility was also calculated, with $\kappa = 1.62 \times 10^{-3} \text{ MPa}^{-1}$ at 500 K, 1 bar. This value matched exactly with experimental data found in ref [251].

Polybutadiene

PVT of PBD is presented in Figure 5.11. Just like the two previous cases, it could be seen that the simulations match the theory, with an AAD% = 0.25. Unlike the two previous cases, data on the radius of gyration for PBD is much more scarce.

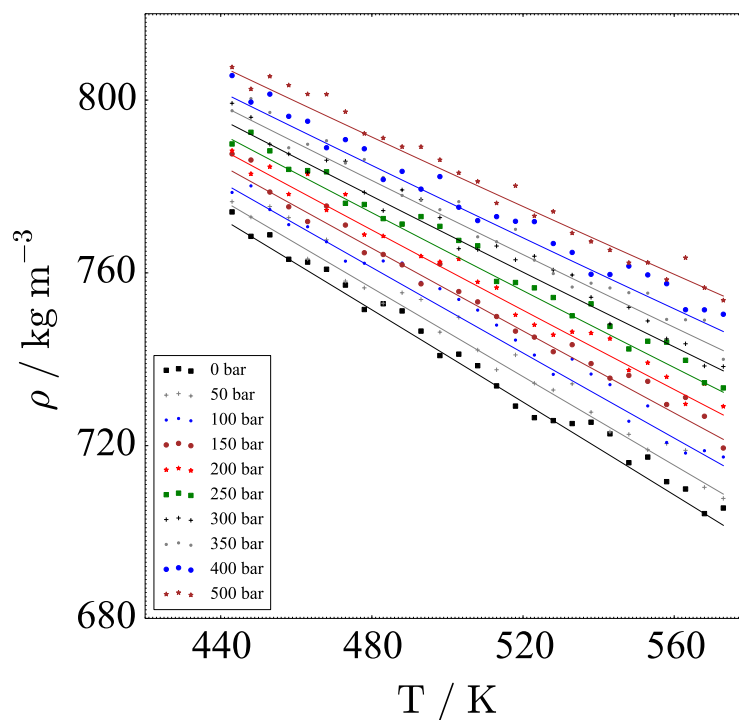


FIGURE 5.9: PVT data of 500 monomer units of PP in melt at different temperatures and pressures. Lines correspond to the calculations of the EoS and symbols are simulations in this work.

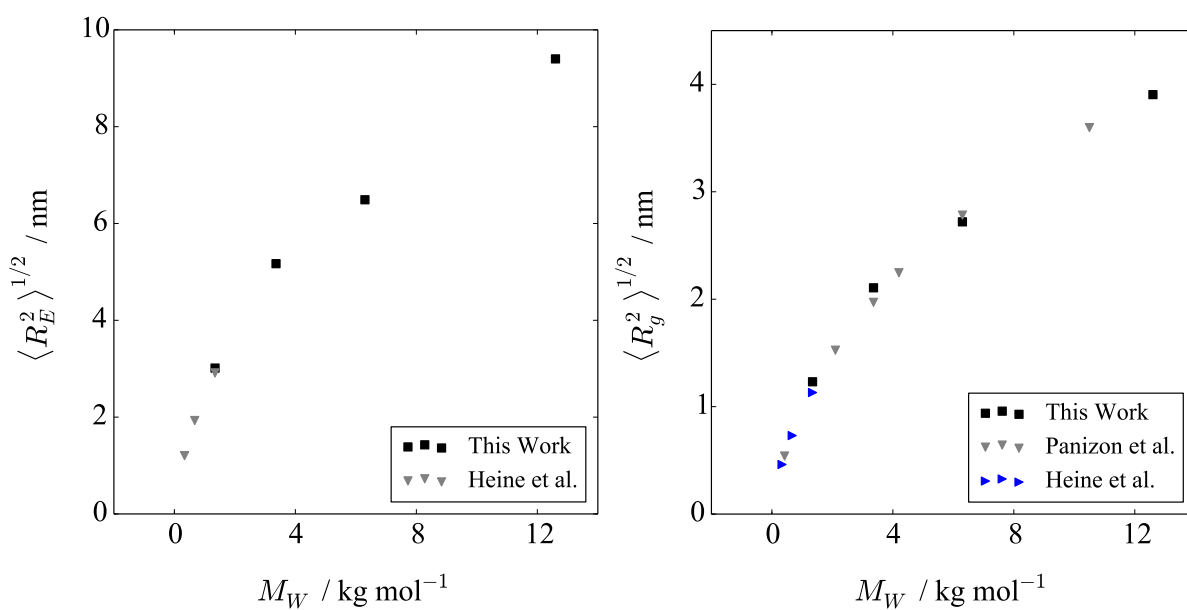


FIGURE 5.10: Radius of gyration, R_g , and End-to-End distance, R_E , of i-PP as compared with simulations of Panizon et al. [139] and Heine et al. [252]

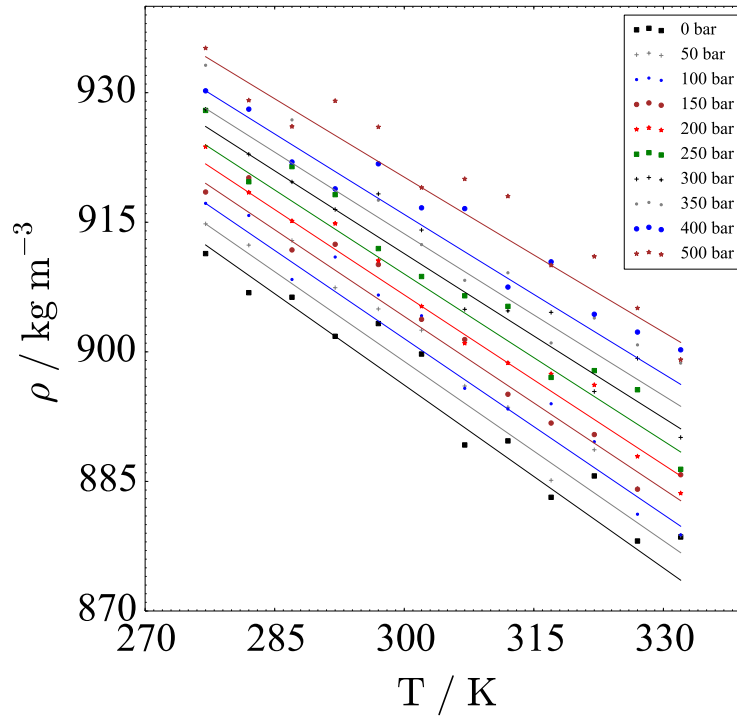


FIGURE 5.11: PVT data of 500 monomer units of PBD in melt at different temperatures and pressures. Lines correspond to the calculations of the EoS and symbols are simulations in this work.

Theodorou et al. have investigated properties of 1,4-cis-polybutadiene with atomistic simulations. Just like the case of polyethylene, the value of k_θ had to be adjusted in order to calculate the radius of gyration accurately. Without adjustment, the radius of gyration was overestimated by almost 40%. Hadjichristidis et al. [253] investigated end to end distances of polybutadiene, which was used to adjust k_θ . The results can be seen in Figure 5.12. The characteristic ratio was calculated to be 4.7, which corresponds to those calculated in literature [254].

Polystyrene

Finally, for polystyrene, the two models proposed were both simulated. Figure 5.13 shows the results for the two cases. For the PS-CG2 model, which is a linear chain, the theory and simulations match. However for the case of PS-CG1, where polystyrene is modelled as a branched polymer, simulations slightly overpredict

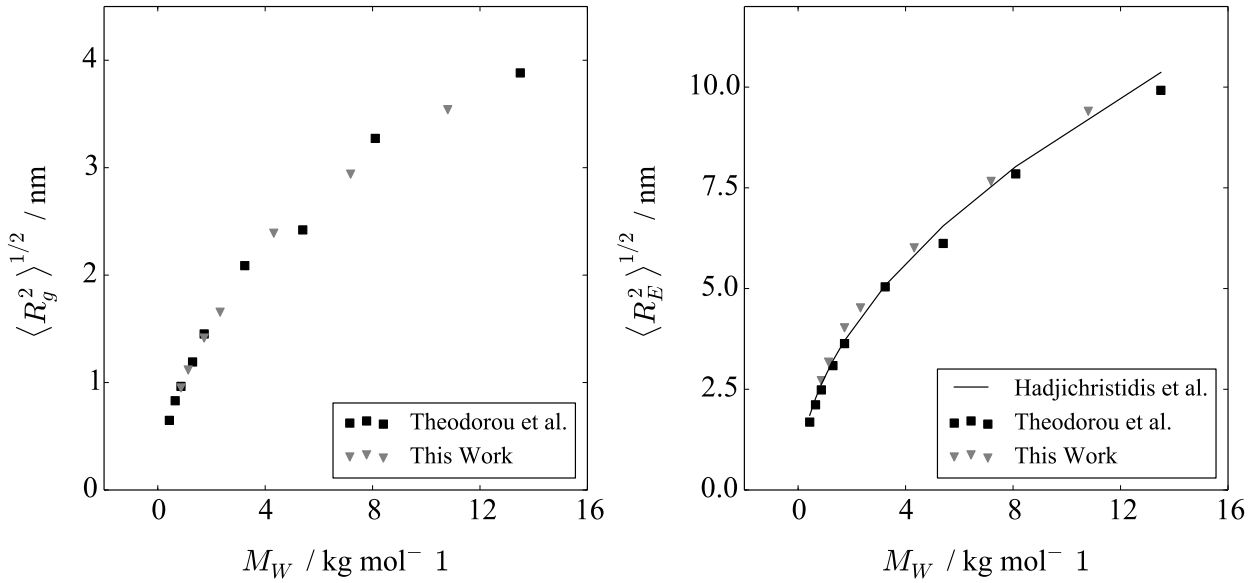


FIGURE 5.12: Radius of gyration, R_g , and End-to-End distance, R_E , of PBD as compared with simulations of Theodorou et al. [254] and experimental data from Hadjichristidis et al. [253]

densities compared with the EoS. However, this overprediction was still less than 1%.

Surprisingly, both models produced same values for the isothermal compressibilities at 500 K and 1 bar, being 2.1×10^{-3} MPa⁻¹ for PS-CG1 and 2.3×10^{-3} MPa⁻¹ for PS-CG2. Experimental values for κ of PS are around 1.13×10^{-3} MPa⁻¹ [255]. Jimenez-Serratos et al. [236] obtained a value of 1.64×10^{-3} MPa⁻¹ with a CG model, and Carbone et al. [131] reporting a value of 0.93×10^{-3} MPa⁻¹ using atomistic simulations. Finally Spyriouni et al. [132] obtained isothermal compressibilities of 25.0×10^{-3} MPa⁻¹ using the IBI method for polystyrene, which was also similar to compressibilities of the CG model proposed by Carbone et al. The fact that κ calculated in our coarse-grained approach is in the same order of magnitude as experimental and atomistic simulation results shows the robustness of the parameters in studying melts.

R_E and R_g for both models were calculated without adjusting the angular potentials, with both models being able to calculate the correct R_g and R_E values. The characteristic ratios for PS-CG1 and PS-CG2 were found to be 8.9 and 8.6 respectively. This is in quantitative agreement with the value of 8.5 reported by Tzounis. The results for R_g and R_E of both PS models can be seen in Figure 5.14.

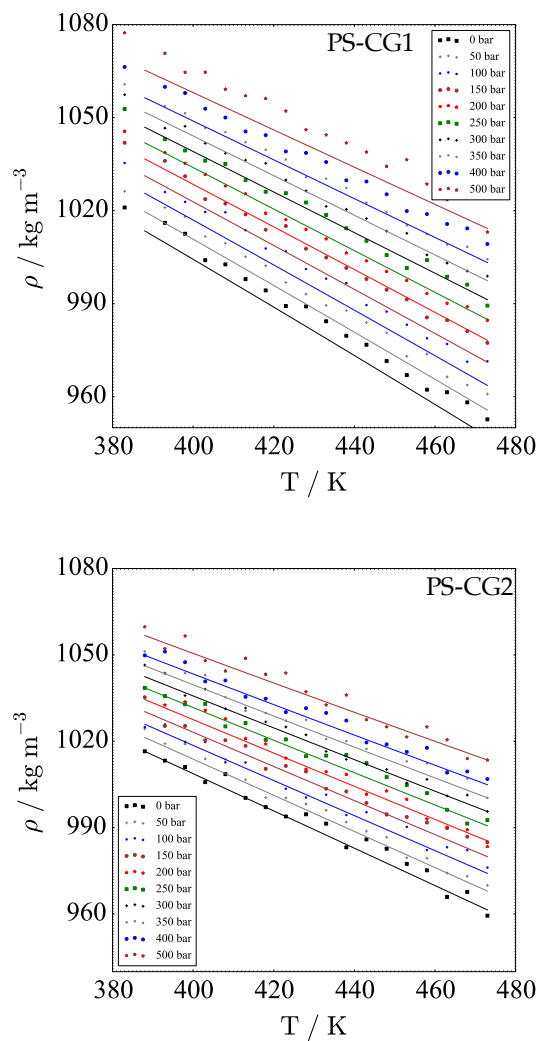


FIGURE 5.13: PVT data of 500 monomer units of PS in melt at different temperatures and pressures. *Left* PS-CG1 model with side chain and *Right* PS-CG2 model, which is linear polystyrene. Lines correspond to the calculations of the EoS and symbols are simulations in this work.

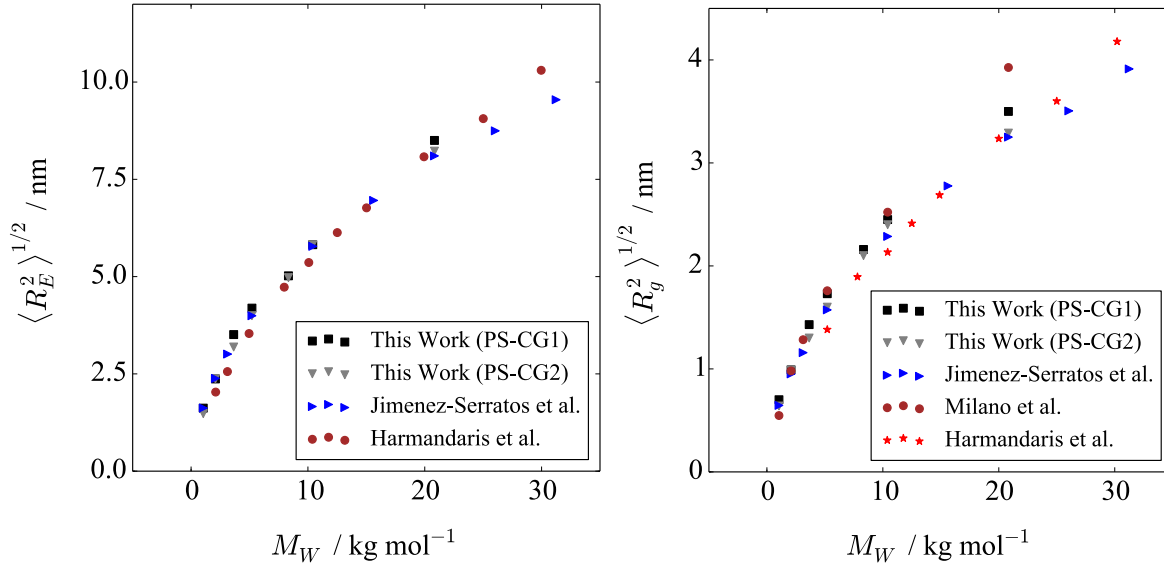


FIGURE 5.14: Radius of gyration, R_g , and End-to-End distance, R_E , of PS as compared with the simulations Jimenez-Serratos et al [236], Harmandaris and Kremer [130] and Milano and Müller-Plathe [129]

TABLE 5.4: Intermolecular potential parameters of n-pentane, n-hexane and n-heptane used in simulations

Molecule	m_{seg}	λ_r	ε [K]	σ [Å]
n-Pentane	2	14.75	307.9	4.258
n-Hexane	2	18.01	371.1	4.517
n-Heptane	2	21.27	427.0	4.766

5.3.3 Polymer-Solvent Phase Behaviour

So far simulations of homopolymer melts have been presented, highlighting the almost identical agreement between densities calculated by the equation of state and molecular simulations. This is a clear indication that SAFT- γ Mie EoS can be an accurate tool to obtain forcefields for polymers. Since the EoS could provide accurate self-interaction parameters, cross interaction parameters obtained from the EoS could also be used directly in molecular simulations to observe the same phase behaviour as predicted by the EoS.

Representability of the Solvent Models

In this section a comparison of the calculations of the EoS is made with the results obtained from simulations for polymer-solvent mixtures. Three solvents namely

TABLE 5.5: Intramolecular potential parameters of n-pentane, n-hexane, n-heptane used in simulations

Molecule	m_{seg}	k_b (kJ mol ⁻¹ nm ⁻²)	$b_{0, SAFT}$ (nm)
n-Pentane	2	6300	4.258
n-Hexane	2	6300	4.517
n-Heptane	2	6300	4.770

n-pentane, n-hexane and n-heptane are used with their Mie potential parameters parametrised in the previous chapter. Each of the solvent molecules are modelled as two spheres tangentially bonded to each other with a distance of σ . The Mie potential parameters presented in the previous chapter are directly used in direct coexistence VLE simulations to assess the representability of the potential parameters in modelling the solvents in simulations. The non-bonded and bonded interaction parameters are given in Table 5.4 and 5.5 respectively.

The value of k_b used to model all solvents was the one fitted for n-alkanes by Rahman et al. [32] and can be seen in Table 5.5. The VLE of these solvents were calculated via direct coexistence simulations, using an elongated box ($L_z = 8 L_x$, $L_x = L_y \approx 5$ nm) in the canonical ensemble, with 2000 molecules. The results can be seen in Figure 5.15. Vapour pressures are slightly over-predicted in the simulations, however saturation liquid densities match experimental results for temperatures away from the critical point. It can be seen that the parameters are robust in representing the fluid properties of the n-alkane solvents.

Polyethylene & Temperature Induced Phase Separation (LCST)

Polyethylene is the simplest of all polymers. For mixtures of PE with solvents, LCST phase behaviour has been experimentally observed at high pressures. [194]. In the previous chapter, it was shown that the solution phase behaviour of PE in n-alkanes could be predicted by the EoS without any adjustable parameters. To assess the correspondence between the calculations from the EoS and the simulations, two different M_W of polyethylene were simulated in a mixture with n-pentane.

The first polyethylene-solvent mixture studied was an oligomer with a $M_W = 2.15$ kg mol⁻¹, corresponding to 39 CG beads. 5 NPT simulations were run at a global

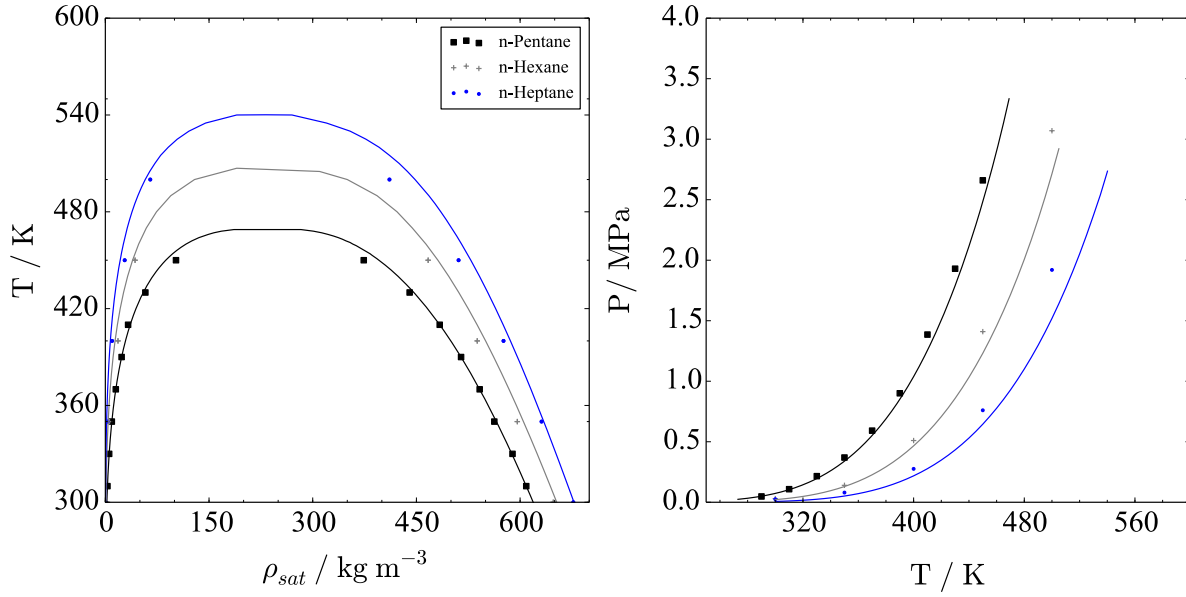


FIGURE 5.15: Comparison of simulation (symbols) with experimental data (NIST). *Left* Temperature-density vapour-liquid coexistence curve, *Right* Vapour pressure.

composition of 20 wt%, with 200 molecules of polymer and 25000 solvent molecules in the system, with a total of 58000 CG segments ($\approx 520,000$ atoms) in the system. 5 different temperatures were run between 450 to 490 K with a constant pressure of $P = 5$ MPa. The simulation box is an elongated box with the dimensions $L_z = 10 L_x$, $L_x = L_y \approx 15$ nm. Each simulation was run in the isobaric-isothermal (NPT) ensemble, with 2000 molecules being in the system. The critical temperature of n-pentane is 470 K and therefore, it was assumed that n-pentane above this temperature would be in the supercritical region. The Gelb and Müller method previously described in Figure 5.3 was used to assess immiscibility and coupled with the visual inspection of the simulation trajectory was used to observe temperature induced LCST phase behaviour. This can clearly be seen in Figure 5.16. The onset of phase separation occurs between 460 and 480 K, as predicted by the EoS. The distribution of the local compositions at 460 K is unimodal, corresponding to a single phase mixture, and at 490 K it can be clearly seen that the distribution is bimodal, corresponding to a system composed of polymer rich and polymer lean phases. At 490 K, the polymer rich phase has a composition of 50 wt% polymer. This is compared to the calculations of the EoS in Figure 5.17. The composition of the polymer rich phase at 490 K is very

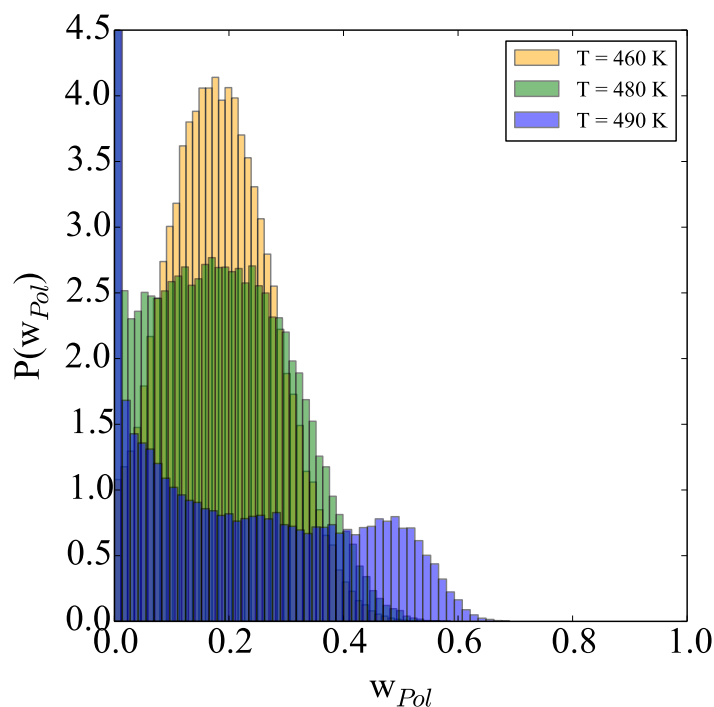


FIGURE 5.16: Local composition distributions of boxes with size of 3 nm^3 for a mixture of PE-n-pentane, with $M_W = 2150 \text{ Da}$, $P = 5 \text{ MPa}$ and global compositions of $w_{\text{polymer}} = 0.2$. A bimodal distribution is observed at 490 K , clearly indicating a phase separation, whereas a unimodal distribution with a peak at $w_{\text{polymer}} = 0.2$ (corresponding to the global composition) is observed at $T = 460 \text{ K}$, indicating full miscibility. The simulations clearly highlight an LCST phase behaviour.

similar in value for both methods, however at 480 K , although there is a phase separation and there is a bimodal distribution, the polymer rich phase has a composition very close to the global composition, around $25 \text{ wt\%}$ polymer. This could mean that the lower critical temperature is slightly overpredicted in the simulations and that phase separation starts at a higher temperature for this molecular weight. The simulation snapshots of the final polymer configurations can also be seen in Figure 5.17, and it could clearly be seen that at 450 K the system is much more isotropic than at higher temperatures.

The onset of phase separation in the first case of low M_W PE in n-pentane is very close to the critical point of the solvent, and consequently phase separation is only observed in a very small region of temperature. By increasing the molecular weight of the polymer, the lower critical point decreases significantly away from the critical point of the solvent. The second case of polyethylene in n-pentane is for a

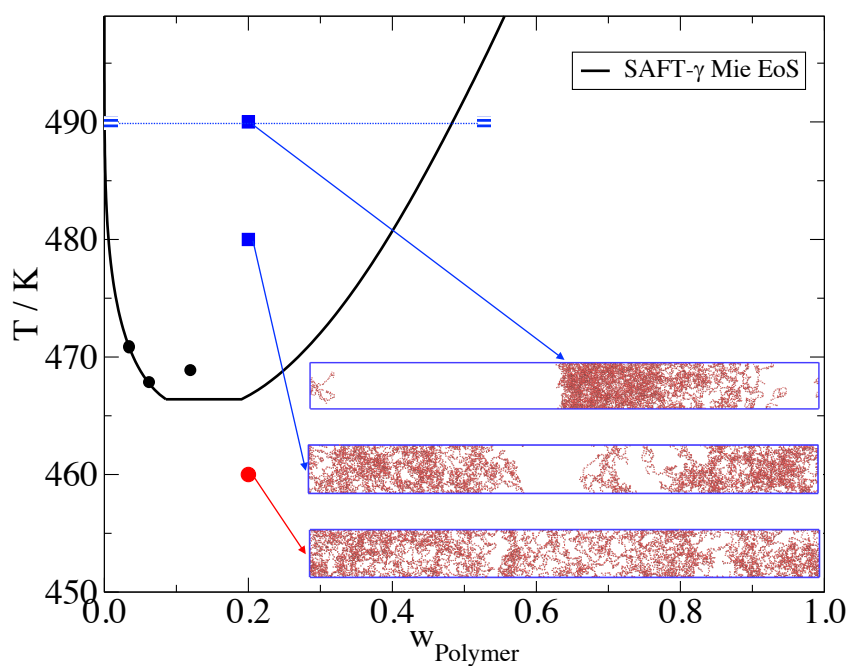


FIGURE 5.17: Phase diagram of PE-n-pentane mixtures, $M_{W, \text{Polymer}} = 2150$ Da (39 CG beads), $P = 5$ MPa. Line corresponds to the calculations of the SAFT- γ EoS, black circles correspond to experimental results from ref [194]. Filled blue squares are the global compositions ($w_{\text{polymer}} = 0.2$) and patterned squares are the compositions calculated from the local density method. Snapshots of the final configurations of the simulations at different temperatures are also presented, clearly demonstrating the LCST phase behaviour.

polymer of molecular weight 16,400 Da, corresponding to 292 CG beads. The LCST is predicted to be 416 K by the EoS. Again like the case of the first PE polymer (low M_W), an NPT simulation at 5 MPa was run at different temperatures for a system with a global composition of 20 wt% polymer, with 25 polymer molecules and 25,000 solvent molecules. The dimensions of the simulation box was kept around $L_z = 10 L_x$, $L_x = L_y \approx 10$ nm. As can be seen from Figure 5.18, it is possible to observe phase separation for a much large range of temperature in this system, as the phase separation starts at temperatures far less than the critical point of the solvent. The comparison between the EoS, the experimental data, and the simulations is clearly shown in the aforementioned figure. There is a close correspondence between all three approaches in calculating the LCST, however, the shape of the phase envelope is slightly narrower in simulations relative to the predictions of the EoS. This could potentially be due to the fact that in the EoS, molecules are assumed to be freely jointed chains and the effect of the chain stiffness and the angular potentials are not taken into account. By simple inspection of the final simulation snapshots as shown in the Figure, it is possible to see that there is a clear phase separation at $T = 430$ K as the temperature is increased from 410 K. Less mixing is also observed at higher temperatures. The local composition distributions can be seen in greater detail in Figure 5.20. It is clearly seen that there is a deviation from the global composition at temperatures higher than 410 K. Therefore, no adjustable parameters are required to model polyethylene-alkane solvent mixtures and that at least qualitatively, the EoS and the simulations are in agreement.

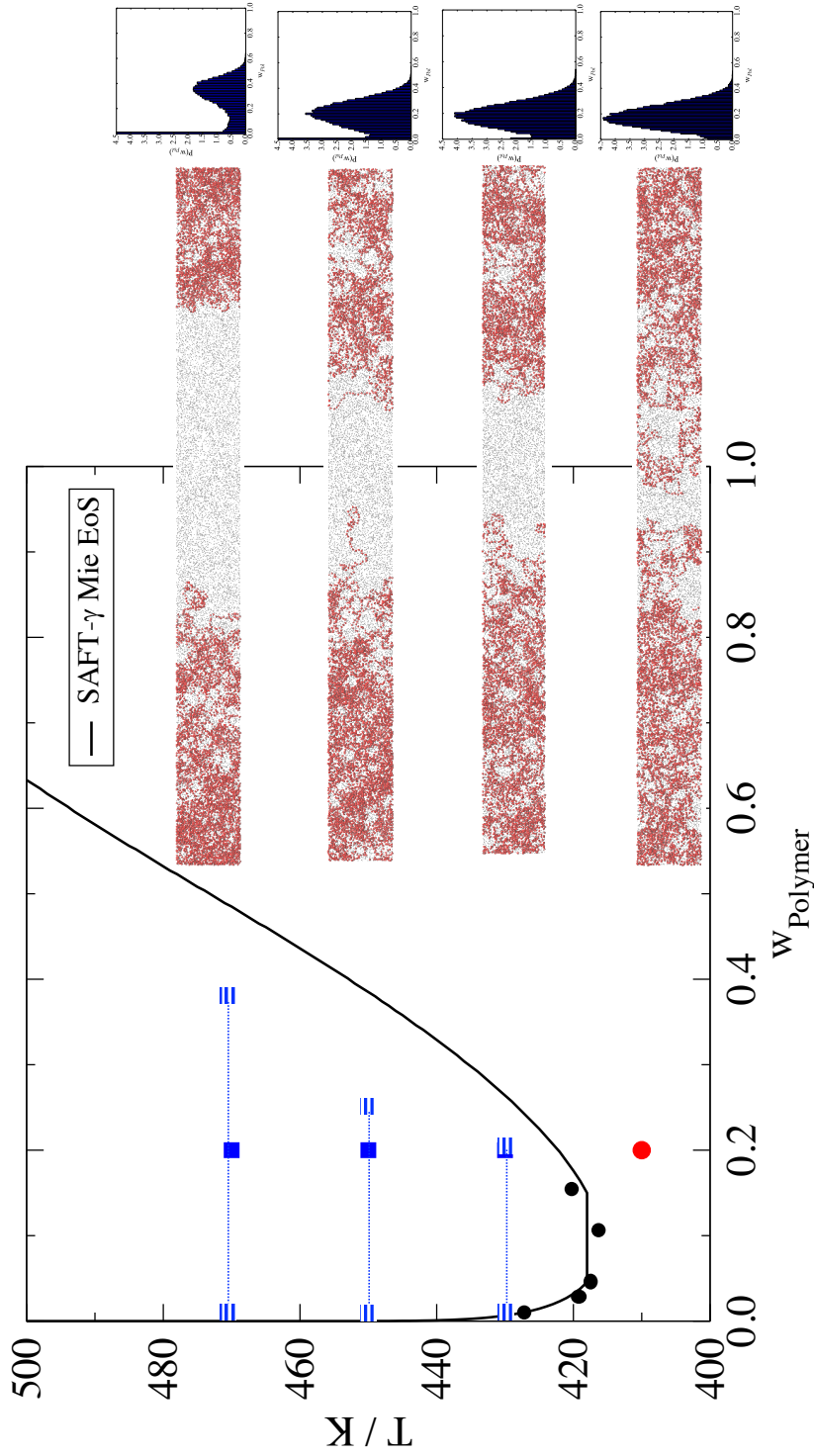


FIGURE 5.18: Phase diagram of PE-n-pentane mixtures, $M_W, \text{polymer} = 16400$ Da (292 CG beads), $P = 5$ MPa. Line corresponds to the calculations of the SAFT- γ EoS, black circles correspond to experimental results from ref [194]. Filled blue squares are the global compositions ($w_{\text{polymer}} = 0.2$) and patterned squares are the compositions calculated from the local density method. Snapshots of the final configurations of the simulations at different temperatures are also presented, clearly demonstrating the LCST phase behaviour without any adjustable parameters.

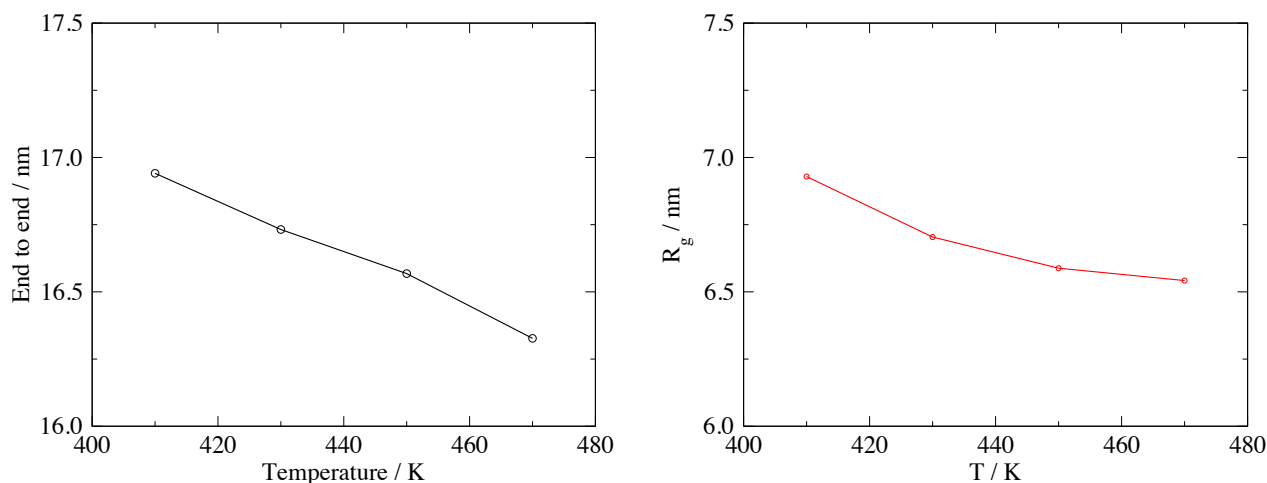


FIGURE 5.19: *Left* R_E and *Right* R_g vs Temperature of 16,400 Da PE in n-pentane

The significance of the study of PE is to demonstrate that this approach presented in this thesis can be used to reliably simulate Type V (LCST) phase behaviour of polymer solutions with quantitative accuracy. This is the main highlight of this coarse-graining approach. Moreover, not only is it possible to observe the same behaviour in simulations as calculated by the EoS, it is also possible to observe transport and structural properties. In terms of conformational properties, it could be seen in Figure 5.19 that R_g and R_E of the long chain PE decreases with increasing temperature. Again this is another indication that the system is undergoing phase separation.

Polypropylene: Pressure Induced Phase Separation (UCSP) & the Effect of k_{ij}

There are many methods that can capture type II (UCST) phase behaviour predictably, as discussed in the 5.1. Type V (LCST) phase behaviour discussed for PE is the first of the other complicated phases that can be predicted with a polymer mixture.

Another complex phase behaviour which is difficult to simulate with conventional techniques such as DPD is that of pressure induced phase separation. As shown in the previous chapter, polypropylene and n-pentane mixtures undergo mixing with increasing pressure. In this section, mixtures of 54 kDa polypropylene (642

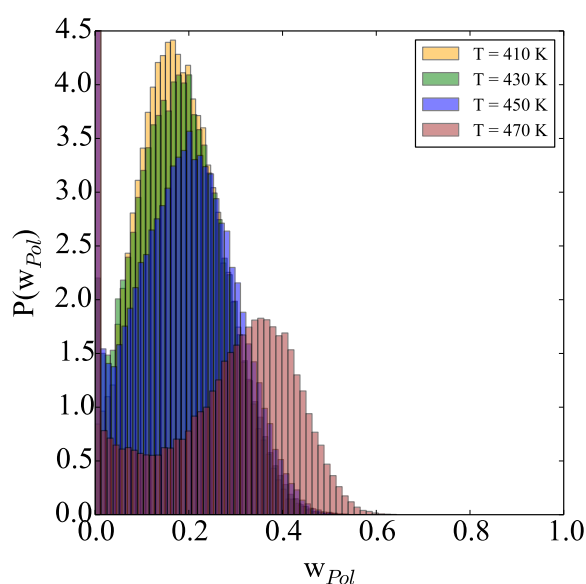


FIGURE 5.20: Local composition distributions of boxes with size of 3 nm³ for a mixture of PE-n-pentane, with $M_W = 16400$ Da, $P = 5$ MPa and global compositions of $w_{polymer} = 0.2$. A bimodal distribution is observed at 470 K, clearly indicating a phase separation, whereas a unimodal distribution with a peak at $w_{polymer} = 0.2$ (corresponding to the global composition) is observed at $T = 410$ K, indicating full miscibility. The simulations clearly highlight an LCST phase behaviour.

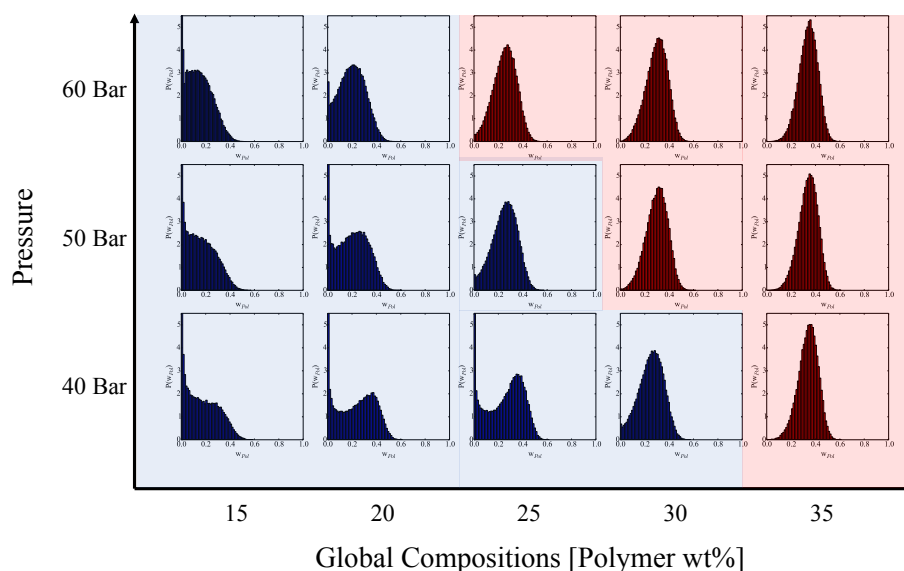


FIGURE 5.21: Local composition distributions of i-PP-n-pentane mixtures, $M_{W, polymer} = 54$ kDa (642 CG beads), $T = 470$ K. Blues indicates regions where phase separation was observed (bimodal distribution) and reds are regions the mixture is miscible (unimodal distribution).

CG beads or 11,000 atoms) and n-pentane were simulated at different global compositions and at different pressures. For each system, polymers were added to 40,000 solvent molecules to have global compositions of 15 to 35 wt% polymer. The box dimensions were around $35 \times 22 \times 22$ nm in order to ensure that the boxes are larger than the R_g . The temperature of the system was set to 470 K and the cross interaction parameter was set to the value of $k_{ij} = -0.061$ calculated in the previous chapter. The full phase diagram of regions of miscibility and immiscibility can be seen in the local composition distributions in Figure 5.21. Where a bimodal distribution was observed, it was assumed the mixture is immiscible, and where a unimodal distribution was observed miscibility was assumed. Of particular interest is the middle column with the global composition at 25 wt%. The distribution diagrams clearly demonstrate a change in miscibility of the polymer in solution at different pressures. Moreover, the row of different global compositions at 40 bar also clearly highlights a change of miscibility with increasing polymer content in the system. The column at a global composition of 15% contains only bimodal distributions, whereas that of 35% shows only unimodal distributions.

The phase map shown in Figure 5.21 is superimposed onto the predictions of the EoS in Figure 5.22. Surprisingly, the EoS and the simulations give identical phase envelopes for the systems studied. This shows that the value of k_{ij} given by the EoS has a real physical meaning and that the state independent parameters can be used realistically to model not only temperature and molecular weight dependent phase behaviour as shown previously, but also the immiscibility due to pressure. Accurate correspondence between the theory and simulation is observed given a single adjustable parameter for all state points in the phase diagram. This transferability of the potential parameters allows the models to be predictable in other regions of the phase space.

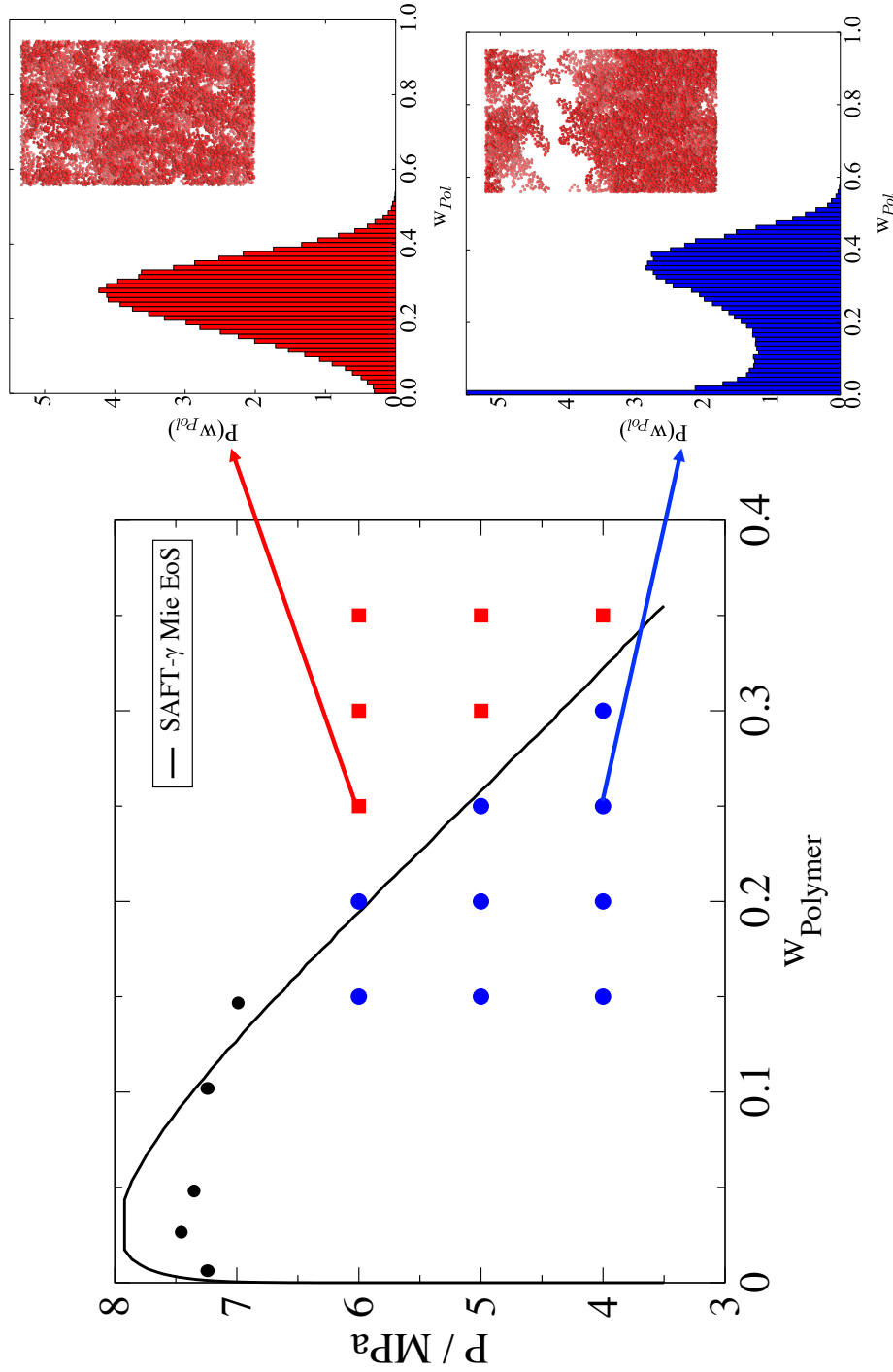


FIGURE 5.22: Phase diagram of i-PP-n-pentane mixtures, $M_{W, \text{Polymer}} = 54$ kDa (642 CG beads), $T = 470$ K. Line corresponds to the calculations of the SAFT- γ EoS, black circles correspond to experimental results from ref [198]. Blue circle are the global compositions (w_{polymer}) at pressures where phase separation was observed and red circles are the global compositions at pressures where phase separation was not observed. Snapshots of the final configurations of the simulations at different temperatures are also presented, clearly demonstrating the pressure induced phase separation, with accurate correspondence between simulations and theory. $k_{ij} = -0.061$ as calculated in the previous chapter.

So far it has been shown that the approach proposed here can successfully model Type II and Type V phase behaviour with state-independent parameters. Type III (hourglass) and Type IV (LCST+UCST) phase behaviour is investigated next, with yet another polymer (polystyrene) in new solvents investigated to explore the extent of applicability of SAFT methodology proposed here.

Polystyrene: Type II (UCST), Type III (Hourglass) and Type IV (UCST+LCST) Phase Behaviours

Given that the SAFT- γ Mie CG methodology can capture LCST of PE-n-pentane mixtures without any adjustable parameters and that it is possible to simulate pressure induced phase separation of i-PP-n-pentane mixtures with a single state-independent cross interaction parameter, other phases in Figure 2.7 are also expected to be simulated. Polystyrene solutions in n-hexane and n-heptane are known to exhibit Type IV at low molecular weights. Upon increasing the molecular weights, the separate phase envelopes of LCST and UCST coalesce forming a single region of immiscibility, i.e. Type V phase behaviour. This has been previously discussed in Section 4.3.6.

In order to assess the effect of chain geometry on phase behaviour, the PS-CG1 (i.e. the branched polymer) was used in mixtures with n-hexane and n-heptane. Two different M_W of PS were used; 2.03 kDa and 4.80 kDa, corresponding to 39 and 92 CG beads per molecule respectively. As with the model proposed in Section 4.3.6, $k_{ij} = 0.0113$ for PS-n-hexane mixture, and $k_{ij} = 0.007$ for PS-n-heptane mixtures. Each system was run with 20,000 solvent molecules with a global composition of 30 or 50 polymer wt%. Like previous cases, simulations were composed of an elongated box ($L_z \approx 8 L_x$) at pressure and temperature fixed in an NPT ensemble. However, unlike previous cases, the system pressure was changed at every temperature so that the system pressure was at the vapour pressure of the solvent ($\approx$ along the 3-phase line), commensurate with the experimental set-up.

The local composition distributions of 2.03 kDa PS-n-hexane (30 wt% Polymer) mixture is presented in Figure 5.24. For the first time in this chapter, there is a qualitative discrepancy between the critical point calculated in the EoS and that shown

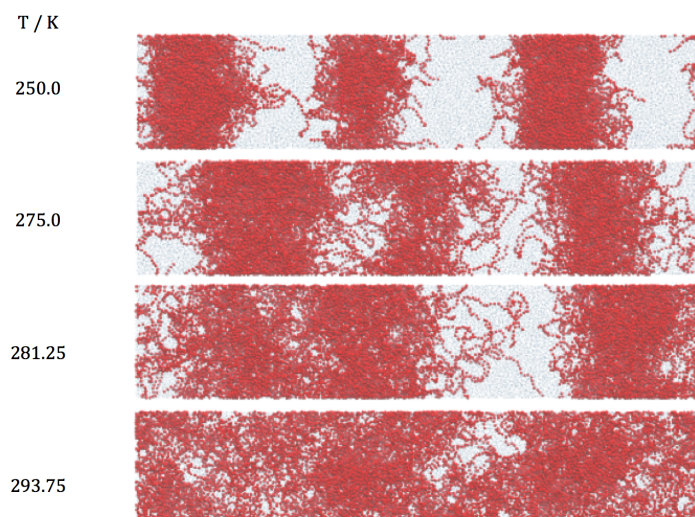


FIGURE 5.23: Snapshots of the UCST behaviour of 2.03 kDa PS in n-heptane solution at different temperatures. As temperature is increased, the two components become more miscible, however, no LCST behaviour is observed at higher temperatures, unlike the prediction of the EoS.

in the simulations. The phase diagram of this system as obtained from simulations does not show any LCST behaviour at higher temperatures. A unimodal distribution is observed for any temperatures above 300 K. However, the UCST phase envelope in simulation and theory are almost the same. For the lowest two temperatures (250 K and 285 K), it was possible to determine the composition of polymer in each LLE phases and they were found to be in quantitative agreement with the theory. One reason as to why no LCST behaviour was seen could be due to the effect of branching of the polymer. As has been previously reported in literature, increases in the degree of branching can lead to more miscibility as the size of the molecule (R_g) is smaller for a branched polymer relative to its linear isomer. This leads to a smaller radius of gyration. In essence the molecule size becomes more similar to that of the solvent molecules and the solvent and the polymer molecules become more alike. Consequently the components of the system become more miscible. [256–260] The exact same behaviour is observed for the same M_W polymer in n-heptane, where it is possible to observe UCST phase behaviour correctly, yet no LCST phase behaviour is observed. The snapshot of the final frame of the simulations are presented in Figure 5.23.

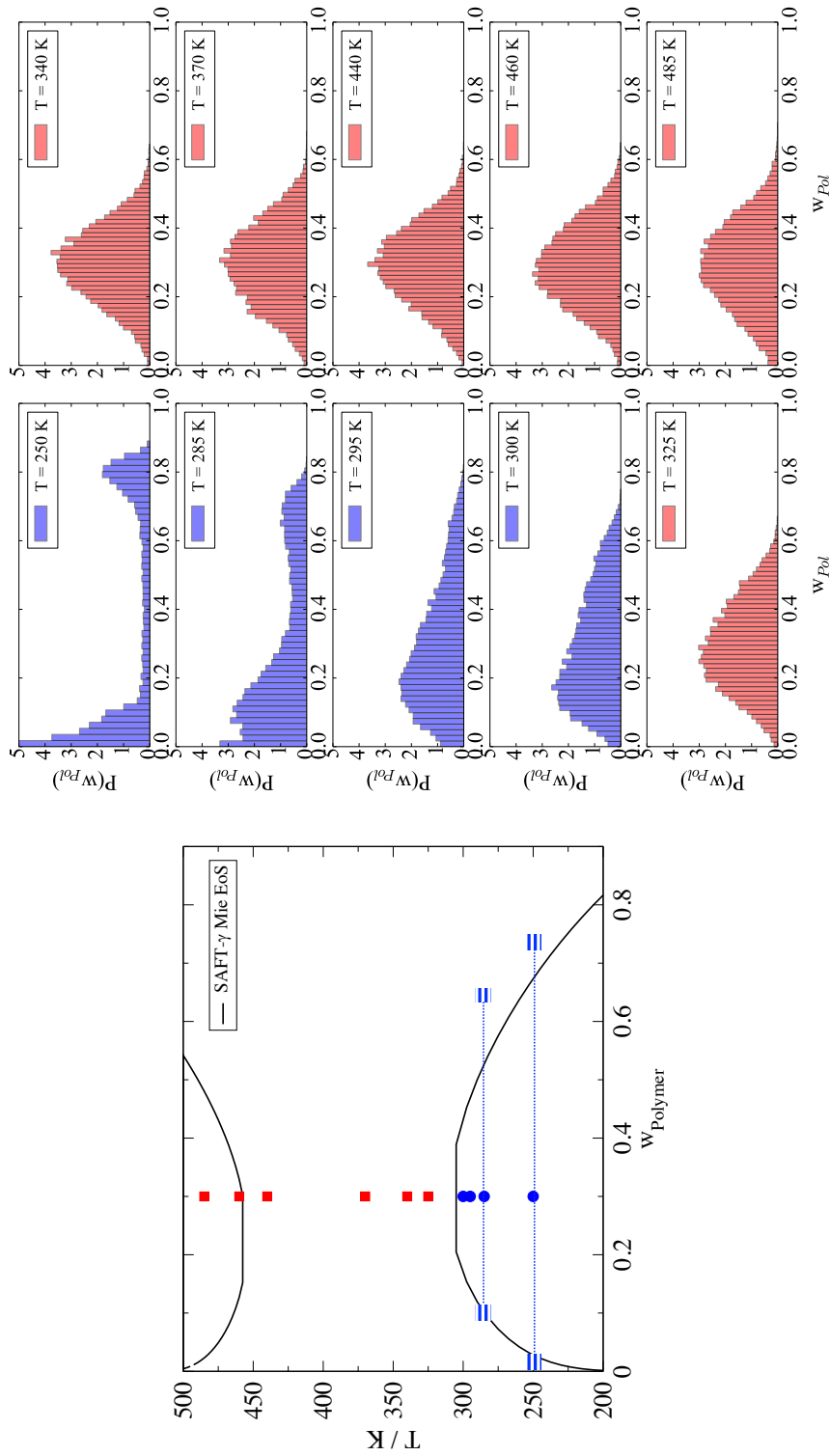


FIGURE 5.24: Phase diagram of PS-CG1-n-hexane mixtures, $M_{W, Polymer} = 2030$ Da (40 CG beads). Line corresponds to the calculations of the SAFT- γ EoS. Filled blue circles are the global compositions ($w_{polymer} = 0.3$) where phase separation was observed and patterned squares are the compositions calculated from the local density method. Red squares are the global compositions at temperatures where phase separation was not observed. The local composition distributions at different temperatures are also presented, clearly demonstrating the onset of miscibility at higher temperatures. Unlike the EoS predictions, no LCST phase behaviour was observed for this system.

As shown in Figures 5.25 and 5.26, for the heavier polymer (4.80 kDa PS), the effect of branching is not as significant and LCST is observed at the critical point as predicted by the EoS.

The phase diagram of 4.80 kDa in n-hexane is that of Type III (hourglass shaped). In this work, two global compositions of 30 and 50 polymer wt% were simulated, with the 30% being fully within the immiscibility region at all temperatures and the 50 wt% being miscible in a temperature range of 350-450 K. As can be seen from Figure 5.25, not only is it possible to observe the hourglass phase behaviour in simulations, there is quantitatively accurate agreement between the theory and simulation. For the 50% polymer composition, the local composition distributions at 370 and 430 K are unimodal, albeit slightly skewed. Conversely, local composition distributions at 30% polymer composition are non-unimodal, indicating phase separation at all temperatures. The composition of the polymer rich phase agrees well with the calculations of the theory, with the polymer rich phase having a higher polymer weight fraction at 250 K than at 470 K, with a minimum in the polymer content of the polymer rich phase at around 370 K. At 370 K, the polymer lean phase is composed of around 10 wt% polymer, which shows the existence of another miscibility region at low polymer weight fractions around that temperature too.

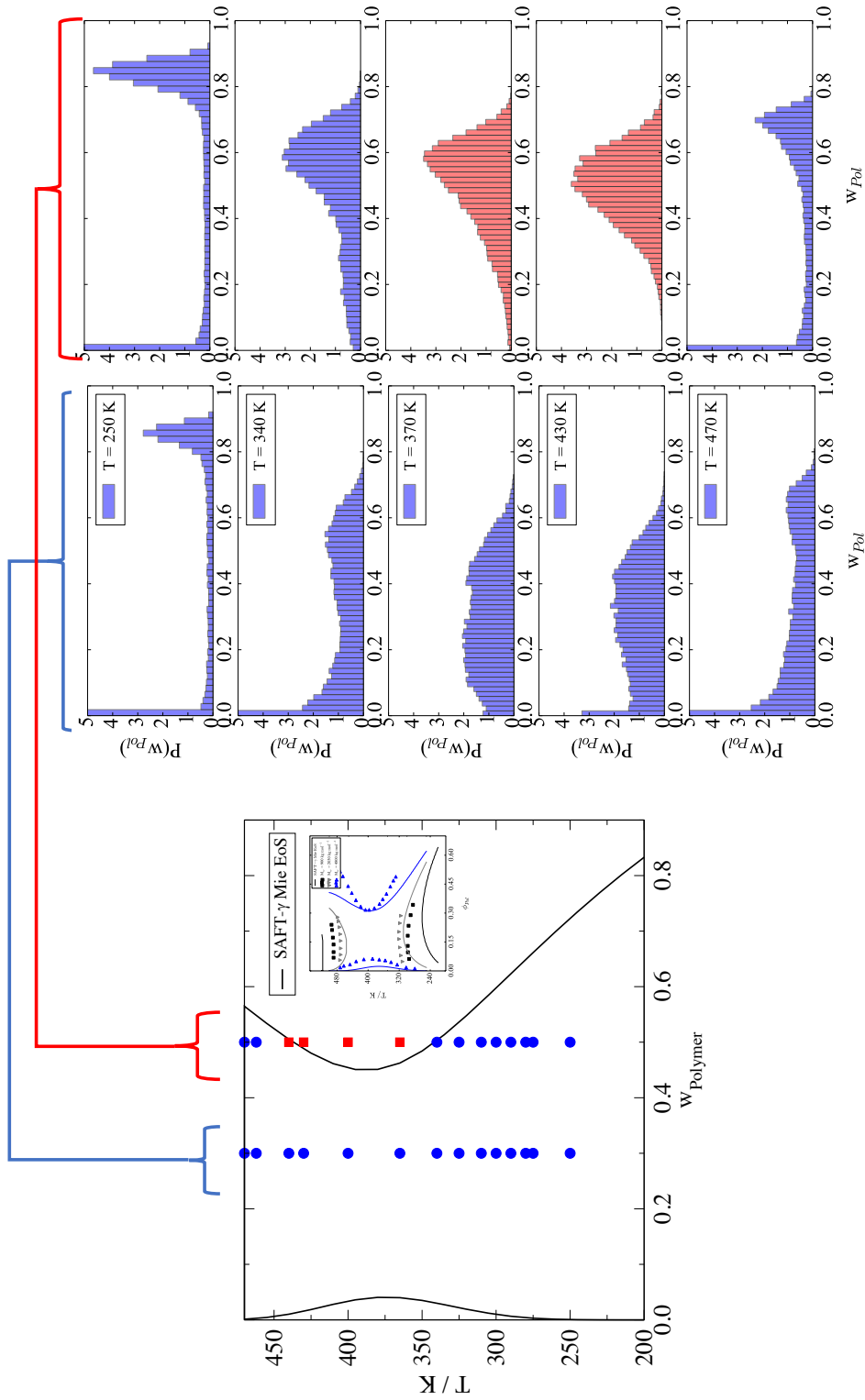


FIGURE 5.25: Phase diagram of PS-CG1-n-hexane mixtures, $M_{W, \text{Polymer}} = 4800$ Da (92 CG beads). Line corresponds to the calculations of the SAFT- γ EoS. Filled blue circles are the global compositions ($w_{\text{polymer}} = 0.3$ and $w_{\text{polymer}} = 0.5$) where phase separation is observed. Red squares are the global compositions at temperatures where phase separation was not observed. The local composition distributions at different temperatures and compositions are also presented, with each row being at the same temperature. It can clearly be seen that for $w_{\text{polymer}} = 0.3$ binodal distributions exist at all temperature, whereas at $w_{\text{polymer}} = 0.5$ unimodal distributions can be observed for T = 370–430 K. Clear correspondence between theory and simulations is observed.

Given that so far it has been possible to simulate Type II (UCST only), Type III (the hourglass) and Type V (LCST only) phase behaviour, only Type IV (UCST+LCST) has not been simulated. Even though Type IV was expected with the low M_W PS solutions in n-hexane and n-heptane, it was not possible to observe LCST phase behaviour. However, as can be seen in Figure 5.26, Type IV phase behaviour can also be simulated for the case of 4.80 kDa PS-n-heptane mixtures. PS is more soluble in n-heptane than it is in n-hexane, meaning that even though the hourglass phase behaviour is observed for mixtures of 4.80 kDa PS in n-hexane, due to greater solubility of PS in n-heptane, the two phase envelopes do not coalesce and therefore type Type IV phase behaviour is observed, with two separated regions of immiscibility in the phase diagram. Simulations were carried out with the global composition being set to 30 polymer wt%. Temperature was set to a range of values with intervals of 25 K. It could be seen in Figure 5.26 that even though the critical temperatures are in accordance with the predictions of the EoS, the shape of the UCST phase envelope is broader with a slight overprediction of the UCST relative to the EoS.

Contrary to the 2.03 kDa PS mixtures with n-hexane and n-heptane, it is possible to observe LCST phase behaviour in simulation for the 4.80 kDa PS. In both simulation and the EoS, the LCST is around 475 K with the phase envelopes being in quantitative agreement. This agreement is impressive given that all interaction parameters are state (temperature, pressure, composition and density) independent and that both inter and intra-species interaction parameters estimated with the EoS can be directly used in simulations to observed the phase behaviour.

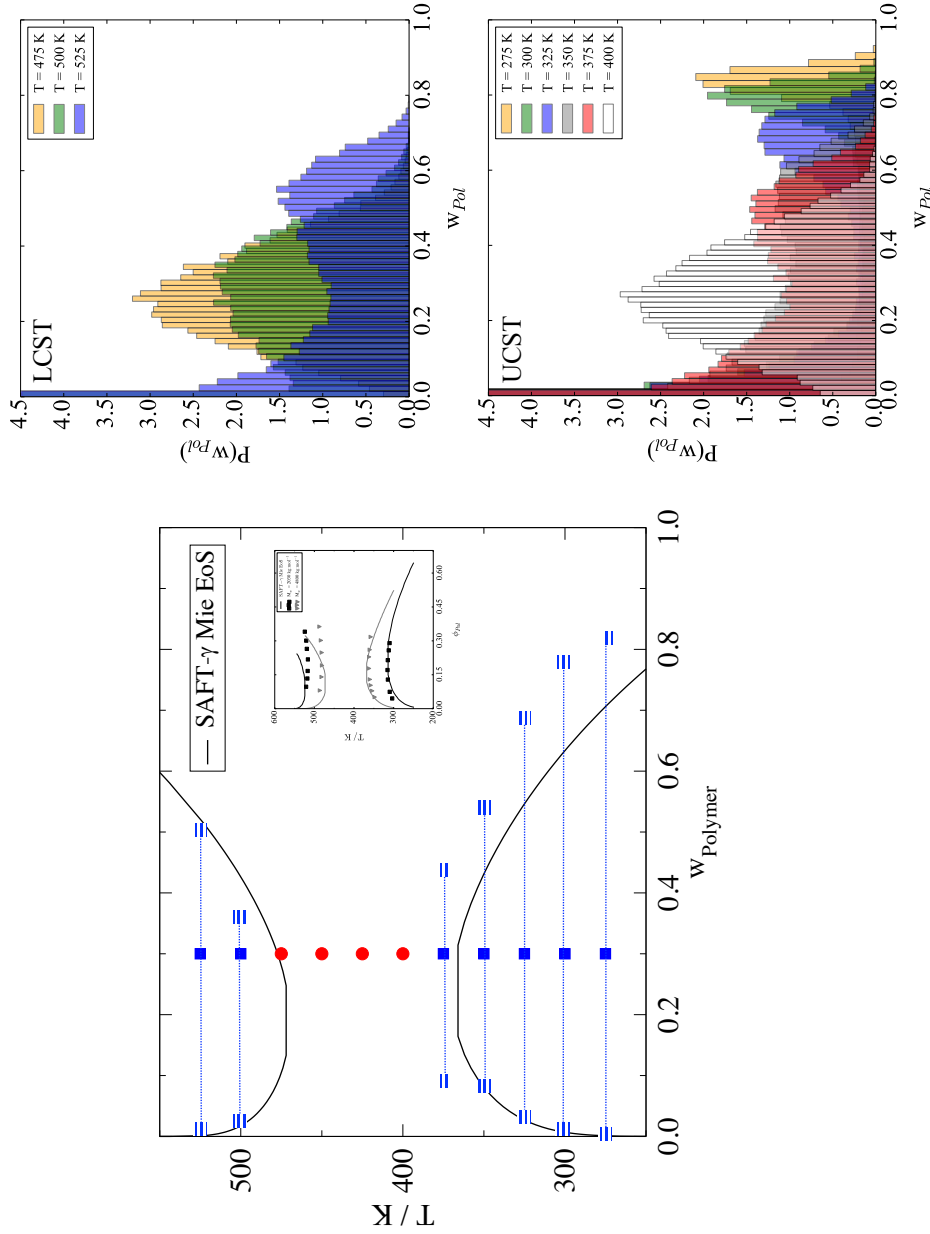


FIGURE 5.26: Phase diagram of PS-CG1-n-heptane mixtures, $M_{W, polymer} = 4800$ Da (92 CG beads). Line corresponds to the calculations of the SAFT- γ EoS. Filled blue circles are the global compositions ($w_{polymer} = 0.3$) where phase separation was observed and patterned squares are the compositions calculated from the local density method. Red squares are the global compositions at temperatures where phase separation was not observed. The local composition distributions at different temperatures are also presented, clearly demonstrating the onset of miscibility at higher temperatures and lower temperature. It can clearly be seen that at intermediate temperatures there is a unimodal distribution corresponding to miscibility.

Overview of the Simulations of Polymer Solvent Systems

It has been shown that the SAFT- γ approach proposed here can be used to model all types of phase behaviour of polymers-solvent mixtures as can be seen in Figure 2.7, with quantitative accuracy. Apart from the case of 2.03 kDa PS in n-hexane and n-heptane, the phase behaviour of the polymers are in exact agreement with the calculations of the EoS. The CG potential parameters used in the EoS can be directly used in simulations to reproduce the same phase envelopes at orders of magnitude faster than atomistic simulations. The robust parameter estimation methodology makes the the potential parameters transferable to a wide range of pressures, temperatures, molecular weights of the polymer and compositions of the mixtures, rendering this method very useful in obtaining reliable forcefields for polymers.

For the cases of polyethylene and polypropylene, the phase diagrams simulated have not been simulated before. However, it is important to note that the PS-n-alkanes mixtures presented in this chapter have already been studied by Serratos-Jimenez et al. [236] with SAFT type potentials. The parameters that were studied by Serratos-Jimenez et al. were not fitted for polystyrene specifically. In that model, the backbone of the branched polymer was modelled as a $(\text{CH}_2)_3$ group. The branches were modelled as a segment of a 2 segment homonuclear toluene model. Thus, there is an issue with extent of the representability of the polymer to a real polystyrene molecule. Moreover, the cross interaction parameters between the n-alkanes and the polystyrene model were manually altered with a random k_{ij} parameter. This means that the experimentally correct phase behaviour might not be observed with the EoS.

In this work, an effort has been made to ensure the representability of the force-field parameters with the equation of state prior to their application in molecular simulations. It has been shown that both inter and intra-species parameters are so reliable that simulations can directly reproduce the same phase behaviour of the polymer as calculated by the EoS without any adjustments to the parameters. Although the EoS might not have the same shape of the phase envelopes as the experiments, the qualitative agreement between experiments, theory and simulation makes this methodology extremely useful in studying polymer solvent systems. In the future it would be possible to study the effects of shearing or confinement on the

phase behaviour of polymers with thermodynamic accuracy. Moreover, dynamic properties like diffusion of solvents in polymers or the monomer diffusions could also be investigated. This has to be one of the key areas of future work.

Another key area that can be investigated is the self-assembly of block copolymers. In order to see the viability of this methodology in studying block copolymers in the future, polymer blends need to be investigated first.

5.3.4 Polymer Blends & Block Copolymers

Given the success of this methodology in modelling polymer-solvent mixtures, two systems of polymer blends were simulated. The first system is that of a mixture of 1.90 kDa PS-CG1 and 2.35 kDa PBD as previously presented in Figure 4.36. Here, like the previous simulations of polystyrene in this work, the polystyrene was modelled as a branched polymer. It has been shown that this model is robust in reproducing the polymer-solvent phase behaviour.

However, given that PS-CG1 represents every monomer of PS with 2 segments and the PS-CG2 model only has one segment per monomer, it is more efficient to use the latter model in future simulations of polystyrene for systems of high molecular weight polymer. This is particularly useful in simulations of copolymers containing polystyrene, where microphase separation is observed at molecular weights in excess of 20 kDa. Therefore, in addition to the PS-CG1-PBD polymer blend, a mixture of 2.10 kDa PS-CG2 and 2.70 kDa PI, commensurate to that presented in Figure 4.37 was also investigated to assess the robustness of the parameters obtained for PS-CG2.

Both of these systems were expected to have UCST behaviour, as presented in Figures 4.36 and 4.37.

For the first case, 1.90 kDa PS-CG1 and 2.35 kDa PBD, simulations were run for a system containing 1,300 polystyrene molecules and 840 1,4-cis-polybutadiene molecules corresponding to a global composition of 50 wt% PS. A total of number of CG segments summed up to 84,000, corresponding to nearly 800,000 atoms. Temperature was changed but the pressure was fixed at 1 bar. The ratio of $L_Z:L_{X,Y}$ was set to 4:1 and each simulation was run for 500×10^6 timesteps, with $\delta t = 0.01 ps$.

Like the previous cases, a cut-off of 2.0 nm was used in all simulations, with no tail corrections.

The adjustable parameter between the two polymers for this mixture is $k_{ij} = -0.025$ as given in the theory (Table 4.18). However, when this interaction parameter was used, significant overestimation of the UCST was found. Polymer blends are much more sensitive to the cross interaction parameters due to the each species being composed of many monomers. So the slightest changes in the cross interaction parameter can significantly affect the miscibility of the two components. This parameter was changed slightly from -0.025 to -.028, with the phase diagram presented in Figure 5.27. This change in the k_{ij} is less than 1 K, and it is not a significant deviation from the predictions of the theory. As shown in the figure, it is possible to observe the UCST behaviour of this PS-PBD mixture, however the shape of the phase envelope is not commensurate with that which was calculated with the EoS. Surprisingly, there is quite a good agreement between simulations and the experimental results from ref [213]. This could be due to the conformational structure of the polymer, namely the branching that not being considered in the EoS but accounted for in the simulations.

This example clearly demonstrates that it is possible to observe UCST phase behaviour in polymer blends as could be predicted from the theory. However, in this instance the correlation between the EoS and the simulations is less robust than the case of the polymer-solvent mixtures.

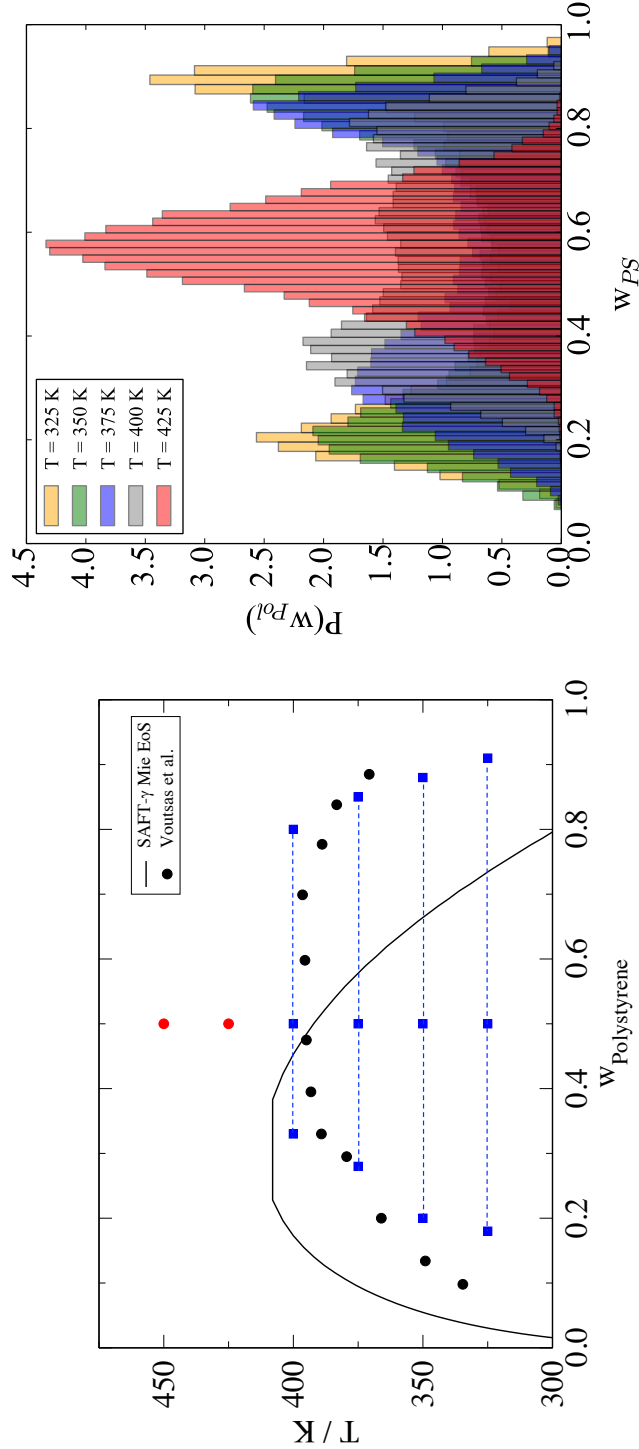


FIGURE 5.27: Phase diagram of low M_W PS-CG1 (1900 Da) - PBD (2350 Da) blend, corresponding to 36 and 43 CG beads respectively. Line corresponds to the calculations of the SAFT- γ EoS. Black circles are experimental data from ref [213]. Filled blue squares are the global compositions ($w_{polymer} = 0.5$) where phase separation was observed and patterned squares are the compositions calculated from the local density method. Red squares are the global compositions at temperatures where phase separation was not observed. The local composition distributions at different temperatures are also presented, clearly demonstrating the onset of miscibility at $T = 425$ K. Even though intermolecular potentials were fitted using the EoS, the shape of the phase envelope matches the experimental data and is different to the EoS. The interaction parameter, k_{ij} was changed from -0.025 to -0.028 in order to observed the correct UCST.

The second mixture of 2.10 kDa PS-CG2 and 2.70 kDa PI was simulated at different temperatures and 1 bar. Each PS molecule contained 20 segments and each PI molecule contained 40 segments. Each simulation contained 600 PS molecules and 500 PI molecules, corresponding to a global composition of 47 wt% of PS. Each simulation was run for 500×10^6 time steps, with $\delta t = 0.01 ps$ with a cut-off of 2 nm. Here a much larger adjustment to the cross interaction parameter was needed to obtain the correct phase behaviour. The cross ε was changed from 523 to 519, with the k_{ij} changing from 0.0027 to 0.01. The results can be seen in Figure 5.28. Here, the phase behaviour calculated from the EoS is in quantitative agreement with that of the EoS. The experimental data from ref [197] is for a polydispersed system. However, here, just like the EoS, the simulations are run assuming monodisperse polymers. It could clearly be seen from the end to end distances in Figure 5.28(d) that the polystyrene at 420 K is in a more expanded conformation than at 325 K. This is further evidence of the phase separation at lower temperatures. However, as previously observed in Figure 5.19 the end-to-end distances do not change significantly from the miscible regime to the immiscible regime. At 420 K, R_E is 2.57 ± 0.04 nm and at 325 K, R_E is 2.52 ± 0.04 nm.

Comparing the two cases of polymer blends studied here, it can be seen that branching has a significant effect on the shape of the phase envelope in polymer blends. The critical point does not seem to be affected by the molecular architecture. However, for both cases, the cross interaction parameters do not match that of the EoS, albeit very close for both cases (less than 1%). However, given that it is still possible to model the UCST phase behaviour of low M_W PS with PBD and PI, it is possible to study microphase separation of poly(styrene-co-isoprene) as first studied by Khandpur et al. [11]

Attempts were made to simulate poly(styrene-co-isoprene), however given the very long chain lengths equilibration remains extremely slow. Equilibration of polymer-solvent mixtures is much faster in simulations given the fast diffusion of the solvent molecules. Even for low molecular weights as presented here it is possible to equilibrate systems with millions of timesteps. However, the only cases where microphase separation could be observed for chain-lengths exceeding 100 segments is by having

very large k_{ij} parameters, inducing spontaneous demixing. With the k_{ij} parameters developed in this work, the unlike interactions are not strongly unfavourable. This makes it difficult to observe microphase separation of block copolymers starting from either a demixed or a mix system. However, given the parameters are derived from an EoS, it is possible to use other simulation techniques such as DFT using the free energy to predict structures. The development of DFT models based on the SAFT- γ Mie is currently being undertaken.

5.4 Conclusions

In this chapter, the parameters obtained in the previous chapter were used in molecular dynamics simulations to assess the validity of the potential parameters in modelling homopolymers and polymer mixtures. Polymers were modelled as chains of tangentially bonded homonuclear segments, where the bond distances and the non-bonded interactions were taken from the EoS, and the angular potentials were calculated using Boltzmann inversion of an atomistic representation of the polymer. It was shown that for polymer melts, it is possible to obtain the same densities as the EoS, and the morphological properties were also calculated and compared with available data. Given that the EoS is a thermodynamic model, it is not necessary for it to predict the correct structural properties. Therefore, to obtain the correct morphologies (R_G , R_E), the angular potential parameters were adjusted to fit to experimental data. In terms of mechanical properties, it was shown that the parameters could calculate the correct isothermal compressibilities.

The main highlight of this chapter is the polymer-solvent behaviour where it was shown that with the same set of parameters calculated by the EoS, it is possible to observe all complex phases of polymer-solvent mixtures with thermodynamic accuracy. LCST, UCST, the "hourglass" phase behaviour, as well as pressure induced phase separation were studied. The parameters were found to be state-independent, meaning that temperature, pressure, molecular weight of the polymer, composition of the polymer did not affect the phase behaviour as predicted with the EoS. This has been a significant challenge in modelling polymers as it is very difficult to find state-independent potential parameters, particularly in terms of the polymer solvent

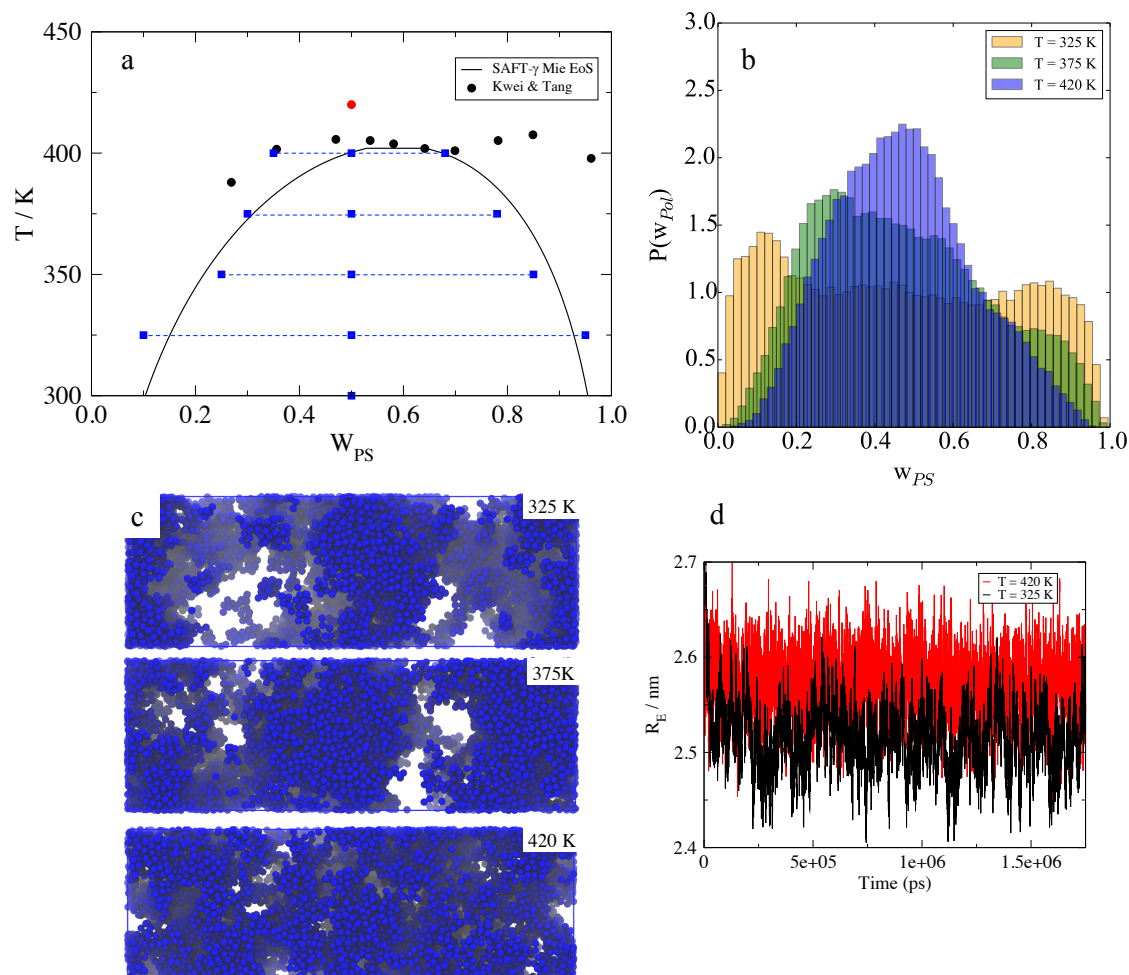


FIGURE 5.28: Phase diagram of 2.10 kDa PS-CG2 and 2.70 kDa PI, corresponding to 20 and 40 CG beads respectively. **a** Temperature-composition phase diagram of the blend, with the line corresponding to the calculations of the SAFT- γ EoS. Black circles are experimental data from ref [197]. Filled blue squares are the global compositions ($w_{\text{polymer}} = 0.47$) where phase separation was observed and patterned squares are the compositions calculated from the local density method. Red squares is the global composition at 420 K where phase separation was not observed. **b** Local composition distributions at different temperatures, indicating phase separation at $T = 420 \text{ K}$. **c** Snapshots of the distributions of polystyrene molecules in the final frame of the same mixture at different temperatures and **d** End-to-end distance vs time of polystyrene chains at two different temperatures.

cross interactions. This is why there are very few simulation studies on the phase behaviour of polymer solvent mixture.

Polymer blends of polystyrene-1,4-cis-polybutadiene and polystyrene-polyisoprene were also modelled. However, for these it was found that the cross interaction parameter had to be slightly adjusted.

5.4.1 Outlook

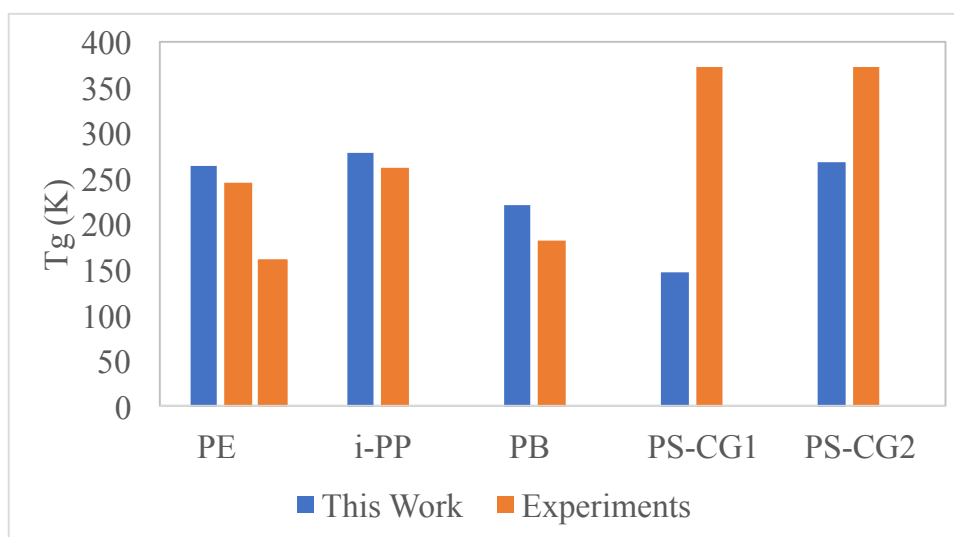
In this work, the primary focus has been on structural and thermodynamic properties of the polymers. Although the main objective of this thesis has been to obtain forcefield parameters that can be used in simulations to correctly calculate structural, thermodynamic and dynamic properties of polymers, in this chapter the main focus has been on studying the former two. Dynamic properties have not been investigated which, given the importance of properties like glass transition temperatures, have to be investigated further in future works. One particular challenge in obtaining robust parameters for dynamic properties is that currently the parameter estimation methodology is solely based on fitting the equation of state to thermodynamic properties. This can significantly affect the robustness of these parameters in studying dynamic properties.

In order to assess the viability of the forcefield in investigating dynamic properties, glass transition temperatures, T_g , of all the polymers were calculated by measuring specific volumes of pure melts, v , and self-diffusion coefficient of polymers segments, D^s , as functions of temperature in NPT simulations at 1 bar. Each polymer was modelled with 60 segments and each simulation contained 200 polymer molecules. Above the transition temperature, D^s is expected to increase with increasing temperature. 10 million time-steps were used for each simulation. Following the work of Walker et al. [261], specific volume vs. temperature data from the NPT simulations were fitted to a 5-parameter hyperbolic function to quantitatively calculate transition temperatures:

$$v(T) = v_g + a(T - T_g) + b \left[\frac{1}{2}(T - T_g) + \sqrt{\frac{(T - T_g)^2}{4} + e^c} \right] \quad (5.11)$$

TABLE 5.6: T_g calculated by fitting Equation 5.11 to NPT simulation data in Figure 5.30.

Polymer	$T_g^{Exp} /$ K	$T_g^{SAFT} /$ K	$v_g /$ $\text{cm}^3 \text{g}^{-1}$	$a \times 10^{-4} /$ $\text{cm}^3 \text{g}^{-1} \text{K}^{-1}$	$b \times 10^{-4} /$ $\text{cm}^3 \text{g}^{-1} \text{K}^{-1}$	c
PE	140-245 [262–264]	264.19	1.07	2.90	9.29	7.83
i-PP	261 [265, 266]	282.89	1.12	2.18	8.11	7.35
1,4-cis-PBD	181 [267, 268]	226.05	1.01	2.57	8.15	6.86
PS-CG1	373 [269]	148.86	0.80	2.89	4.28	5.43
PS-CG2	373 [269]	270.81	0.83	1.68	6.34	7.95

FIGURE 5.29: Comparison between experimental T_g and ones calculated in this work.

As mentioned in the study by Walker et al., the gradient of this hyperbolic function changes smoothly from a to $(a + b)$, with the transition in gradient occurring at the glass transition temperature (T_g, v_g). This methodology allows for a quantitative measurement of transition temperatures from simulation data. v_g vs. temperature plots for each polymer can be seen in Figure 5.30 and D^s vs. temperature can be seen in Figure 5.31. For linear polyethylene, it is a challenge to calculate T_g due to high degree of crystallinity. Experimental studies [262–264] typically give two ranges of values for T_g : one range of T_g is 160–190 K and the other is 240–250 K.

It could be seen that for PE, i-PP and 1,4-cis-PBD, glass transition temperatures are overpredicted. For polypropylene, this overprediction is around 7%, and for polybutadiene the calculated T_g is 20% larger than the experimental value. For polyethylene, T_g is in agreement with the higher value of T_g observed experimentally.

However, for the case of PS, both models significantly underpredict the glass transition temperature, and the results are totally incomparable to experimental measurements. This clearly highlights the importance of incorporating dynamic properties such as glass transition temperatures in parameter estimations.

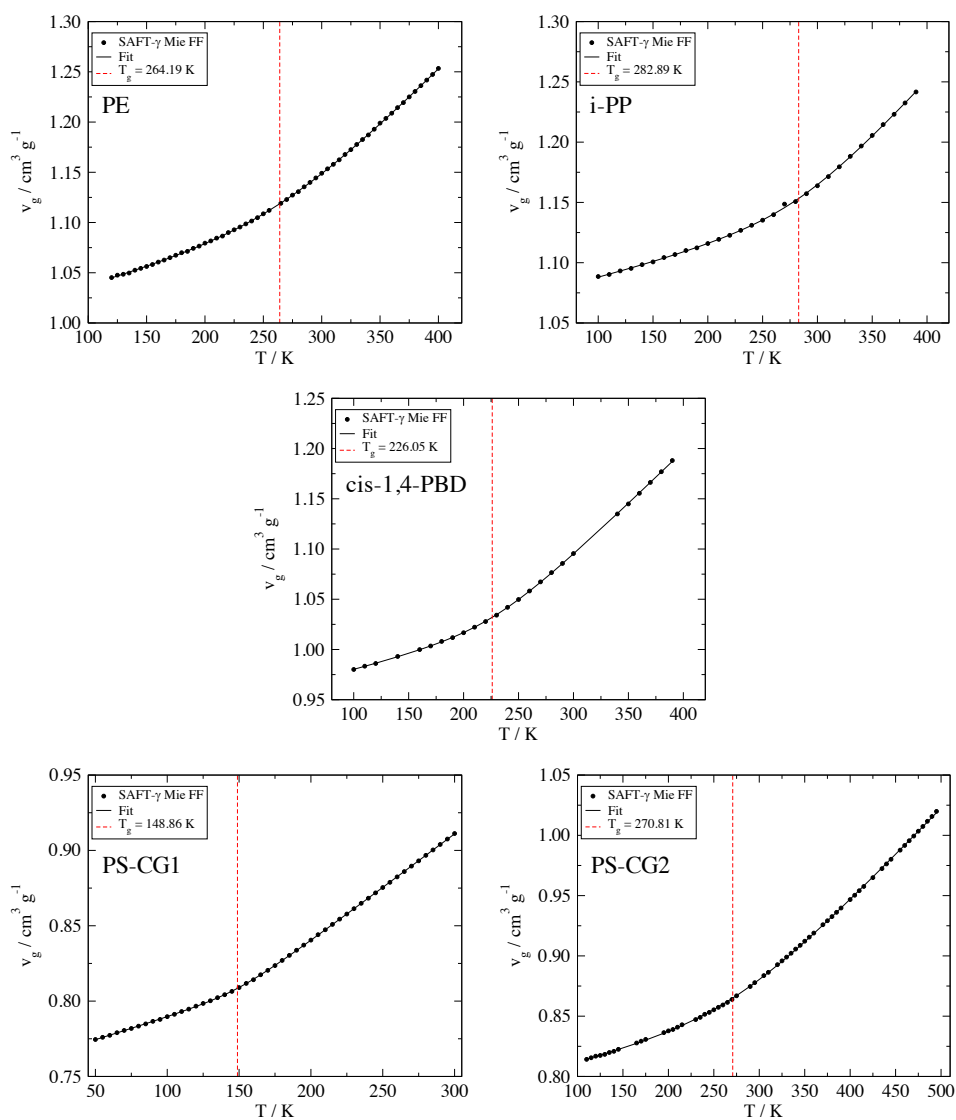


FIGURE 5.30: Specific volume, v_g , vs. temperature for the different polymers studied in this work. The black line is from fitting Equation 5.11 to the simulation data (black circles). Red dashed line highlights the value of T_g calculated in this work.

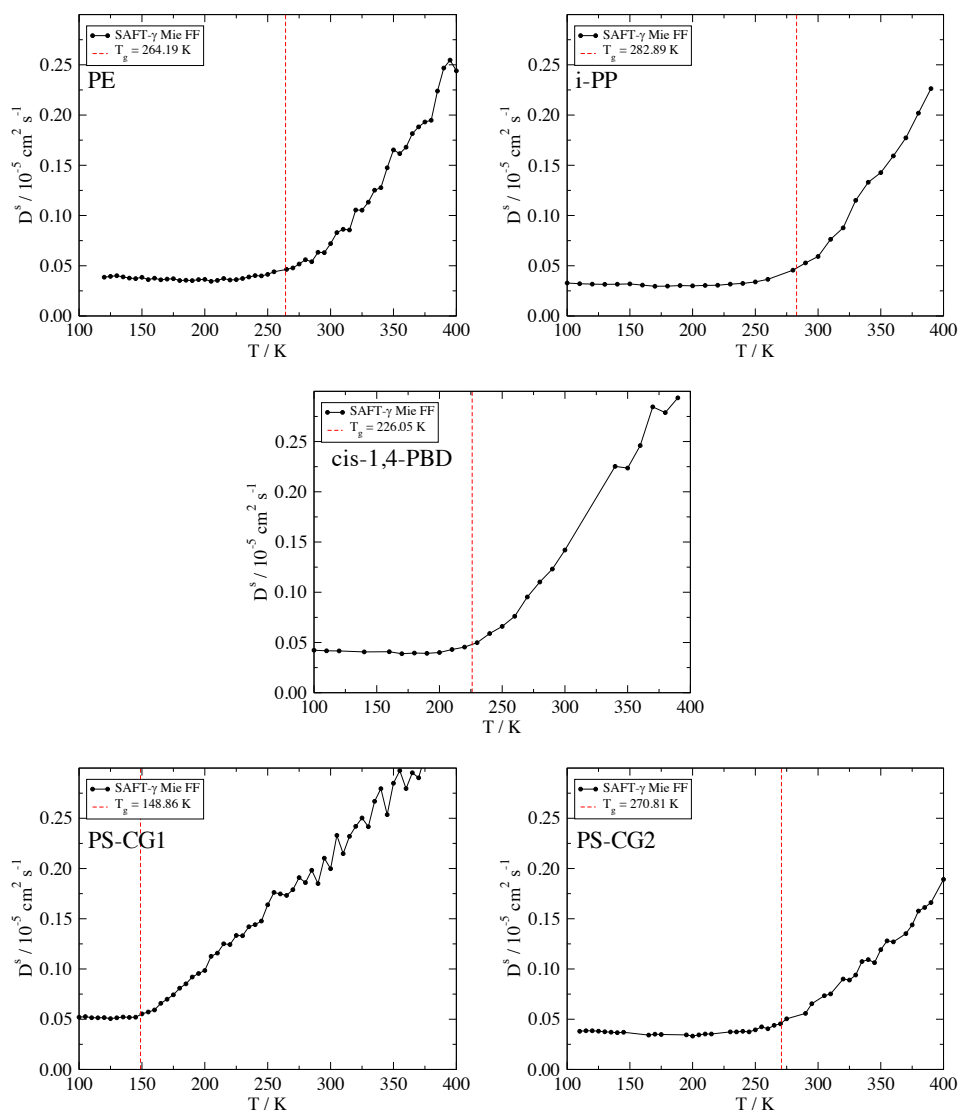


FIGURE 5.31: Self-diffusion coefficient, D^s , vs. temperature for the different polymers studied in this work. Black circles are calculated from simulation data and the black line is a guide to the eye. Red dashed line highlights the value of T_g calculated in this work.

Preface to Studies of Liquid Crystals

The previous two chapters focused on a *homonuclear* representation of molecules, where each polymer or solvent was composed of a single repeat unit. It was shown that this homonuclear representation is valid for polymers. However, with added complexity, such as the existence of drastically different functional groups in a given molecule, the homonuclear philosophy breaks down. Each functional group needs to be parametrised separately, and molecules would be represented as a *heteronuclear* model.

The main focus of the following chapters is to build upon the accurate models of homonuclear polymers to develop parameters for *heteronuclear* models of polyphilic liquid crystals. Here, not only molecular weights of different moieties are variables, but there is variety in the structure and the interactions of different functional groups in the liquid crystalline molecule. Just like the previous studies on polymers, the focus will be more on thermodynamics and structural properties rather than transport properties, and the aim is to predict structural properties of liquid crystals and compare them to experimental data where available. If the models could accurately predict the phase behaviour of the liquid crystals, a systematic study of the phase space is carried out.

Chapter 6

SAFT- γ Mie MD Study of the Self-Assembly of Polyphilic Bolaamphiphiles

6.1 Introduction

Synthesis of materials that can self-assemble into ordered structures has become a ubiquitous field of physical sciences and engineering [3, 270, 271]. The mesostructure of a material can significantly affect its physical properties [272], and this makes self-assembling materials attractive in many applications such as catalysis [273, 274], heat insulation [161], display devices [275], semiconductors, electronic, optical and photovoltaic devices.

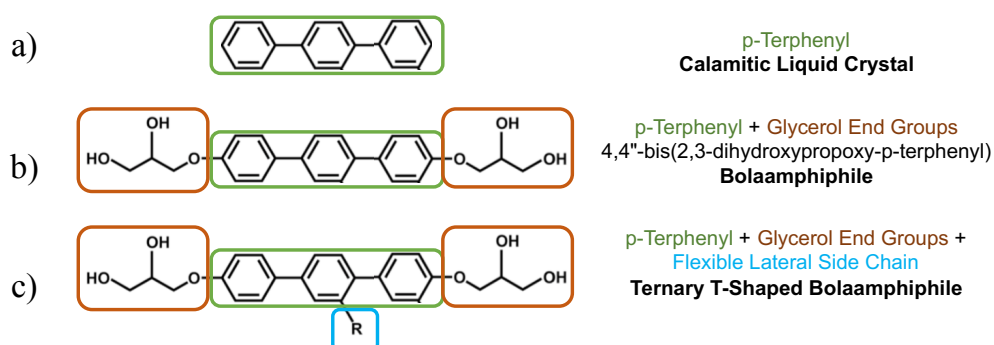


FIGURE 6.1: *a*) The chemical structure of p-terphenyl, a calamitic liquid crystal. *b*) bolaamphiphile 4,4''-bis(2,3-dihydroxypropoxy-p-terphenyl). *c*) T-shaped BA, composed of the same bolaamphiphile with a lateral side chain.

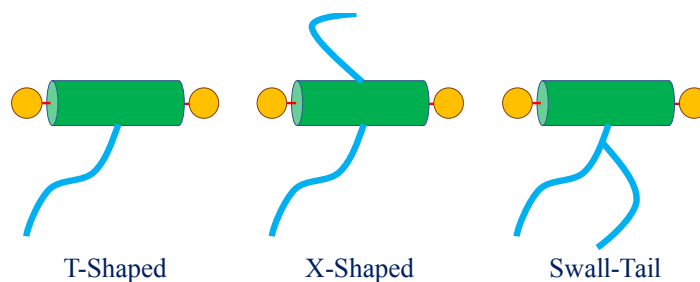


FIGURE 6.2: Structural variety of polyphilic BAs

Bolaamphiphilic liquid crystals (BAs), such as that shown in Figure 6.1(b), are a group of molecules composed of two hydrophilic end groups (e.g. glycerol), and a rigid hydrophobic group (e.g. p-terphenyl) forming the rod like backbone. The phase map of rigid bolaamphiphiles has been previously explored [121], with smectic A (SmA), nematic and isotropic phases observed (Figure 2.8), commensurate with previous studies of both attractive [276, 277] and hard [74, 278] calamitic liquid crystals. Simulation studies [121] have demonstrated that stronger self-attraction of the end groups of rigid bolaamphiphiles can reduce the region of isotropic-nematic phase transition, and lead to greater region of isotropic-SmA phase transition at lower temperatures. For molecules similar to the one presented in Figure 6.1(b), the hydrogen bonding strength of the end groups is so strong that only isotropic-SmA phase transitions are observed experimentally [279].

Adding flexible side chain(s) to bolaamphiphilic liquid crystals, as presented in Figures 6.1(c) and 6.2, leads to a variety of complex mesophases. The lateral side chains disrupt the phase, leading to formation of columnar phases with complex two-dimensional tiling patterns for shorter chains, and lamellar or three-dimensional network phases for the longer chains. Experimentally, side chains have been composed of alkyl chains [279, 280], semiperfluorinated alkyl chains [281–287], ethoxylated alkyl chains [288], or siloxanes [289]. As presented in Figure 6.2, not only is there variety in the chemistry of the lateral side-chains, the structure of the lateral side chains can be different.

T-shaped BAs with a single lateral side-chain have been most extensively studied experimentally with 15 unique structures discovered. For experimental reviews of these systems one could refer to refs [290, 291]. The sequence of some of the most

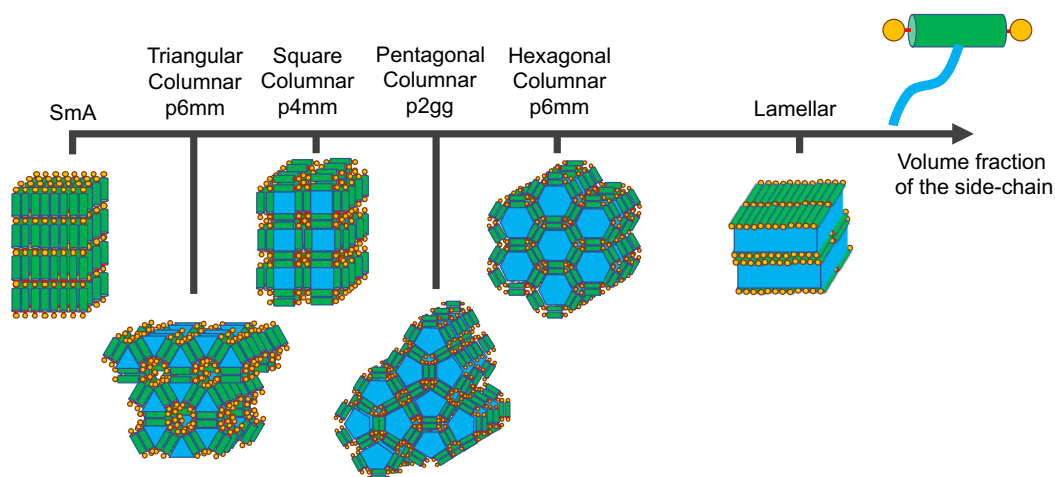


FIGURE 6.3: Liquid crystalline phases formed by self-assembly of T-shaped BAs as observed upon increasing the volume fraction of the side-chain, adapted from ref [291].

common liquid crystalline phases upon increasing the size of the lateral chain are highlighted in Figure 6.3. Very small side chains induce triangular columnar phases with a hexagonal $p6mm$ symmetry. Increasing the size of the side chain leads to formation of square ($p4mm$), pentagonal ($p2gg$) and hexagonal ($p6mm$) columnar phases. Upon further increasing the length of lateral side chains, lamellar, hexagonally organised nano-wires and gyroid phases have also been observed [291]. X-shaped bolaamphiphiles (Figure 6.2) with either the same moieties for the lateral chains or different groups can lead to combinations of these tiling patterns tessellating the 2-D plane perpendicular to the direction of the columns. For example, one of the side chains could be a short ethoxylated chain which can form a triangular columnar phase, and the other a longer alkyl chain which can form square columnar phases ($p4g$ phase) [288]. A particular system of X-shaped BA with semiperfluorinated chain and siloxane was shown to be able to produce upto three different polygons tessellating the plane: a square, a triangle and a rhombus [292], demonstrating the complexity of the self-assembling structures observed with BAs.

Given the the laborious and exhaustive process of manufacturing these materials, developing a complementary theoretical or *in situ* methodology to predict the

structures for a given system *a priori* can be a more cost effective and efficient approach in designing BAs. Moreover, mesophase characterisation is carried with experimental techniques such as polarising microscopy, calorimetry and different X-ray scattering techniques which can be time consuming. The complexity of these molecules in terms of chemical composition, the level of rigidity and flexibility of each functional group and the size and the arrangements of these building blocks means that developing a theory to predict the mesophase behaviour would be a significant challenge. Conversely, molecular simulations can be a reliable pathway in understanding the mesophase behaviour of these materials. A particular advantage of molecular simulations is that provided one has a realistic representation of the molecular system, one could directly observe the self-assembly of the BA without inference from indirect observations.

Atomistic simulation of these systems is not feasible with current computational capacities and the length and time scales required to observe self-assembly renders this method redundant. Subsequently, coarse-grained methodologies are a more appropriate approach in studying mesophase behaviour of BAs.

There has been a number of simulation studies on the self-assembly of BAs, with all of them being phenomenological studies, i.e. with no attempts in developing thermodynamically accurate potential parameters for the building blocks. The first studies on the self-assembly of T-shaped BAs via molecular dynamics simulations were the works of Crane et al. investigating the phase behaviour of pure component [293] and mixtures [294] of BAs. The model proposed was based on Lennard-Jonesian (LJ) type potentials. For weak interactions, the LJ potential was cut-off and shifted (Weeks-Chandler-Anderson (WCA) [90] potential), which included all cross interactions and the self-interaction of the segments of the backbone, assuming weak π - π interaction of the phenyl groups. The end groups were modelled as very attractive beads with a self-interaction of ϵ and the segments of the lateral side chain had an $\epsilon_{Lateral}$ of 0.5ϵ . All building blocks had the same size σ , with no efforts in relating the sizes of the segments to real molecules. A particular advantage of this methodology is the fast equilibration times and the simple approach to the phenomenological study of T-shaped BAs. For short side-chains with contour lengths of $< 5\sigma$, triangular, square and hexagonal columnar phases were observed. For chains with contour

lengths of 12σ , lamellar phases were observed. Even though triangular, square and hexagonal phases were observed, it was not possible to observe regular pentagonal columnar phases. For intermediate chain lengths, a combination of pentagonal and hexagonal columns were present, which was attributed to the fact that pentagons cannot tessellate planes. This is contrary to experimental observations [288].

The work of Crane et al. [293] was complemented by the studies of Bates and Walker [295–297], who developed DPD models to study T-shaped and X-shaped BAs. The phases discovered by Bates and Walker for T-shaped bolaamphiphiles were commensurate with those observed by Crane et al. Again, all segments in the model were of the same size, and here the backbone and the end groups were softer than the lateral side chain in terms of self-interaction. With a symmetric bolaamphiphilic molecule, only triangular columnar, square columnar, hexagonal columnar and lamellar phases were observed for T-shaped BAs [296]. For X-shaped BAs, Archimedean tiling patterns combining triangles with hexagons and triangles with squares were observed. Their model was also not able to predict regular pentagonal columnar phases either. By modifying the bolaamphiphile backbone and making it chemically asymmetric (with more hydrogen bonded segments on one side), it was possible to observe pentagonal columnar phases [298]. This underscored the discrepancy between experimental observations and DPD simulations with the model developed by Bates and Walker, as none of the BA liquid crystals studied by experiments have been asymmetric. Liu et al [299] carried out another DPD study of T-shaped BAs with a variable size of the hydrogen bonding end-groups. Again, triangular (p6mm), square (p4mm), hexagonal (p6mm), lamellar phases were observed. Just like the work of Crane et al., highly irregular pentagonal columns were found, with the irregularity attributed to the incompatibility of the mesophase periodicity with the size of the box. It could be concluded that with particle based simulations, obtaining regular pentagonal columnar phases has been challenging. Only a recent self-consistent field theoretic (SCFT) study has been able to predict pentagonal columnar (p2gg) phases [300].

These coarse-grained particle-based studies using toy-models have the advantage of being very fast simulations that can give insight into the mesophase behaviour of these materials qualitatively. The coarse-graining philosophy that different functional groups are incompatible with each other is shared among all three models, but representability of physical systems remains an issue. It is not known the extent to which the assumptions in the models affect the phase behaviour observed in the simulations. For example, regular pentagonal columnar phases have only been observed in systems that are not chemically representable of the symmetric bolaamphiphiles used in experimental studies.

One key assumption that is universal to all previous models is the equal size of all segments in a molecule. The extent of the validity of this assumption has not been assessed. Moreover, there are discrepancies in the description of the interactions between the models themselves. For example, in the Bates and Walker model, the rigid backbone has a softer self-interaction (i.e. less self-repulsive) than the lateral side-chains, but in the Crane et al. model, the rigid backbones are fully repulsive, yet the aliphatic chains are self-attractive. Naturally it seems that these interaction parameters are somewhat arbitrary, as long as they can be used to give qualitatively realistic descriptions of the system. Consequently, relating the results of these simulation to real systems becomes significantly challenging. Even though it is possible to study properties such as phase transition temperature and diffusion via simulations using the aforementioned models, but these cannot be related to real system. For example, it has been shown that the chemistry of the side-chain can affect the isotropic-ordered transition temperature of thermotropic BAs [121]. However, none of these models could predict the phase transition temperature of T-shaped BAs with different chemistries of the side-chain.

6.1.1 SAFT & Swall-Tail BAs

The main aim of this chapter is to develop a coarse-grained model of BAs that is structurally and thermodynamically consistent with real experimental systems, with each moiety having its own size and interaction parameters which is derived from its underlying thermophysical properties. This more representable model can then

be used in more intelligent design of BAs. In order to do this, the SAFT- γ approach presented in the previous chapters is employed to obtain parameters for the different moieties.

In order to test the validity of our models, SAFT- γ Mie CG simulations will be run to predict the structure of the most recently studied family of BAs, which are swallow-tailed (Figure 6.2(c)).

Recently, a new class of BAs (not T or X shaped) has gained significant attention, due to an interesting phase behaviour not observed previously. The phase behaviour of T-shaped and X-shaped BAs is usually understood using the volume fraction of the lateral side chain as the key metric (Figure 6.3). For different volume fractions, one could expect different structures. Swallow-tail BAs, as presented in Figure 6.2, are a class of liquid crystals that have a branched lateral side-chain. The effect of branching is highly significant as can be seen in Figure 6.4. This Figure is adapted from the recent work of Poppe et al. [301], where the volume fraction of the moiety constituting the lateral side-chain was kept constant, with the key variable being the degree of branching. All three molecules presented in Figure 6.4 have the same molecular weight. Poppe et al. discovered some of the most complex tiling patterns with BAs, with pentagonal-hexagonal and pentagonal-octagonal tiles tessellating the plane. This was achieved by transforming a BA with a single side chain of 20 carbons into one with 2 alkyl branches of different length but with the same total number of carbons (20).

The main characteristic feature of swallow-tail BAs is that unlike all previous studies where the volume fraction of the side chains was the key factor in determining the mesophase structure, the volume fraction of the flexible chains is kept constant, and the geometry of the side chain is the key factor in self-assembly.

The fact that such subtle changes in the geometry of the side-chain could lead to such drastic changes, coupled with the fact that these new mesophases have regular pentagonal structures and pentagonal columnar phases have been challenging to simulate with the aforementioned models, SAFT- γ Mie could be used as a viable alternative to study swallow-tail BAs. Additionally, unlike the phenomenological studies undertaken previously, SAFT- γ Mie CG simulations is a predictive approach

where the transition temperatures and the size of the ordered structures could be directly related to the physical molecule studied, as the parameters are directly fitted to the properties of each functional group. The sizes of the different segments do not necessarily have to be the same, and are dependent on the density of the functional group represented. Thus as a first study on the application of SAFT- γ Mie in studying BAs, these swallow-tail BAs are ideal candidates.

There has recently been one simulation of study swallow-tail BAs, with focusing on very long lateral side-chains [302]. The work presented by Sun et al. focused on the three-dimensional periodic structures of long swallow-tail chains, using the Crane et al. model. No attempt was made to study any of the complex phases presented in Figure 6.4 or to test the ability of the Crane model in predicting the two-dimensional tiling patterns of these zeolite-like liquid crystals. Moreover, like the previous studies, the effect of the volume fraction of the side-chain segments was the focus of that study, and not the effect of the degree of branching on mesophase behaviour. In that study, gyroid phases and plumbers nightmare phases were observed, which are novel for liquid crystalline materials.

In the next section, for the molecules presented in Figure 6.4, the methodology of coarse-graining is explained, as well as the simulation details. A list of order parameters are also given to quantitatively observed the phase behaviour of these systems. The predictions of the simulations for the molecules in Figure 6.4 are then presented in section 6.3, with a study of the transition temperatures. Finally, a full phase map exploration of T-shaped bolaamphiphiles of different swallow-tail chain lengths are carried out, followed by conclusions in section 6.4.

6.2 Methodology

In this work, the molecule that will be coarse-grained is an alkyl substituted 4,4'-bis(2,3-dihydroxypropoxy-p-terphenyl) (Figure 6.1(b)). In order to coarse-grain this molecules, first the three main functional groups are defined.

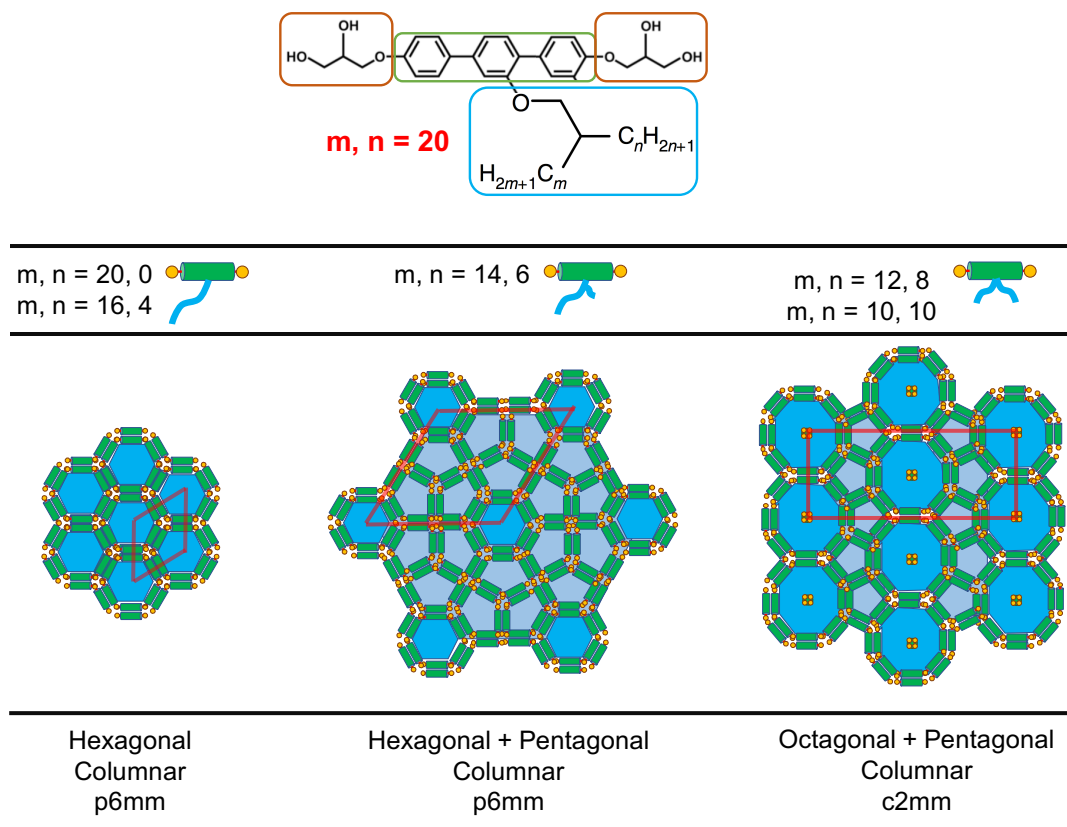
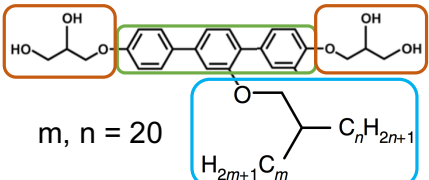
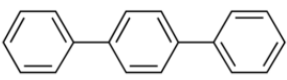
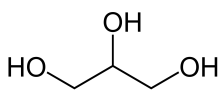
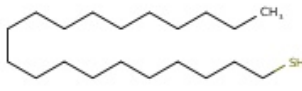


FIGURE 6.4: Swallow-tail BAs studied with SAFT- γ Mie CG forcefield in this work. Different mesophases are observed not by changing the volume fraction of the lateral side chain, but by changing the degree of branching, whilst conserving the volume fraction of all moieties. This system has been experimentally studied, with the schematic of the mesophases adapted from ref [301]

TABLE 6.1: Segmentation of the swallow-tail BA studied in this work into three distinct functional groups.

LC Molecule	Moieties	
 $m, n = 20$	p-Terphenyl (Backbone)	
	Glycerol (End Groups)	
	Icosane (C ₂₀ H ₄₂) (Lateral Side-Chain)	

6.2.1 Defining the Moieties

Table 6.1 is a summary of the coarse-graining philosophy undertaken in this work. The swallow-tailed bolaamphiphile is segmented into three distinct functional groups: a rigid backbone which has the same parameters as a p-terphenyl molecule, two end groups that are modelled as two glycerol molecules, and a swallow-tail moiety which has the same parameters as icosane, or C₂₀H₄₂ alkane. Although, these functional groups are not exactly the same as the molecules mentioned, it is assumed that the true physical interaction of these functional groups are not drastically different to the whole molecules. Given a lack of experimental data for such systems, group contribution theories cannot be employed to fit parameters exactly to bolaamphiphiles. So by looking at properties of whole molecules instead of functional groups, one could at least infer the values of parameters that are more realistic than toy-model systems.

6.2.2 CG Representation of the BA

Given the definitions of the moieties, the next step is to define a CG representation of the molecule. Since these simulations are based on SAFT- γ Mie forcefield, each moiety will be modelled as a chain of tangentially bonded coarse-grained segments. The number of segments representing each of the groups is decided heuristically,

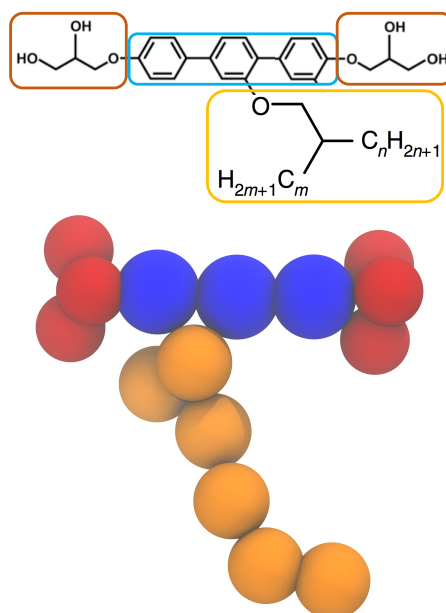


FIGURE 6.5: CG representation of the BA studied in this work, with the p-terphenyl backbone being represented by 3 segments (1 segment per benzene ring), the glycerol group being represented by 3 segments (one segment per hydrogen bonding group) and 6 segments for the lateral chains.

attempting to minimise the number of segments to reduce computational expenses, whilst keeping the model as representable of the real system as possible.

The rigid backbone of the molecule is p-terphenyl with three phenyl rings attached to each other linearly. In the CG representation, each phenyl ring is represented by a CG sphere. The icosane like the previous studies on alkanes [241], will be modelled as a chain of 6 beads. glycerol will also be modelled as a 3 segment model, given that there are three hydrogen bonding sites in the molecule.

The schematic of the CG representation of the BA can be seen in Figure 6.5.

By looking at Figure 6.4, it could be seen that there are three types of structures observed in the study by Poppe et al., depending on different lengths of each chain of the swallow-tail. To simulate these systems, first one needs to translate the chain lengths from the number of carbons into the number of CG segments. Given that a 6 bead model is used in representing icosane, every 3.7 (≈ 4) united atom carbons is coarse-grained into a segment. The number of CG segments in each chain of the swallow-tail for each of the molecules in Figure 6.4 is given in Table 6.2.

TABLE 6.2: Translation of the number of carbons in each chain of the swell tail in the molecules presented in Figure 6.4 to number of CG segments

Molecule	m	n	m _{CG}	n _{CG}
1 (T-shaped BA)	20	0	6	0
2	14	6	5	1
3	10	10	3	3

6.2.3 Interaction Parameters

Non-Bonded Interactions

Knowing the molecules representing each moiety, it is now possible to obtain SAFT- γ Mie CG models of these molecules. As seen in the previous chapters, each moiety is modelled as tangentially bonded spheres, having non-bonded interactions based on the Mie potential:

$$u^{Mie}(r) = C\varepsilon \left[\left(\frac{\sigma}{r} \right)^{\lambda_r} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (6.1)$$

$$C = \left(\frac{\lambda_r}{\lambda_r - 6} \right) \left(\frac{\lambda_r}{6} \right)^{6/(\lambda_r - 6)} \quad (6.2)$$

with ε being the minimum of the potential energy between two segments, σ being the touching distance between two segments and λ being the location of the potential minimum.

For obtaining self-interaction parameters, pure component properties, namely vapour pressure and saturation liquid densities of the mentioned molecules are used, with the EoS being used as an optimisation algorithm to find the best set of parameters that minimise the error with experimental data. For the parameter estimation procedure, one could refer to section 3.3.2. Cross interaction parameters are calculated as previously described in section 3.3.1, with arithmetic mean (Equation 3.58) and geometric mean (Equation 3.60) used to calculate the cross σ and λ respectively without any adjustable parameters. Adjustable parameters are used when fitting the cross interaction parameter ε_{ij} to experimental data.

$$\varepsilon_{ij} = (1 - k_{ij}) \frac{(\sigma_{ii}^3 \sigma_{jj}^3)^{1/2}}{\sigma_{ij}^3} \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \quad (6.3)$$

Again given a lack of experimental data, it is not possible to find experimental

data of mixtures containing p-terpheylnl, icosane and glycerol. To obtain cross interaction parameters, two pathways are taken:

1. Finding experimental data for mixtures of components most similar to the molecules presented in Table 6.1: For example instead of icosane using n-heptane, and instead of glycerol using ethanediol, where experimental solubility of p-terphenyl in those solvents are known, and using the k_{ij} parameters obtained there in for the moieties in the BA.
2. Using the current SAFT- γ library of united atom groups to build the molecules similar to molecules in Table 6.1 and generating pseudo-experimental data. Using the pseudo-experimental data, cross interaction parameters are then fitted to these data. The current SAFT- γ library has many small united atom groups, but these models cannot be used in simulation due to the presence of parameters that currently cannot be modelled in simulation. This methodology has not been implemented before and is a novel way of generating experimentally rare data. For the set of united atom models and their parameters one could refer to ref [117].

Intramolecular Interactions

Like the work in Chapter 5, intramolecular potential is defined as a sum of all bonding and angle potentials. Harmonic potentials are used to bonding and angle potential : In this work, harmonic potentials are used to model angle and bond stretching:

$$U_{Intra} = \sum_i^{all\ bonds} \frac{1}{2} k_{b,i} (b_i - b_{0,i})^2 + \sum_j^{all\ angles} \frac{1}{2} k_{\theta,j} (\theta_j - \theta_{0,j})^2 \quad (6.4)$$

When b_0 and θ_0 is the mean value of the bond and angle stretching for segments. Since the CG representation contains tangentially bonded segments, b_0 is the same as σ in the non-bonded interactions. k_b and k_θ are the constants of the harmonic potentials, with a higher value meaning a more stiff intramolecular potential.

For the flexible lateral chain, the k_b and k_θ parameters are the ones previously studied for alkyl chains [32]. However, for the backbone, the value of k_θ was calculated using Boltzmann inversion from atomistic simulations using the OPLS-AA

forcefield [237] as previously done for polymers in Chapter 5. For glycerol, given that each segments represents one united atom carbon and one OH group, the angle potential is modelled with the same parameters as the angle potential of the three backbone carbons in the TraPPE UA model of 1,3-propanediol [303].

6.2.4 Simulation Details

Once inter and intramolecular interaction parameters were obtained for the moieties, for each simulation, 2,400 BA molecules (corresponding to $\approx 100,000$ atoms) were randomly put in a large box which was compressed at a high pressure of 100 bars isotropically. After producing an isotropic liquid phase, N σ T Simulations were run with Nosé-Hoover thermostat [242, 243] and Parrinello-Rahman barostat [244] with a time-step of 0.01 ps. The equilibration temperature was set to 340 K, which is known experimentally to be in the liquid crystalline region of the phase diagram for all molecules. During the equilibration, due to the anisotropic nature of the interactions, an anisotropic barostat was used (N σ T ensemble). Each pressure tensor was fixed independently from other pressure tensors, allowing the simulation box to expand or compress in different directions with the angles of the box also relaxed. Not only this helps in faster equilibration of the system, this type of expansion of the simulation box allows for the system to find the correct periodicity for the system, preventing molecules from being trapped in local minima.

The SAFT model, unlike previous studies, uses soft Mie interactions to simulate real systems. This means that equilibration times can take very long. Most of the simulations presented in this work required more than 800 million timesteps. Given the current computing capacities, equilibration from random position of molecules takes about a week on a 48 core cluster. Moreover, the cut-off employed in the system has to be at least 3σ of the largest segment to observe realistic phase behaviour.

It should be noted that the reason each system contained 2,400 BA molecules is because of the large scale of the size of each unit cell of the pentagonal-hexagonal columnar and pentagonal-octagonal columnar phases.

All simulations were carried out using GROMACS 4.5 [238] on Imperial College HPC clusters and GROMACS 5.1 [240] on the Thomas cluster.

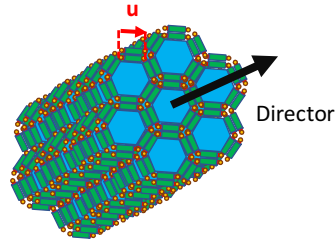


FIGURE 6.6: The director of hexagonal columnar BAs with side-chains is approximately perpendicular to the backbone.

6.2.5 Phase Characterisation and Order Parameters

Structural Metrics

In order to quantify the structures observed in simulations, it is important to develop metrics that can give a more robust understanding of the phase behaviour. For columnar self-assembled mesophases, a key parameter is the director, which is a vector defining the preferred direction of the alignment of the liquid crystals. For the case of T-shaped BAs, the director is approximately perpendicular to the rigid backbone as can be seen in Figure 6.6.

There are many methods to calculate the director relying on vector calculus. Crane et al. [293] used singular value decomposition to calculate the director. It is also possible to calculate the director of individual clusters by using principal component analysis of the position of individual particles.

In this work, the director is calculated not by looking at the position of the individual segments but following the previous study of Avendaño and Müller [304]. It is calculated knowing the vector defining the direction of the rigid backbones. Diagonalisation of the second-rank Saupe order tensor, $\mathbf{Q}$, can be used to find the director. $\mathbf{Q}$ is defined as [304–307]:

$$\mathbf{Q} = \frac{1}{N_m} \sum_j \left(\frac{3}{2} \hat{\mathbf{u}}_j \otimes \hat{\mathbf{u}}_j - \frac{1}{2} \right) \quad (6.5)$$

where $\hat{\mathbf{u}}_j$ is the unit vector describing the principal axis of the backbone of the j^{th}

molecule, which is perpendicular to the normal and $\otimes$ is the outer product. The tensor is diagonalisable and eigenvalues and eigenvectors can be calculated for the tensor. Sorting the eigenvalues in descending order of their absolute values, the eigenvector corresponding to the first eigenvalue is the director. Moreover, the eigenvalue of the largest absolute value is the P_2 nematic order parameter (refer to Equation 2.14), giving a value of 1 if the principal axis of the backbone is parallel to the director and a value of -0.5 if all the the backbone is perpendicular to the director [304].

Once the director is calculated, it is possible to calculate the S_2 nematic order parameters:

$$S_2 = \frac{1}{N_m} \sum_j^{N_m} \left(\frac{3}{2} \sin^2 \theta_j - \frac{1}{2} \right) \quad (6.6)$$

where θ_j is the angle between the principal vector of molecule j and the director. S_2 is 1 when the the principal vector of all the backbones are perpendicular to the director and a value of -0.5 when where are all aligned with the director. This value of the S_2 is the opposite to the P_2 order parameter:

$$P_2 = \frac{1}{N_m} \sum_j^{N_m} \left(\frac{3}{2} \cos^2 \theta_j - \frac{1}{2} \right) \quad (6.7)$$

when all the molecules are aligned parallel to the director, the value of P_2 is 1 and when perpendicular to the director, the value is -0.5.

The director and the nematic order parameter allow one to calculate a degree of alignment in columnar phases. To clearly characterise the specific structures of the LC phases seen in simulations, other metrics are required. For regular polygonal columnar phases, the planar orientational order parameter can be used:

$$\Psi_L = \left\langle \left| \frac{1}{N} \sum_{j=1}^N \exp(iL\theta_j) \right| \right\rangle \quad (6.8)$$

θ_j is the angle between an arbitrary axis orthogonal to the director and the projection of the principal vector of the backbone onto the plane orthogonal to the director. This orientational planar order parameter gives a value of 1 for perfectly ordered polygons in the system and a value of zero for no orientational order. For different

polygonal tiling patterns, the value of L takes different values, being 3, 4 and 6 for triangular, square and hexagonal columnar phases respectively.

For combination of tiling patterns, such as the pentagonal-hexagonal phase presented in Figure 6.4, and for 3-dimensional network phases, it is not possible to use the planar orientational order parameter. Therefore, for these phases distribution functions and structure factors are more relevant.

Planar 2-D radial distribution function is calculated using the following equation:

$$g^\perp(r) = \frac{A}{N^2} \sum_{i=1}^N \sum_{j=1}^N \frac{\delta(r_{ij} - r)}{2\pi r} \quad (6.9)$$

where A is the area of the plane orthogonal to the director.

Following the work of Sun et al. [302], the structure factor is calculated using the following definition:

$$S(\mathbf{q}) = \frac{1}{N} \left[\left(\sum_j^N \cos(\mathbf{q} \cdot \mathbf{r}_j) \right)^2 + \left(\sum_j^N \sin(\mathbf{q} \cdot \mathbf{r}_j) \right)^2 \right] \quad (6.10)$$

where $\mathbf{r}_j$ is the position of the j^{th} particle in the system. This could be used to calculate the structure factor as a scalar function of a scalar q or a scalar field of $\mathbf{q}$.

Dynamic Metrics

To observe the phase transition temperature, a key metric that has been previously studied is the diffusion coefficient as a function of temperature. Diffusion coefficient of species A , D_A is calculated using the Einstein relation [87]:

$$\lim_{t \rightarrow \infty} \langle \|\mathbf{r}_i(0) - \mathbf{r}_i(t)\|^2 \rangle_{i \in A} = 6D_A t \quad (6.11)$$

Where r_i is the 3-dimensional position of particle i and t is time. For calculating the diffusion constant in a particular direction x , the following equation is needed:

$$\lim_{t \rightarrow \infty} \langle (x_i(t) - x_i(0))^2 \rangle_{i \in A} = 2D_{x, A} t \quad (6.12)$$

TABLE 6.3: Non-bonded self-interaction parameters of the moieties fitted to experimental data using the SAFT- γ Mie EoS.

Molecule	N_{CG}	$M_{W,CG}$	λ_r	ε [K]	σ Å	AAD ρ^{SatLiq} %	AAD P^{vap} %
p-Terphenyl	3	76.77	30.15	703.48	4.929	0.8	2.4
Glycerol	3	30.69	24.00	615.90	3.385	2.3	4.5
Icosane	6	47.09	24.70	453.10	4.487	4.6	9.6

Visualisation

All visualisations of simulations used in this work were generated using the VMD visualisation package [308].

6.3 Results

6.3.1 Parameter Estimation

Self-Interaction Parameters

Non-bonded self-interaction parameters are presented in Table 6.3. Unlike icosane which has been previously parametrised [241], the equation of state was used to fit the self-interaction parameters of p-terphenyl and glycerol to experimental data taken from NIST [309].

The comparison between the calculations of the EoS using the fitted parameters and experimental data is presented in Figure 6.7. Simulation data are also presented in the mentioned figure, with calculations done after intramolecular interactions were obtained from underlying atomistic simulations.

The shape of the T- ρ phase envelope for icosane is slightly different in the EoS to that of the experimental data, which could be due to the different method of parametrisation using a corresponding states approach [189] instead of directly fitting the parameters directly to experimental data. Moreover, for glycerol the theory overestimates the liquid densities at lower temperatures. This is an effect of hydrogen bonding in real glycerol molecules, where the structural changes at lower temperatures cause the fluid to have more order and therefore less packing. This leads to a lower density than expected (same reason as water having a higher density at 4 °C than at 1 °C). Since the parameters fitted here are non-associative, it is not

TABLE 6.4: Literature data used for obtaining cross interaction parameters of the three species using Method 1.

Mixture Needed	Mixture Found in Literature	Property	Ref
p-Terphenyl - Glycerol	p-Terphenyl - Ethanediol	Solubility (SLE)	[310]
p-Terphenyl - Icosane	p-Terphenyl - n-Heptane	Solubility (SLE)	[310]
Icosane - Glycerol	n-Heptane - Ethanediol	LLE	[311]

possible to capture the densities correctly over the whole range. Having said that, the overall error in density is low with an AAD of 2.3% for saturation liquid density.

A particular advantage of the SAFT model presented here is the fact that all segments have a size rationally obtained via fitting the potential parameters to experimental data. Segment sizes are chemistry dependent, which makes the models more realistic than previous models studied where all segments had equal size. Here it could be seen that the end groups are particularly smaller in size than the rigid backbone and the lateral side chains.

Cross Species Parameters: Method 1

As discussed in the methodology section, there is a lack of literature data for phase behaviours of mixtures containing p-terphenyl, icosane and glycerol. So there are two methods of obtaining cross interactions parameter. Table 6.5 is a summary of the literature data found for calculating the cross interaction parameters.

The first method is finding literature data of mixtures of molecules similar to those under investigation here. For the cross interactions between p-terphenyl glycerol, the closest experimental data found in literature was that of the solubility or solid liquid equilibrium (SLE) of p-terphenyl in ethanediol.

Solubility was calculated using following equation is used [117, 312]:

$$\ln(x_i(T, p)) = \frac{\Delta H_m^{fusion}}{R} \left(\frac{1}{T_m} - \frac{1}{T} \right) - \frac{\Delta c_p(T_m)}{R} \left[\ln \frac{T_m}{T} - \frac{T_m}{T} + 1 \right] - \ln \gamma_i(T, p, \mathbf{x}) \quad (6.13)$$

where x_i is the solubility of species i , ΔH_m^{fusion} is the molar enthalpy of fusion at melting point, T_m is the melting point and $\Delta c_p(T_m)$ is the difference in heat capacity of the solid and the liquid phases at the melting point. γ_i is the activity coefficient of species i in solution, which is calculated by the SAFT- γ Mie EoS and is therefore

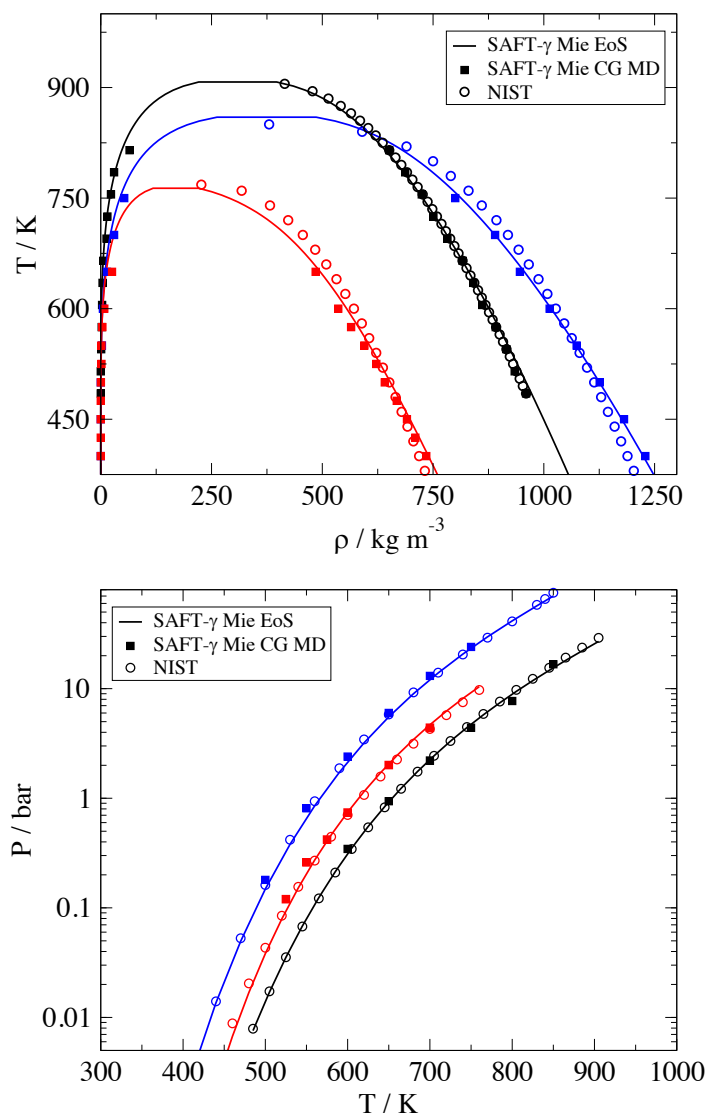


FIGURE 6.7: Comparison of theory, experimental data and MD simulation for the three different molecules used to model the BA. The black, blue and red plots represent p-terphenyl, glycerol and icosane respectively. *Top* Temperature vs density and *Bottom* Vapour Pressure vs temperature.

TABLE 6.5: Melting point properties of p-terphenyl used in solubility calculations in glycerol and n-heptane, taken from DIPPR 801 [313].

Property	Value
T_m	485 K
ΔH_m^{fusion}	33.70 kJ mol ⁻¹
$\Delta c_p(T_m)$	34.82 J mol ⁻¹ K ⁻¹

a function of the cross interaction parameter between the solvent and the solute i . Since the solid phase here is p-terphenyl, the values of the melting point properties for terphenyl are presented in Table 6.5.

To calculate activity coefficients using SAFT, the self-interaction parameters of p-terphenyl as given in Table 6.3 were used. However for ethanediol, new parameters were fitted to NIST data, with the potential parameters being $N_{seg} = 3$, $\varepsilon = 503.67$ K, $\sigma = 3.04$ Å and $\lambda_{rep} = 22.26$. The cross interaction parameter was optimised to minimise the error for solubility of the solute. The optimal k_{ij} was found to be -2.8% which means a favourable interaction between the two species. The comparison between calculated and experimental solubilities is presented in Figure 6.8(a). In general there is good agreement between the fit and the experimental data. Given the strong self-interaction of ethanediol and glycerol due to hydrogen bonding, a favourable cross interaction is slightly surprising, however, without favourable cross-interaction, the solute was found to be insoluble in the ethanediol.

The same procedure was carried out for the cross interaction of p-terphenyl in n-heptane. For n-heptane, the same parameters of icosane was used, with two icosane segments representing an n-heptane. Here, the rationale was to ensure a transferability of the cross interaction parameter to use when modelling icosane and p-terphenyl, and therefore the self-interaction parameters were not altered. Solubility of p-terphenyl in n-heptane is presented in Figure 6.8(b). This set of experimental data has very few data points and it is not possible to assess the robustness of the cross interaction parameter over the whole temperature range, however, it is possible to find a cross interaction parameter that can give solubilities in quantitative agreement with the 3 data points that exists in literature.

Finally for n-heptane and ethanediol, the same parameters used in the solubility

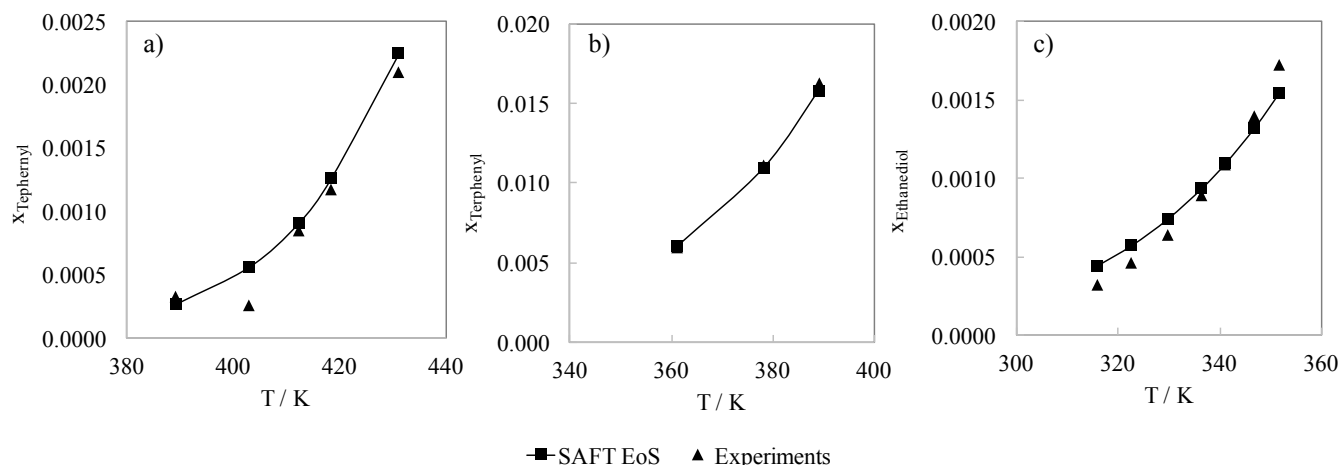


FIGURE 6.8: Comparison of the calculations of SAFT- γ Mie with experimental data for binary mixtures with components similar to the moieties of the bolaamphiphile studied here: *a*) Solubility of p-terphenyl in ethanediol, *b*) Solubility of p-terphenyl in n-heptane, *c*) T-x diagram of ethanediol-n-heptane mixtures (LLE) at P = 1 bar. The experimental data for *a* and *b* are from ref [310], and for *c* are taken from ref [311]. A k_{ij} of -0.028, 0.021 and 0.132 was used for the mixtures in *a*, *b* and *c* respectively.

calculations were used, with the cross interaction fitted to experimental data of T-x diagram of ethanediol-alkane mixtures at P = 1 bar. The results can be seen in Figure 6.8(c). The results are only in qualitative agreement, with the slopes of the calculations of the EoS and the experimental data being different. It could thus be concluded that away from the temperature ranges plotted, the EoS and experiments would most likely not agree. However, temperatures of 320 to 380 K is within the temperature range where liquid crystalline phases of BAs are observed, and so the cross interaction parameters is valid for temperature ranges of 300 to 400 K.

The optimal k_{ij} for the interaction of alkanes with ethanediol was found to be 0.138, which is much larger than the k_{ij} for the other binary mixtures. This shows that unlike previous studies of BAs where all moieties are strongly immiscible, with very high repulsions, here only the interaction of alkanes and polar groups deviate considerably from values obtained by combining rules.

Cross Species Parameters: Method 2

Given a lack of experimental data for the binary mixtures of the components in Table 6.3, it is possible to generate pseudo-experimental data by building the molecules

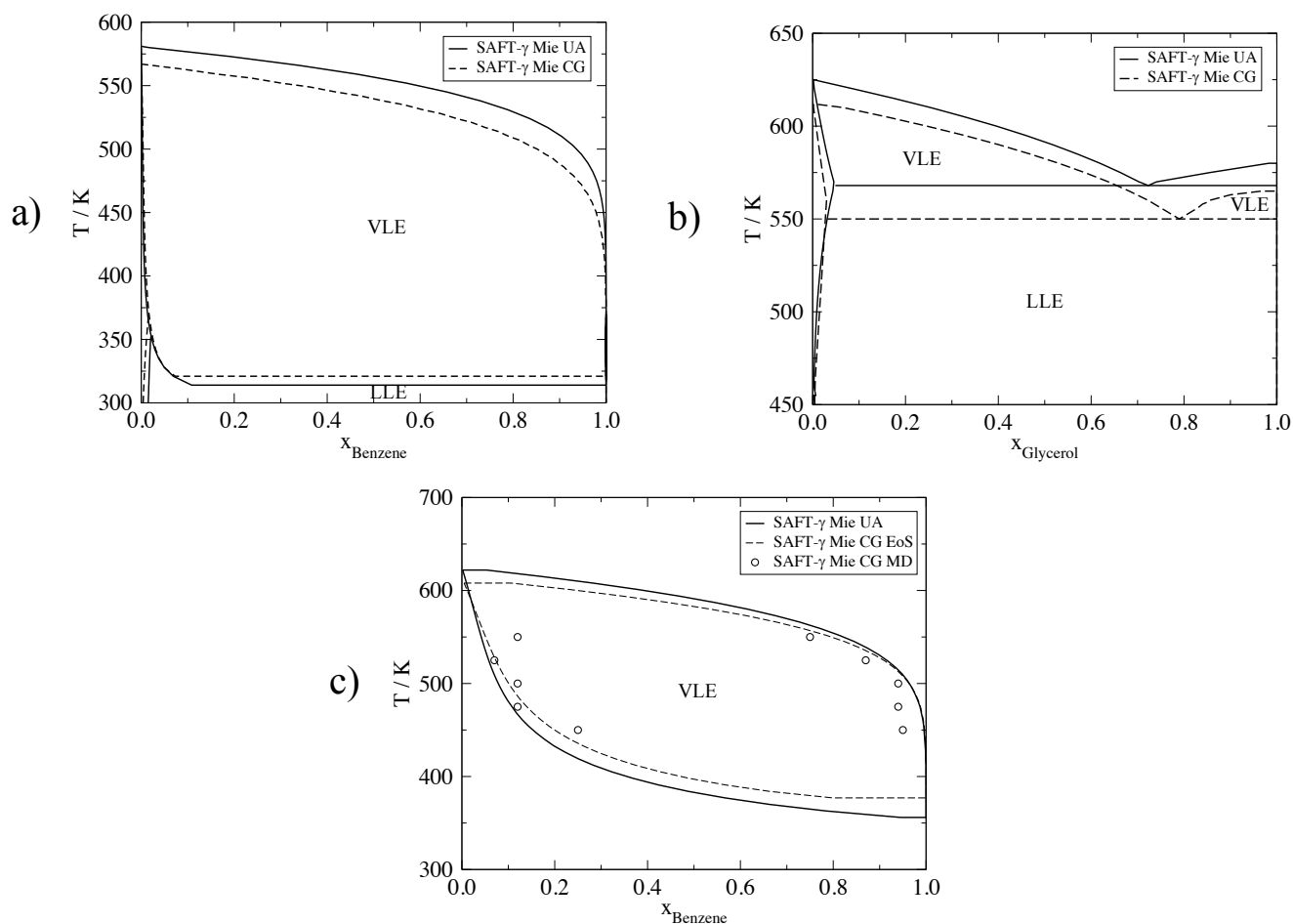


FIGURE 6.9: Comparison of T-x diagrams at $P = 1$ bar for binary mixtures of *a*) benzene and glycerol, *b*) glycerol and icosane and *c*) benzene and icosane as calculated using the parameters estimated in this work (SAFT- γ Mie CG) and the united atom models of Hutacharoen et al. [117] (SAFT- γ Mie UA). For the SAFT- γ Mie CG models, k_{ij} of 0.036, 0.145, 0.028 was used for the mixtures in *a*, *b* and *c* respectively.

using united atom groups previously parametrised and validated with SAFT- γ Mie. In this work, this SAFT representation of molecules will be described as SAFT- γ Mie UA (united atom). These united atom models have parameters such as the shape factor and association which means that they cannot be used directly in molecular simulations. However, it has been shown that their parameters are transferable among a range of hydrocarbons and complex pharmaceutical molecules, and can therefore be used as building blocks of new molecules. For a review of the prediction capabilities of phase behaviour of complex molecules and the latest table of parameters one could refer to refs [117, 314]. It is possible to build SAFT- γ Mie UA models of icosane and glycerol using these UA groups. However for p-terphenyl this is not possible since there are no parameters for the carbons connecting the phenyl rings to each other (aC group). It is possible to build a benzene model using six aromatic aCH groups.

For p-terphenyl it could be assumed that each CG segment of the 3-segment model represents a benzene molecule, and therefore benzene-glycerol and benzene-icosane binary mixtures can be appropriate mixtures to find cross interaction parameters between p-terphenyl, icosane and glycerol. In this method, therefore, the fluid phase properties (namely T-x diagrams at $P = 1$ bar) for mixtures of icosane-glycerol, as well as benzene-glycerol and benzene-icosane are first calculated using the UA groups specified in Table 6.6. Once pseudo-experimental data for each of the mixtures is generated, the same T-x diagrams are generated using the SAFT- γ CG parameters in Table 6.3. Again, the self-interaction parameters of benzene was assumed to be the same as one segment of p-terphenyl. The cross interaction parameters were then adjusted to minimise the error between the T-x diagrams generated using the two different approaches.

The results can be seen in Figure 6.9, with both sets of parameters generating very similar phase diagrams. For mixtures containing glycerol, the VLE and LLE regions merge with a VLLE line separating the two regions observed. It is known that for mixtures of benzene and glycerol, no azeotropes are observed experimentally at $P = 1$ bar [315]. For mixtures of heavier alkanes with alcohols, however,

TABLE 6.6: Molecules used in Method 2 to find cross interaction parameters of the three moieties studied in this work and their SAFT- γ Mie UA groups used to build these molecules to generate pseudo-experimental data of mixtures. The Mie interaction parameters for these groups could be found in ref [117].

Molecule	UA Groups (N^{repeat})
Bezene	aCH (6)
Glycerol	OH (3); CH ₂ (2); CH (1)
Icosane	CH ₃ (2); CH ₂ (18)

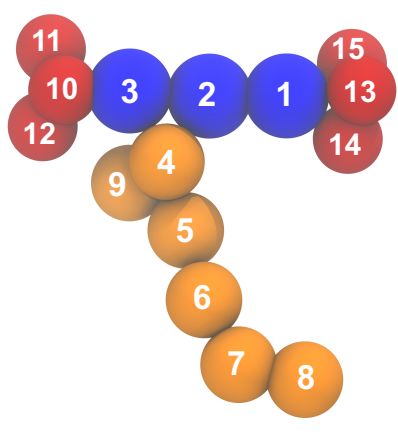
TABLE 6.7: Values of k_{ij} obtained from both methods. The k_{ij} values obtained by method two were used in simulations of the liquid crystallines systems in this work.

Mixture	Method 1	Method 2
p-Terphenyl - Glycerol	-0.028	0.036
p-Terphenyl - Icosane	0.021	0.028
Glycerol - Icosane	0.132	0.145

homogeneous azeotropes have been observed, such as mixtures of ethanol with n-heptane [316] and ethanediol with tetradecane [317]. This is predicted by the SAFT- γ UA models, for both binary mixtures of glycerol. It can be seen with the help of adjustable parameters that both approaches produce the same shape of phase envelope for all three mixtures. For the mixture of benzene-glycerol, the optimal value of k_{ij} was found to be 3.60%. This indicates a slightly unfavourable cross interaction between the species, which is different to the k_{ij} obtained in method 1, where the interactions were more favourable than predicted using combining rules. However, for the mixtures of benzene-icosane and glycerol-icosane, the k_{ij} values agree with those calculated in the previous section, being 2.80% and 14.5% respectively. Again this methodology indicates that alcohol and alkane moieties interact extremely unfavourably with each other, whereas the cross interactions between the benzene groups and other groups are not significantly different to the geometric mean of the self-interaction ϵ_s .

A summary of all the k_{ij} parameters obtained from both methods is given in Table 6.7. In this work, it was decided to use the k_{ij} parameters obtained using method 2 in the simulation of bolaamphiphiles. This is because of the more unfavourable interaction between glycerol and p-terphenyl groups.

TABLE 6.8: The angle potentials used to model the swallow-tail bolaamphiphile.



Beads	Angle / °	k_θ / kJ mol ⁻¹ rad ⁻²
1 – 2 – 3	180	225
2 – 3 – 10	180	225
2 – 1 – 13	180	225
11 – 10 – 12	109	420
14 – 13 – 15	109	420
1 – 2 – 4	120	22
4 – 5 – 6	158	22
5 – 6 – 7	158	22
6 – 7 – 8	158	22

Intramolecular Interactions

Given that SAFT- γ Mie CG is a top down thermodynamic CG model, it is not possible for the molecules modelled with SAFT to have the same correct structural properties as bottom up approaches relying on structure matching have. However, for anisotropic molecules (e.g. liquid crystals), it is important for any CG model to capture, albeit qualitatively, the key aspects of the structure of the molecule. The key intramolecular interactions affecting the self-assembly of these liquid crystalline molecules are the angle potential of the backbone (affecting the stiffness of the rod-like component of the LC), and to a lesser extent the angle potential of the lateral side chains, affecting the conformation the moieties.

Previous simulation studies of alkanes using SAFT- γ Mie have extensively studied the intramolecular potentials of the alkanes, using a Boltzmann inversion method. Rahman et al. [32] used TraPPE UA [318] models to find optimal intramolecular interaction parameters for n-alkanes, with each CG segment representing 3 UA carbons. In this work, therefore, it was deemed unnecessary to fit the angle potentials of icosane, and the angle potentials fitted for n-alkanes by Rahman et al were used directly in this work. For alkanes, it was found that the optimal angle, θ , between three neighbouring CG groups, each representing three UA carbons, was 158° with k_θ of 22 kJ mol⁻¹ rad⁻².

For the glycerol group, the angle potentials parameters were assumed to be the

same as the angle between three backbone carbons of 1,3-propanediol as parametrised by TraPPE [303]. Although this approximation is not strictly valid, the angle potential of the glycerol groups is not expected to significantly affect mesophase behaviour as the size of each glycerol segment is much smaller than the size of each icosane or p-terphenyl segments, meaning chain stretching is not significant for glycerol. Therefore, an approximate set of parameters were used to qualitatively describe the intramolecular potentials of glycerol end groups.

For the rigid backbone, no literature studies of intramolecular potentials of CG models were found, and it was difficult to assume parameters for the angle potentials. Therefore, it was decided to find realistic angle potentials using two methods, both using atomistic OPLS-AA simulations [237].

The first method was to fit the angle distribution to atomistic simulations using Boltzmann inversion. Atomistic simulations were run for a system containing 500 p-terphenyl molecules at $P = 1$ bar and $T = 500$ K, with 500,000 steps for equilibration and 2,000,000 time steps ($\delta t = 1$ fs) for analysis. The centre of mass of each phenyl ring in the atomistic simulation was then taken as the centre of mass of each segment of the CG model and the angle distributions between the three CG segments were calculated. Using the probability distributions of the angles, θ and k_θ , CG were calculated using Boltzmann inversion. θ_{terph} was found to be 180° with the optimal k_θ being $225 \text{ kJ mol}^{-1} \text{ rad}^{-2}$. The results of the probability distributions can be seen in Figure 6.10(top). Even though the angular distribution is correctly captured, it could be seen in Figure 6.10(bottom) that the p-terphenyl centre of mass-centre of mass (CoM-CoM) radial distribution function (rdf) of the CG segments with the aforementioned angle potential parameters is very different to the rdf of the same atomistic simulation used in the Boltzmann inversion. The peaks occur at the same distances, but the magnitude of the peaks of the rdf is much higher for the CG model relative to the atomistic rdf. The logarithm of rdf is the potential of mean force between two p-terphenyl molecules, with a higher peak describing a stronger attraction between the molecules. This suggests that a more rigid CG model can capture the correct structure of the molecule, but at the same time attractions between two rigid molecules as modelled with SAFT are much stronger than the atomistic representation of p-terphenyl.

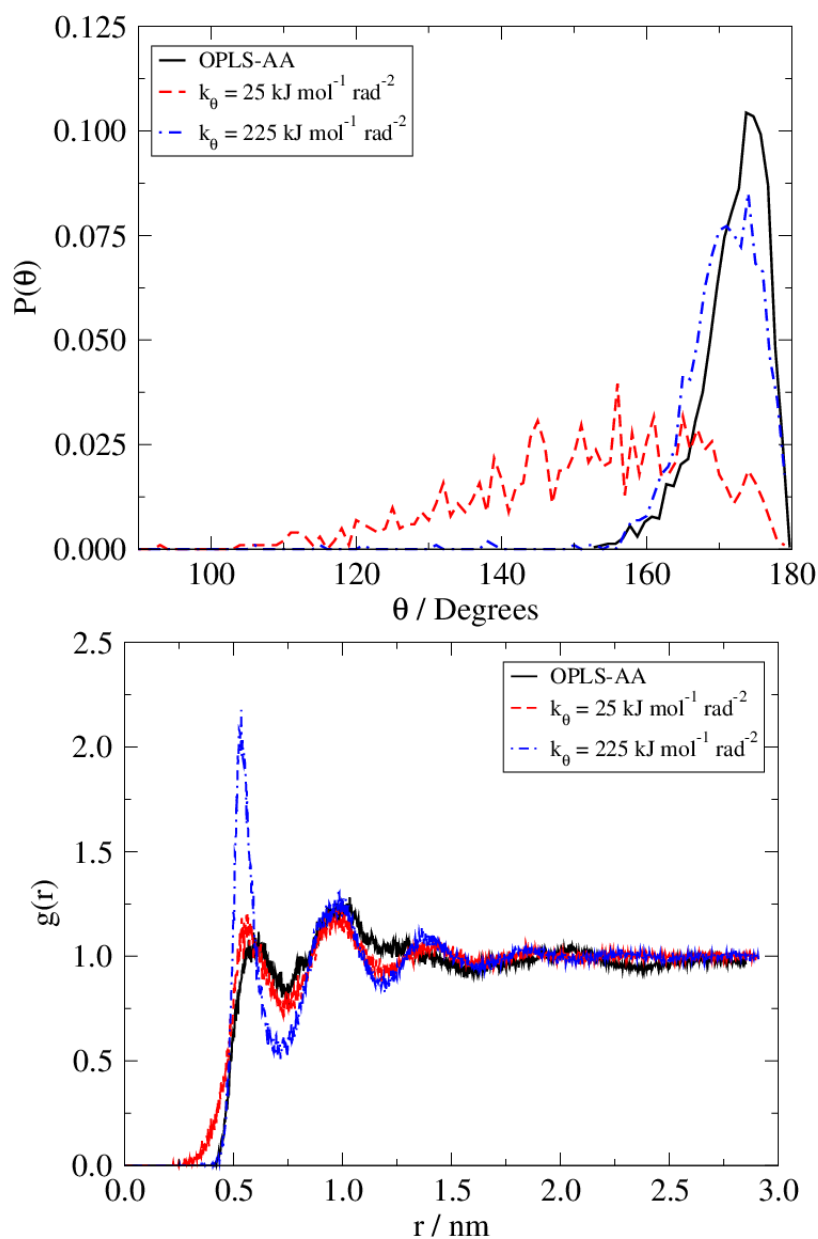


FIGURE 6.10: Comparison between the properties of two coarse-grained models of p-terphenyl with atomistic simulations of p-terphenyl. Two CG models differ in intramolecular potential only, with blue dash and dot line representing a model with $k_\theta = 225 \text{ kJ mol}^{-1} \text{ rad}^{-2}$ and the red dash having $k_\theta = 25 \text{ kJ mol}^{-1} \text{ rad}^{-2}$. Both CG models have $\theta = 180^\circ$. **Top** Angle distributions of the three phenyl rings in p-terphenyl, **Bottom** CoM-CoM RDF of p-terphenyl.

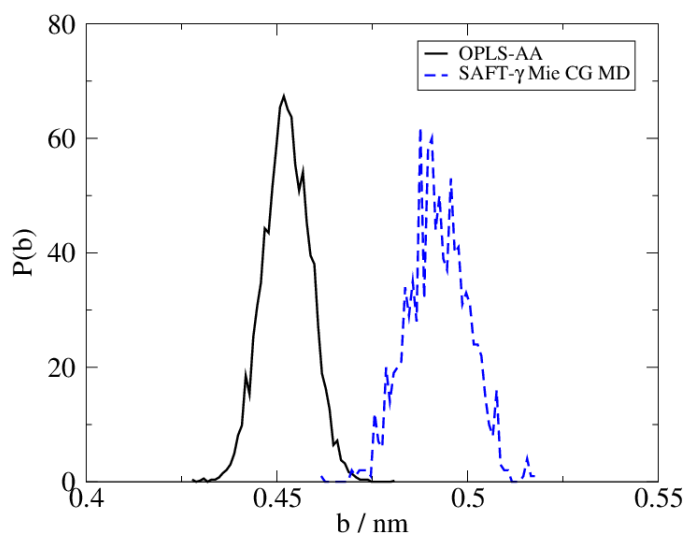


FIGURE 6.11: The bond distances between the two neighbouring phenyl rings in p-terphenyl as calculated by atomistic OPLS-AA simulations (black line) and the CG model (dashed blue lines).

The second method therefore involved fitting k_θ to the CoM-CoM rdf of the atomistic simulations, instead of the distribution of the angles of the three benzenes in the backbone. Using this approach, k_θ was found to be an order of magnitude smaller than previously calculated ($225 \text{ kJ mol}^{-1} \text{ rad}^{-2}$). The rdf of the CG model and the atomistic simulations remarkably agree (6.10(bottom)), however the distribution of the angle and therefore the structure of the molecule clearly deviates from the atomistic representations. It was decided to use intramolecular parameters obtained using the first method, as it accounted for the correct structure of the backbone, important in studying self-assembly.

In terms of bonded potentials, SAFT- γ Mie theory assumes a molecule to be composed of tangentially bonded spheres and therefore bond distances were not fitted to atomistic data, and σ s presented in Table 6.3 were used as bond distances for segments of the same moieties. For CG segments of different groups attached to each other, the arithmetic mean of the σ s was used as the bond distance. Assuming bond distances being the same size of σ is not strictly valid, however since the CG parameters are fitted to thermodynamic properties, instead of structural properties, it is expected that bond distances would be different to the underlying atomistic simulations. This could be seen in Figure 6.11 where the bond distances between two neighbouring phenyl groups is around 10% higher in the CG models than in the

atomistic simulations.

From previous works, it has been shown that the value of k_b does not significantly affect the phase behaviour of SAFT- γ Mie CG models, and therefore all values of k_b were set to $6130 \text{ kJ mol}^{-1} \text{ nm}^{-2}$ used in previous simulation studies [32, 33].

Comments on the Interaction Parameters

Pure component simulations were run using the inter and intramolecular parameters presented before. Each simulation involved a system containing 1000 molecules of each component, with an equilibration run of 200,000 steps and 500,000 steps of the main simulation run using an elongated box ($L_Z > 5 L_{X,Y}$). The cut-off for each simulation was 5σ with no tail corrections.

As can be seen in Figure 6.7, for pure components the calculations of the simulation agree remarkably well with the results of the EoS, with less than 0.5% error between simulations and the calculations of the EoS.

Moreover, for the mixture of benzene (i.e. one p-terphenyl CG segment) and icosane, simulations were run with global composition of 50 mol% of icosane, with the calculations of the VLE presented in Figure 6.9(c). It could be seen that the parameters are robust for simulating both pure components and mixtures.

However, as previously mentioned, structural properties of CG models parametrised by top down approaches are not guaranteed to match the structural properties of real molecules. Moreover, coarse-graining in itself can affect the properties of the materials under study. For example, non-associating CG models are not realistic for hydrogen bonding molecules, as directional interactions cannot be averaged out into an isotropic spherical interaction [319]. A particular consequence of coarse-graining associating molecules as non-associating spheres can be seen in Figure 6.12, where the surface tension of glycerol is significantly overestimated. This is not observed for molecules that do not have hydrogen bonding such as p-terphenyl. Surface tension can have significant effects on the self-assembly structural properties of amphiphilic molecules, such as the curvature of the interfaces. An underlying problem is that the parameter estimation employed in this work is based on fitting the parameters

to VLE data. Future work is currently being undertaken to improve parameter estimation of glycerol and other hydrogen bonding molecules.

Having highlighted these problems, the models presented in this work are still robust in simulating BAs as the parameters are thermodynamically consistent and are transferable over a wide range of state points. As will be shown in the following sections, these models can predict many properties of BAs. First, simulations of the T-shaped bolaamphiphile ($m = 6, n = 0$) are carried out to assess the predictability of the model presented. This is followed by studying swallow-tails BAs.

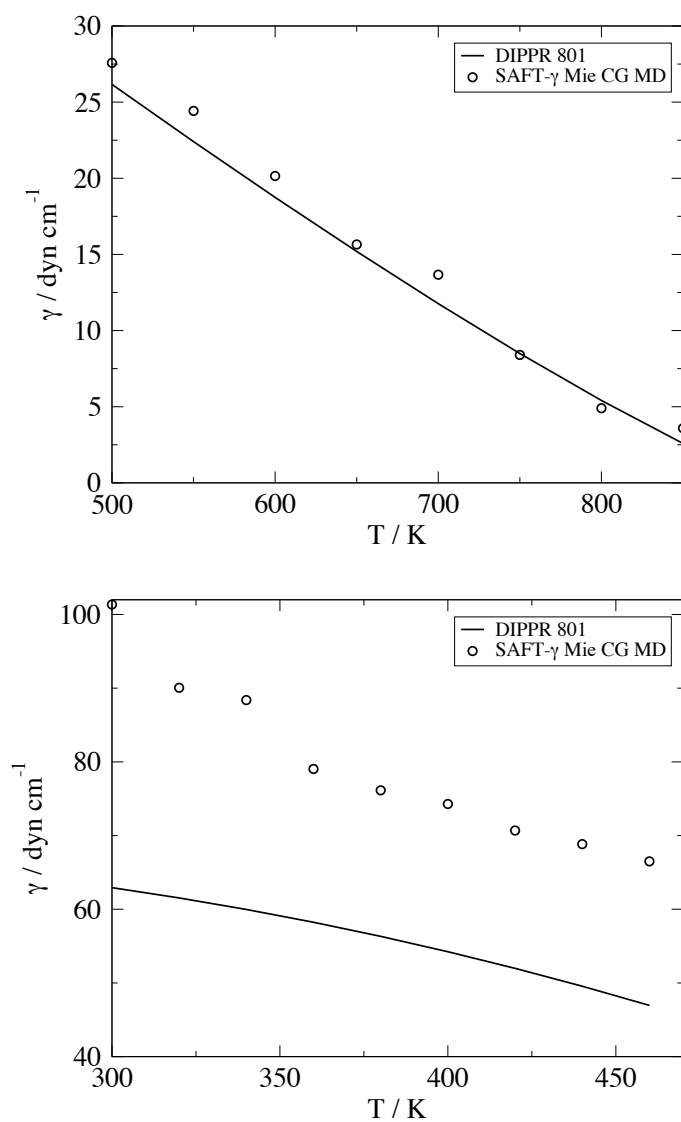


FIGURE 6.12: Comparison of simulations of surface tension of **Top** p-Terphenyl and **Bottom** Glycerol with experimental data [313]. Developing non-associating models of molecules with hydrogen bonding using VLE data leads to CG models with very high surface tensions.

6.3.2 Model Validation: Simulation of Bolaamphiphiles

Phase Behaviour of the Backbone with or without the End Groups

Before the studies of swallow-tailed simulations can be carried out, it is imperative to investigate the phase behaviour of the rigid backbone and the backbone with glycerol end groups.

From previous studies, it is known that systems containing p-terphenyl exhibit nematic and smectic phase behaviour [93] at high temperatures and high densities. However, it is known from previous studies that nematic phases cannot be observed for molecules with chains lengths smaller than 5 [320]. This is due to the fact that the isotropic-nematic phase transition occurs at packing fractions higher than the isotropic-solid transition [321]. According to the OVL-LH theory developed by van Westen to study isotropic-nematic phase behaviour of hard-chains composed of tangentially bonded spheres [321], for linear hard sphere trimers the isotropic-nematic coexistence packing fractions are $\eta_{iso} = 0.541$ and $\eta_{nem} = 0.551$ respectively, which is higher than the isotropic-solid coexistence point calculated from molecular simulations of Vega et al [320], i.e. $\eta_{iso} = 0.430$ and $\eta_{iso} = 0.529$.

In this work, two sets of simulations were set up to study the phase behaviour of the rigid backbone. First set of simulations was set up by randomly inserting 500 molecules in the simulation box allowing the system to equilibrate at 390 K and 1 bar in an N σ T ensemble. The second set of simulations was run with a smectic initial configuration.

The results for the the first set of simulations can be seen in Figure 6.13. After 80 million time steps (0.8 μ s), there was no drift in the energy (Fig 6.13(c)) with an average nematic order parameter is -0.0176 (Figure 6.13(b)). In Figure 6.13(a) every molecule is highlighted with a different colour and it can be visually observed that no nematic phase could be observed. After 80 million timesteps, the system pressure was changed only in the Z direction, at pressures of up to 10,000 bar at different temperatures. No nematic phase could be observed, agreeing with previously studies.

To further assess the phase behaviour of the backbone, the second set of simulations were run, where the initial configuration was a smectic phase. As can be seen

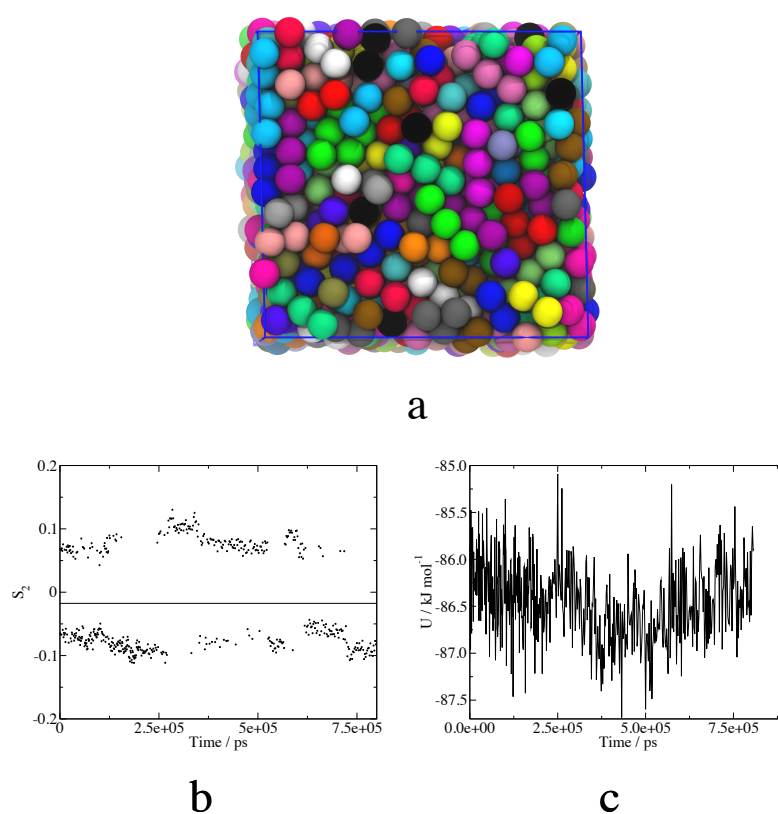


FIGURE 6.13: 800 ns N σ T simulation of p-terphenyl at $T = 390$ K and $\sigma = 1$ bar starting with a configuration of randomly inserted molecules: **a** The final configuration where each p-terphenyl molecule is highlighted in a different colour, **b** S_2 vs time indicating an average nematic order of -0.0176, **c** potential energy, U , vs time for the system

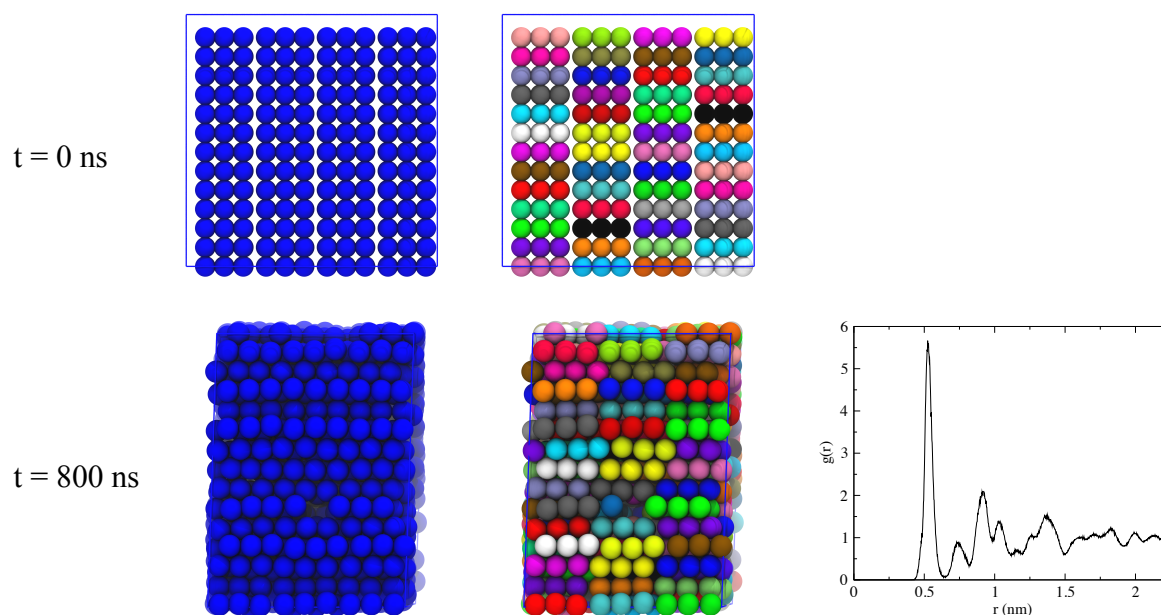


FIGURE 6.14: 800 ns $N\sigma T$ simulation of p-terphenyl at $T = 390$ K and $\sigma = 1$ bar starting with a smectic configuration: it can be seen from the RDF that instead of a smectic configuration, molecules arrange themselves so that the segments form an FCC lattice.

in Figure 6.14, after 800 ns, the smectic layer is disrupted as the individual segments form an FCC lattice, forming a solid.

It can be concluded therefore that the backbone model used in this work is not representative of the real p-terphenyl molecule in terms of liquid crystalline phase behaviour, as it is not possible to observe smectic layering or nematic liquid phases. This can be improved in the future by implementing better models, such as using a five bead model for p-terphenyl, or anisotropic models based on the Gay-Berne potential.

Having said that, using the three bead model for p-terphenyl can still be used in modelling the phase behaviour of bolaamphiphiles, as the unfavourable cross interaction between the moieties can induce smectic layering. The phase behaviour of the pure bolaamphiphile, without any lateral side chains, was investigated with the potentials developed in the previous section. For the first set of simulations, 500 molecules were randomly inserted in a simulation box, with the system equilibrated at 400 K and $\sigma = 1$ bar. The simulation was run in the $N\sigma T$ ensemble. As can be seen in Figure 6.15, a lamellar phase is observed after 1 μs .

To investigate this more accurately, the temperature of the same simulation box

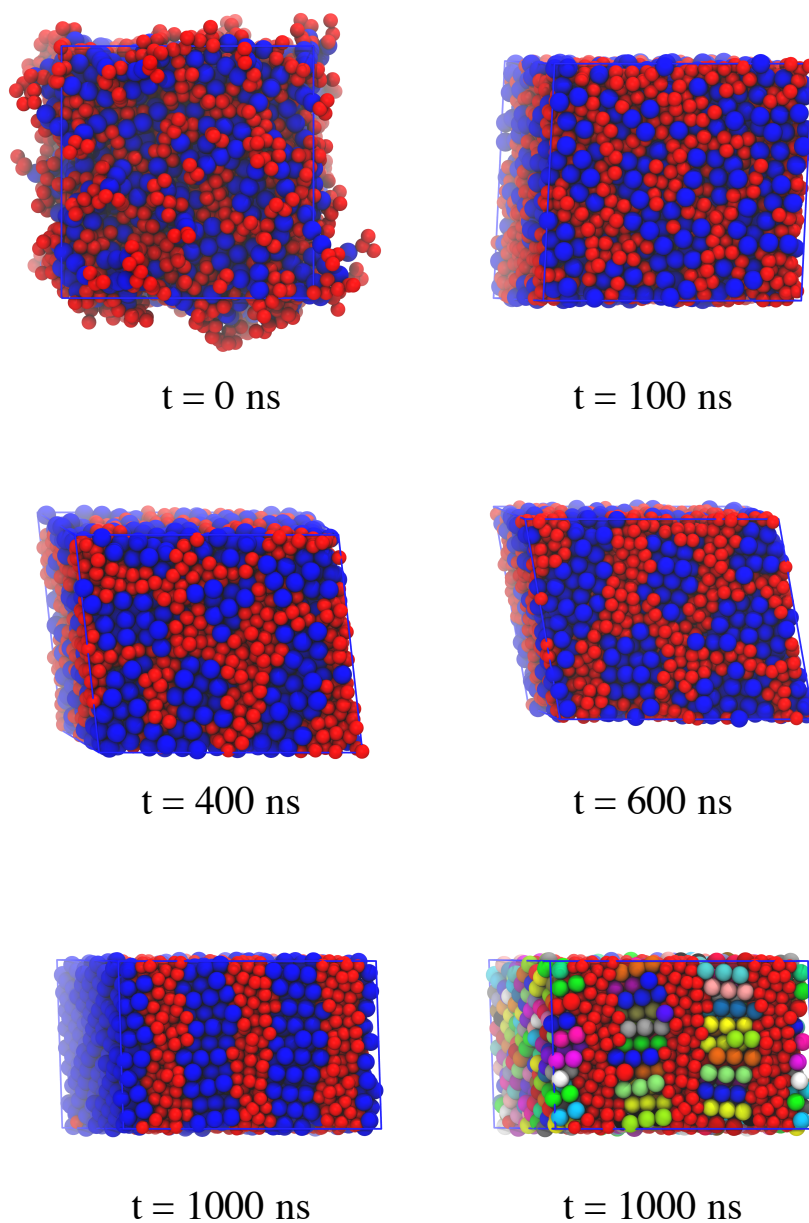


FIGURE 6.15: Snapshots of the equilibration of the BA molecule at 400 K and $\sigma = 1$ bar at different times. After $1 \mu\text{s}$ a smectic phase is observed.

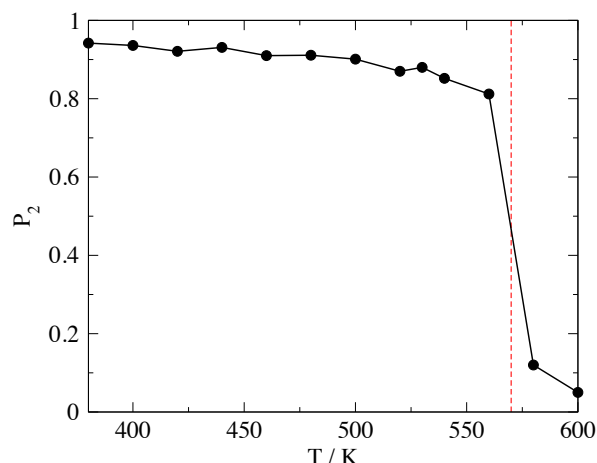


FIGURE 6.16: The P_2 order parameter vs temperature for the bolaamphiphile without any lateral side chains.

was raised to 600 K and slowly cooled at a rate of 20 K per 3 μ s. As can be seen in Figure 6.16, there is an isotropic-smectic phases transition at around 570 K. This value is comparable to that experimentally measured, which for a biphenyl based bolaamphiphile with no lateral side chain is 260 °C or 563 K [281].

Study I: T-Shaped BA ($m_{CG} = 6$, $n_{CG} = 0$)

To check if any self-assembly could be predicted, $N\sigma T$ simulations were run at $T = 340$ K and $P = 1$ bar using a box filled with 2,400 randomly inserted molecules. For the T-shaped BA composed of a single lateral chain of $C_{20}H_{41}$, ($N_{CG} = 6$), the simulations correctly predict a hexagonal columnar phase. Snapshots of the final frame can be viewed in Figure 6.17. From a visual point of view, the hexagonal columnar phase can be most easily understood by looking at the two-dimensional patterns of the alkyl moieties, where each column is surrounded by 6 other columns. Therefore, to analyse the structure using $g_{\perp}$ or $S(q)$, the CG segments of the alkyl moiety were analysed. It is interesting that each column composed of the alkyl moiety is a cylindrical column. This is different to the triangular columnar phase of the glycerol end groups. This triangular shape is due to the way the rigid backbones join each other at their ends. The rigid backbones, highlighted in blue in Figure 6.17, form a honeycomb structure. This can clearly be seen in Figure 6.18, where histograms of the

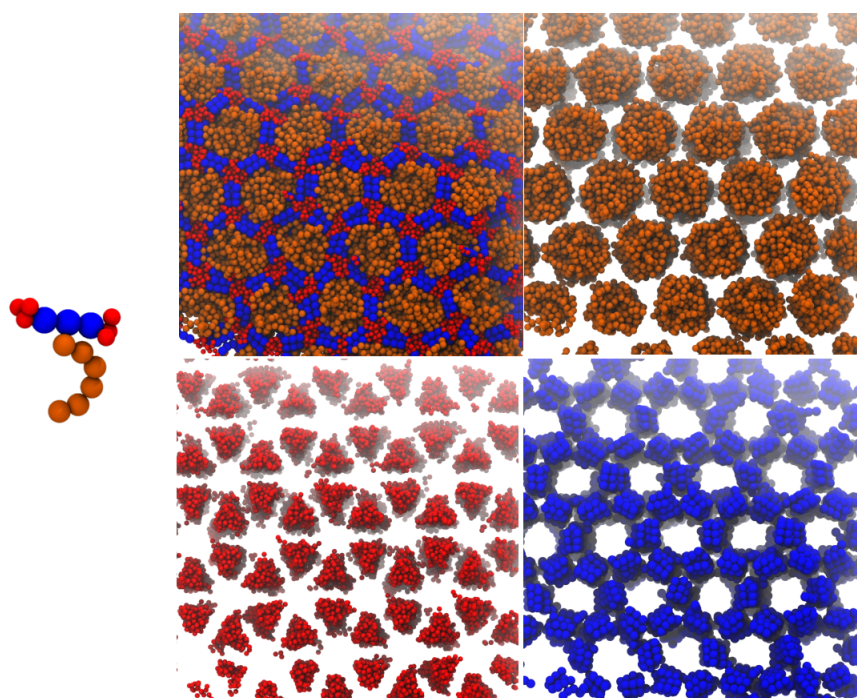


FIGURE 6.17: Snapshots of the final frame of self-assembly of T-shaped BAs composed of side chain of $C_{20}H_{41}$ ($m = 6$, $n = 0$) at $T = 340$ K. The BAs self-assemble into a hexagonal columnar phase. From top right clockwise the snapshots show the alkyl side-chain only, the p-terphenyl rigid backbone only, the glycerol end groups only, and all moieties together respectively.

distribution of the angles between an arbitrarily chosen backbone and all other backbones in the system at different temperatures are presented. It could be clearly seen that at temperatures less than 430 K there are peaks at multiples of 60° , indicating a honeycomb like structure.

Given that a self-assembled structure is observed, it is important to compare this to experimental data, to assess the validity of the model parameters proposed. The first point of direct comparison with experiments is a visual one. To categorise the phases observed experimentally, Poppe et al. [301] generated electron density maps, as well as two-dimensional diffraction patterns using XRD to observe the hexagonal columnar phase. These could be seen in Figures 6.19(a) and 6.19(c) respectively. Therefore, to compare the snapshots to experimental data, a heatmap of the local mole fraction of the alkyl chain moieties in the plane perpendicular to the director was generated, as well as a 2D diffraction pattern of the alkyl moieties on the same plane. The results are presented in 6.19(b) and 6.19(d). The simulation results visually match with the experimental observations. This shows that it is possible to correctly predict the structure of the $p6mm$ hexagonal columnar phase using this CG methodology.

With the qualitative agreement between the visual characteristics between simulation and experiments, the next step is to compare the quantitative agreements between the simulations and the experiments. Two types of quantitative comparisons were carried out. The first property to compare to experiments was a structural property, specifically the inter-column distances. The second property to investigate was the predictions of the transition temperature.

For the hexagonal columnar phase, Poppe et al. reported an inter-column distance of 4.2 nm between two neighbouring columns. To calculate this inter-column distance, the planar radial distribution function, $g_\perp$, of the alkyl CG segments was calculated for the plane orthogonal to the director. It was assumed that the value of the first peak corresponds to the inter-columnar distance, and as could be seen in Figure 6.20, the simulations predict an inter-columnar distance of 4.2 nm, which is exactly the same as that observed experimentally. It is to note that none of the parameters in this work were fitted to the experimental data given by Poppe et al. and therefore this exact agreement is very impressive. The structure factor of the

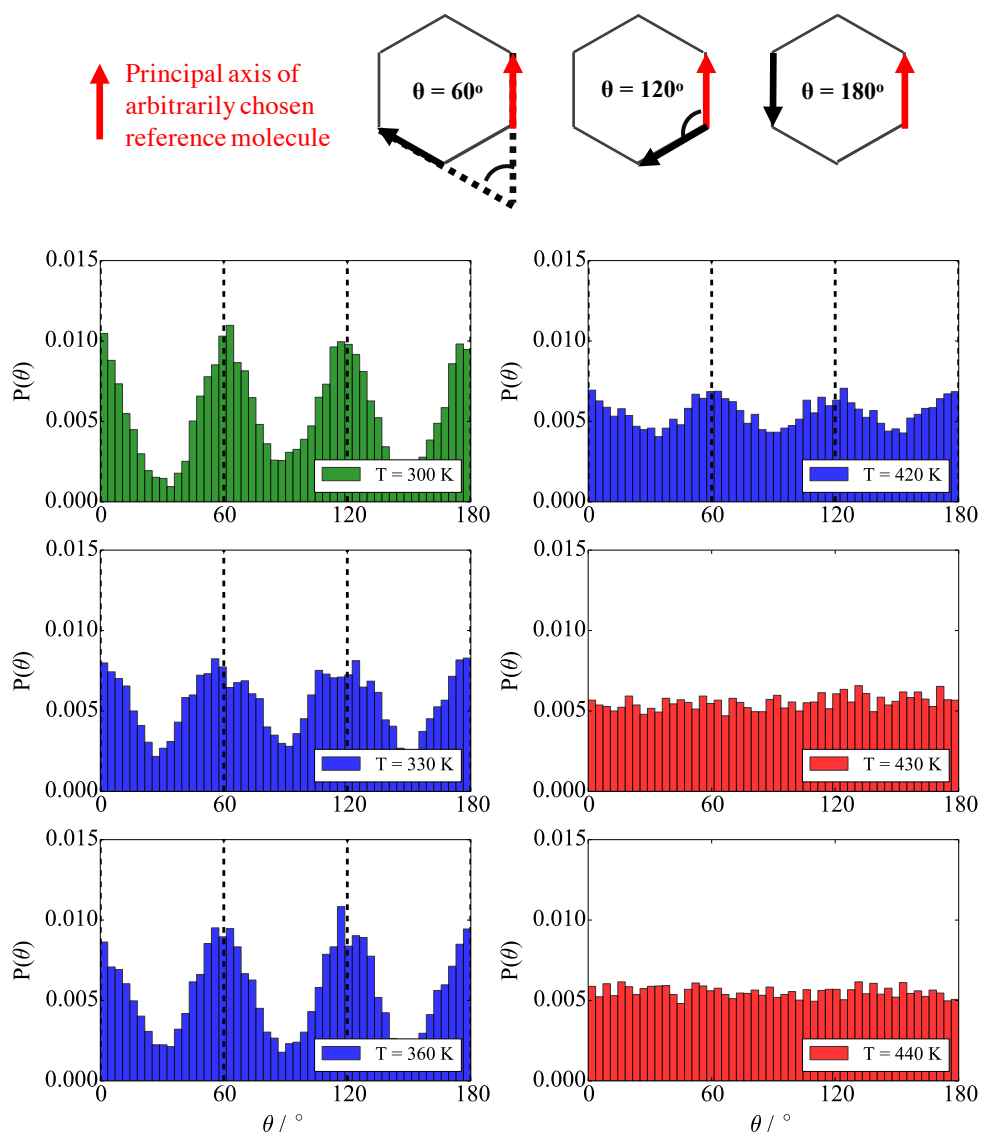


FIGURE 6.18: The distribution between the principal axes of the backbone of an arbitrary BA and the rigid backbones of all other BAs in the simulation at different temperatures. Green represents a crystalline solid phase, red represents isotropic phase where no peaks are observed, and blue represents the liquid crystalline phase.

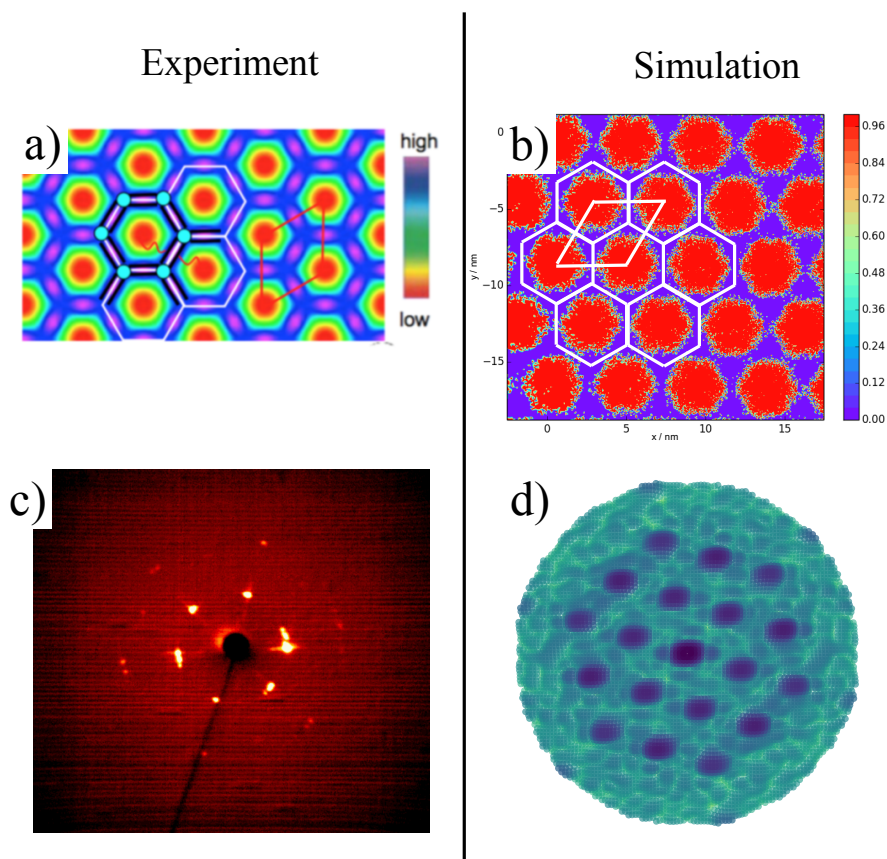


FIGURE 6.19: Comparison of experimental and simulations observations of the hexagonal columnar phase: *a* Electron density map taken from ref [301], where red shows regions of low electron density (i.e. alkyl chains) and blue shows regions of high electron density (i.e. the π conjugation of the rigid backbone). *b* Heatmap of local mole fraction of alkyl moieties on the plane perpendicular to the director observed in simulations at T = 340 K, with red representing a local mole fraction of 100% and purple representing regions void of alkyl side-chains. *c* Diffraction pattern observed using XRD at T = 135 °C taken from ref [301] and *d* Diffraction pattern generated in this work at T = 400 K.

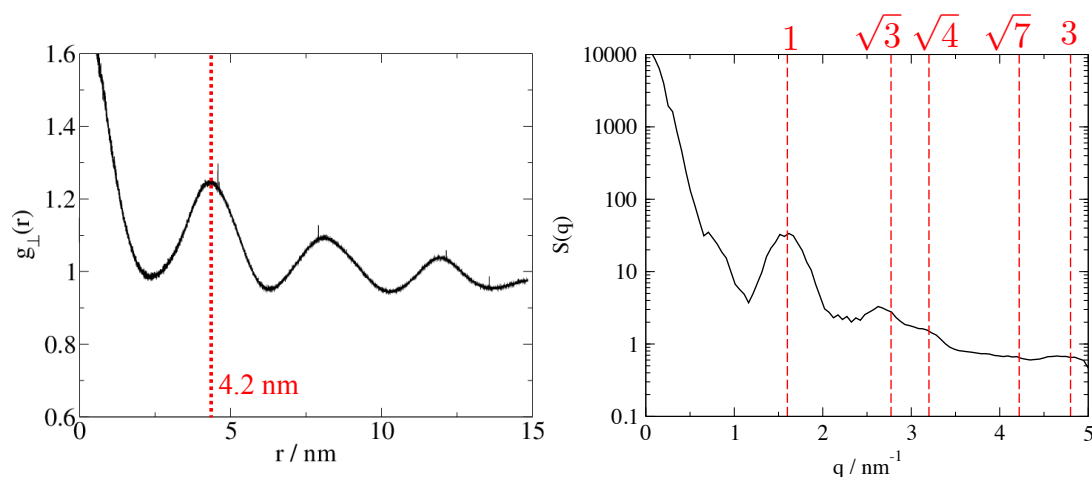


FIGURE 6.20: **Left** planar radial distribution function, $g_{\perp}$, of the alkyl moieties on the plane orthogonal to the director. **Right** Structure factor of the alkyl group in the same system, clearly indicating a hexagonal ordering.

TABLE 6.9: Comparison of the phase transitions of the T-shaped BA as observed experimentally [301] and predicted with simulations in this work.

Phase Transition	$T_{Trans, Exp} / K$	$T_{Trans, Sim} / K$
Crystalline Solid to p6mm Hex Col	310	300
p6mm Hex Col to Isotropic	452	430

alkyl moiety is also shown in the aforementioned figure, with the peaks with a ratio of $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}$ clearly indicating a hexagonal ordering.

In terms of temperature dependent phase behaviour, it is known from experimental and previous simulation studies that T-shaped bolaamphiphiles have a crystalline solid phase at low temperatures, an isotropic phase behaviour at high temperatures and a liquid crystalline fluid at intermediate temperatures. To investigate this, simulations were run at different temperatures from 280 K to 460 K for the hexagonal columnar phase. In order to calculate phase transition temperatures, five parameters were calculated at different temperatures: density, constant volume heat capacity, nematic and orientational planar order parameters as well as the diffusion coefficient of all CG segments. The diagrams can be seen in Figure 6.21.

For all the parameters investigated, there are clear changes in the value of the properties calculated at the onset of phase transition. The phase transitions are most clearly visible in the heat capacity vs temperature plot where two large peaks are

observed at $T = 300$ K and $T = 430$ K. At these temperatures, an order of magnitude increase in the diffusion coefficient is observed with increasing temperature by 10 K. This is further backed by the density vs temperature plots where the slope of the curve changes at $T = 300$ K and again at $T = 430$ K, with the change being more pronounced at the lower temperature. These two temperatures are the transition temperatures. The lower transition temperature is the transition from the crystalline solid phase to a liquid crystal, as the diffusion coefficient becomes an order of magnitude higher at $T = 320$ K than at $T = 300$ K, but S_2 and Ψ_6 remain unchanged. This is also seen in Figure 6.18, where the histograms at temperatures below 430 K had very similar distributions, with 4 peaks at 0° , 60° , 120° and 180° . At $T > 430$ K, a flat distribution is observed indicating an isotropic phase. This is commensurate with the sharp drop in the values of the order parameters at $T = 430$ K, clearly indicating a p6mm-isotropic phase transition. The predictions from the simulations as reported here show a very good agreement between this work and the experimental data published by Poppe et al. [301]. The comparison is presented in Table 6.9, with the solid-liquid crystal transition temperature being almost the same. The columnar-isotropic phase transition is underestimated by 20 K, which is due to the cross interaction parameters between all groups, and can be further refined in the future by having better experimental data to fit the cross interactions.

The diffusion coefficient presented in Figure 6.21 is the average diffusion in all direction for all segments in the simulation box. Closer analysis of the diffusion coefficient, parallel and perpendicular to the director, clearly indicates faster diffusion along the director. This anisotropy in the value of the diffusion coefficient can be seen in Figure 6.22. The two lower temperatures represent the liquid crystalline system, and the higher temperature is for an isotropic system. It could clearly be seen that at lower temperatures, the slopes of the mean square displacements (MSD) vs. time are smaller indicating smaller diffusivities. For the LC phases, the displacements of the molecules parallel to the director are twice as high than displacements perpendicular to it. At 440 K, there is no difference in the value of the diffusivities in different directions, indicating an isotropic phase.

It could be clearly seen that with the given model presented in this work, it has been possible to predict the correct hexagonal columnar self-assembly structure for

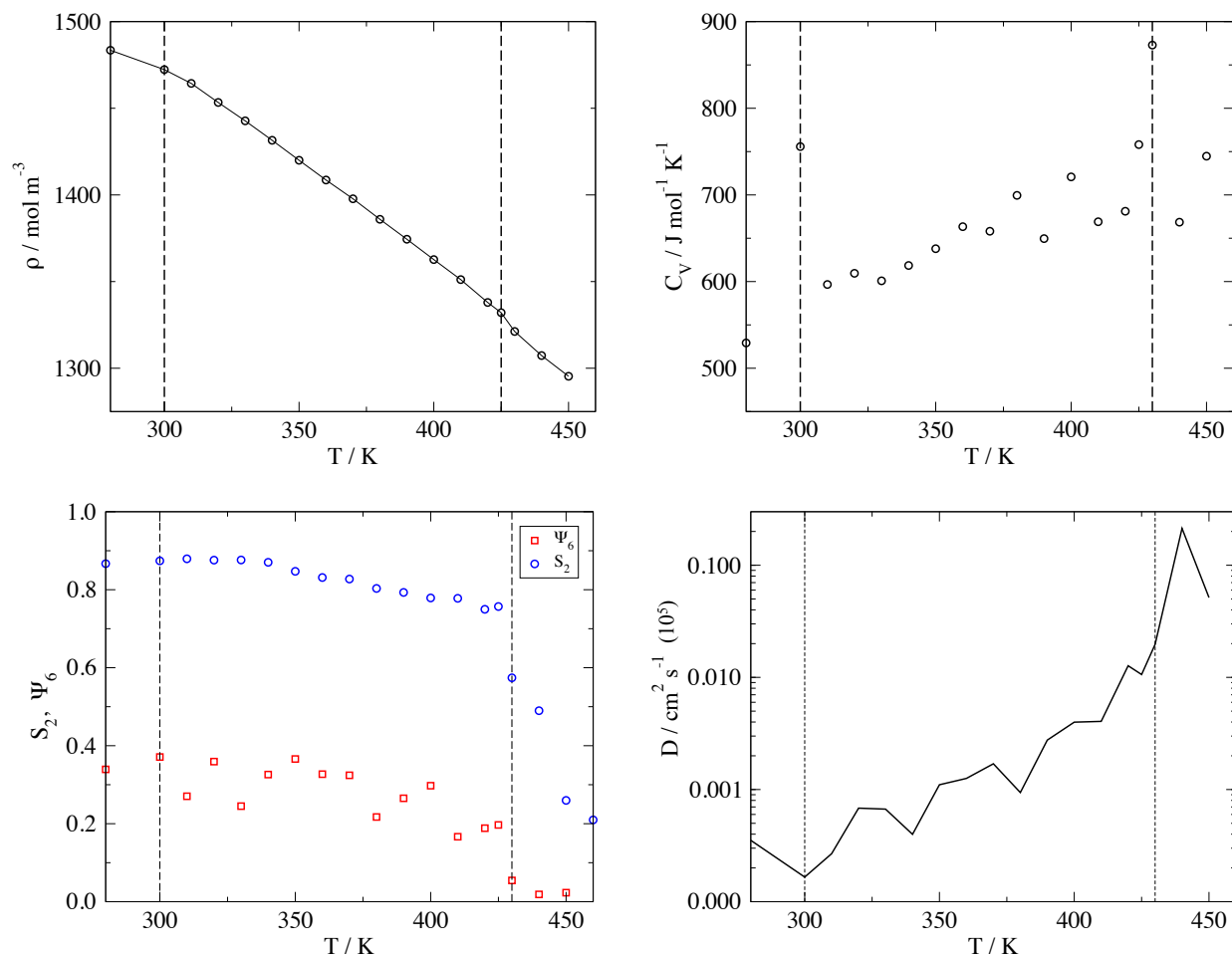


FIGURE 6.21: Plots of 5 parameters vs temperature for the T-shaped BA ($m=6$, $n=0$), used to calculate the transition temperature, T_{trans} . **Top Left** Density vs T , **Top Right** Isochoric heat capacity vs T , **Bottom Left** Nematic order parameter, S_2 , and the hexagonal orientational planar order parameter, Ψ_6 , of the principal axis of the rigid backbone vs T , **Bottom Right** Diffusion coefficient of all CG segments vs T . The dashed lines indicate the transition temperatures.

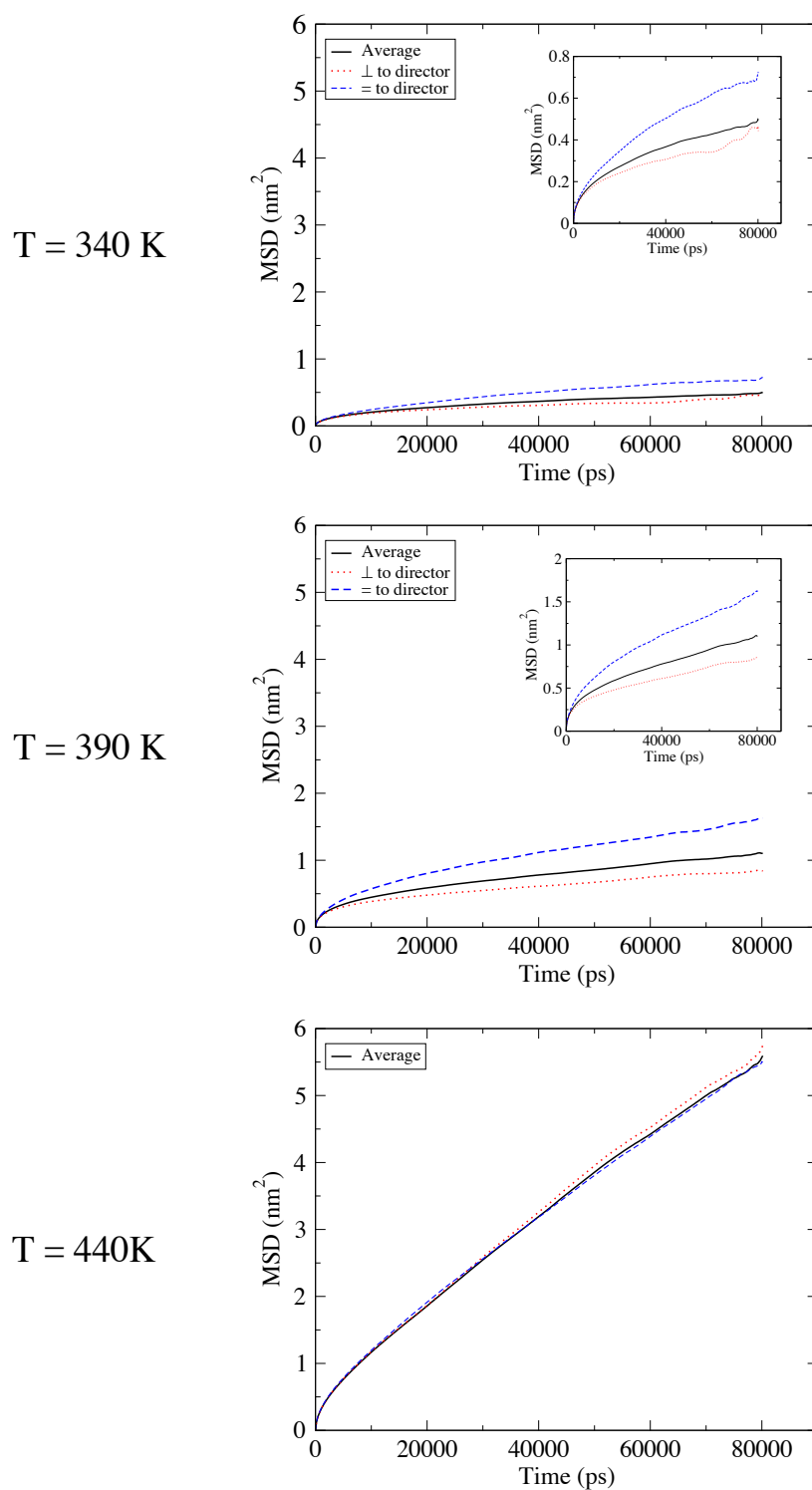


FIGURE 6.22: Mean square displacements of the BA molecules parallel and perpendicular to the director at different temperatures, with the insets being the same plots with readjusted scale for the y axis. $T = 440 \text{ K}$ is the isotropic case.

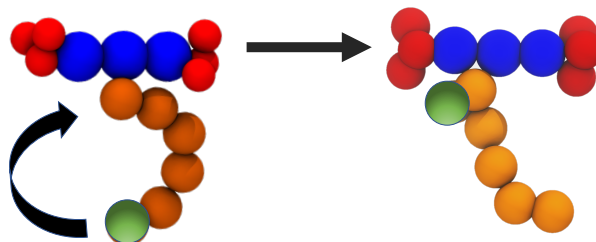


FIGURE 6.23: The asymmetric swallow-tail molecule investigated here, where the last segment is moved and placed next to the first segment, conserving the volume fraction of the moieties whilst changing degree of the branching.

T-shaped BAs, with the correct inter-columnar distances and approximately the correct transition temperatures. The close agreement between simulations and experiments for T-shaped BAs clearly demonstrates the advantage of using the SAFT- γ Mie methodology presented in this work relative to previous simulation studies. Here all moieties are carefully fitted to experimental data and a more realistic model is developed. This is particularly useful in studying more complex phases, such as those of the swallow-tail BAs as presented in Figure 6.4. This would be the focus of the next part of the results.

Study II: Asymmetric Swallow-tail ($m_{CG} = 5$, $n_{CG} = 1$)

As mentioned before, the interesting aspect of the self-assembling behaviour of swallow-tail BAs is that the volume fraction of the moieties are not different to each other. By modifying the structure of the side chain, it is possible to observe different structures. Here, a new molecule is investigated with 6 segments representing the alkyl chain moiety. However, instead of having a single side chain of 6 segments, the BA has an asymmetric swallow-tail side chain with one chain having 5 CG segments and the other having one. This could be seen in Figure 6.23.

N σ T Simulations for this molecule were run as described for the T-shape BA, at

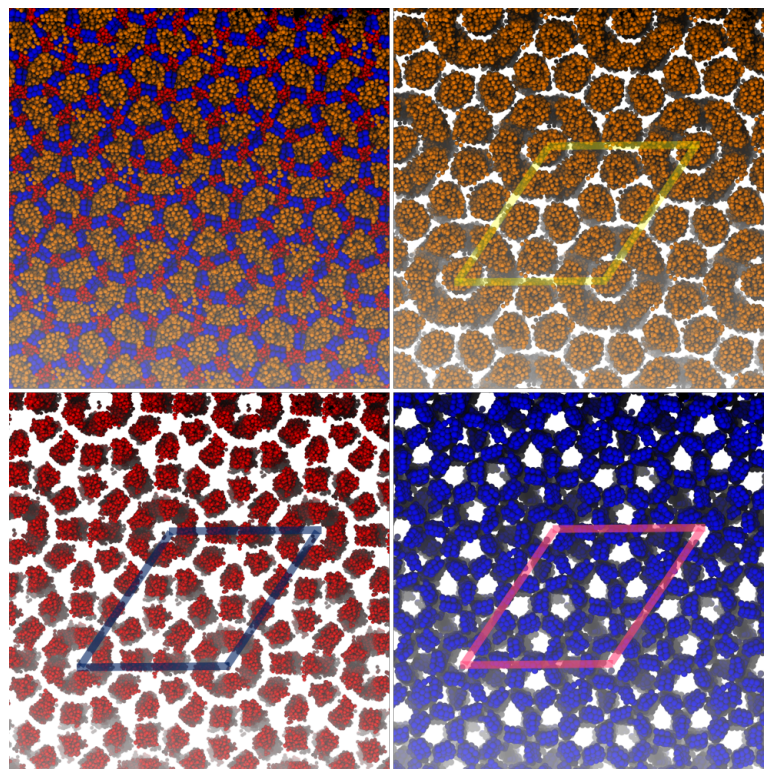


FIGURE 6.24: Snapshots of the final frame of self-assembly of swallow-tail BAs with one tail being $C_{14}H_{29}$ and the other being C_6H_{13} ($m = 5$, $n = 1$) at $T = 340$ K and $P = 1$ bar. The BAs self-assemble into a combination of hexagonal and pentagonal columns, with a central column being surrounded by an inner ring, which is itself surrounded by a ring of 12 pentagonal columns. From top right clockwise the snapshots show the alkyl side-chain only, the p-terphenyl rigid backbone only, the glycerol end groups only, and all moieties together respectively. The unit cell defining the superlattice is sketched on each frame too.

$T = 340$ K and $\sigma = 1$ bar, with a system composed of 2,400 molecules. The snapshots of the final frame of the simulation can be seen in Figure 6.24. As can be seen, a very large superlattice with a hexagonal $p6mm$ symmetry was observed. To the best of our knowledge, this type of phase behaviour has never been observed in simulation work of polyphilic molecules, be it liquid crystals, surfactants or block copolymers. Once again, like the previous case of the T-shaped BA, the columnar phase behaviour can be best understood by looking at the side-chain moiety, depicted using the orange colour in the mentioned figure.

Looking at the alkyl group, a central column is surrounded by a disordered ring. This ring is then surrounded by 12 pentagonal columns. This three layered structure form the basis of the columnar patterns, with these ringed structures forming a

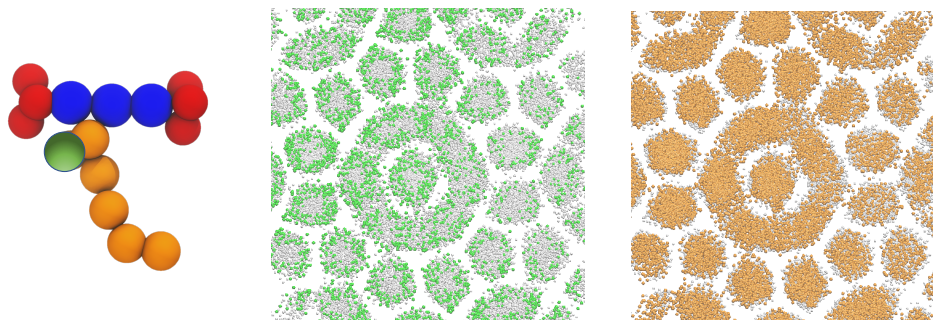


FIGURE 6.25: Distribution of the different branches of the side chain in the columns, with green highlighting the shorter chain and orange highlighting the longer chain.

hexagonal structure. The visual comparison between the predictions of the simulation and the structure observed experimentally is presented in Figure 6.26. It could be seen that again, the proposed model has predicted a structure very similar to that observed experimentally. However, here, the structures are not identical, with the key difference being the number of layers between each central column. In the experimental observations, every two central columns are separated by 2 rings of pentagons. However, in simulations the distance between every two central columns is three layers of either pentagonal or the disordered rings. This can be understood more easily using Figures 6.26(a) and 6.26(b) plotted with the same scale. The radius of the black ring gives the lattice length in experiments, and the white ring gives the lattice length observed in simulations. The lattice length in simulations is clearly an extra layer of pentagons longer. This could be a system size effect. To study this, simulations with 1,600 and 2,000 particles were run. For those systems, it was not possible to observe any pentagonal columns and only the central column was observed. Given the very expensive simulations required, larger system sizes were not investigated. Another reason for the differences between simulations and experiment could be due to the system being trapped in a local minimum of the free energy. Experimentally, the central column is meant to be a hexagonal column, whereas here it is a twisted pentagonal column. Moreover, the ring forming around this central column seen in simulations is not observed experimentally, which could mean the system has not equilibrated or is trapped in a local minimum. Given the chemical and structural complexity of these molecules, it is not possible to access

the free energies of all mesophases to identify the global minimum *a priori*. However, this does not mean that the ring structure observed here is necessarily not the correct structure for the given molecular model. Experimentally, the pentagonal columns of the superlattice were found to be disordered, and this disorder was explained as an entropic effect. Entropy could be used to explain the ring formation around the central column instead of columns, however this would have to be verified in future work, if it is possible to calculate entropies and free energies.

To calculate the lattice length of the hexagonal structure, the planar RDF was calculated for alkyl group, with the fourth peak corresponding to lattice length of the hexagonal columnar phase, as explained in Figure 6.26. As also presented in the aforementioned figure, experimentally the third peak of the planar RDF corresponds to the lattice length as only two pentagonal rings separate the central columns from each other. Poppe et al. calculated a lattice length of 9.7 nm, which is in agreement with the distance given by the third peak calculated in this work at 10.1 nm. However, the lattice length in this work was calculated using the fourth peak of the RDF, and was found to be 13.6 nm. The structure factor was also calculated (Figure 6.27(c)), with only two peaks being visible, as highlighted in the figure, with the ratios of the peaks ($3.82 \text{ nm}^{-1} : 1.94 \text{ nm}^{-1}$) being the same as the ratio of the fourth to the second peak ($13.6 \text{ nm} : 6.9 \text{ nm}$) of the rdf. It was not possible to determine any structures from the structure factor. However, the 2D structure factor (i.e. diffraction pattern) shown in Figure 6.27(d) clearly shows the twelve peaks corresponding to the twelve pentagons surrounding the central column.

To compare the thermotropic behaviour of the asymmetric BA, simulations were run at different temperatures as previously done for the case of the T-shaped ($m = 6$) BA. Parameters used to investigate transition temperatures are presented in Figure 6.28. Again for the solid to liquid crystal phase transition, density and the diffusion coefficient were used, and for the LC columnar to isotropic phase transition, the nematic order parameter was used. The comparison between transition temperatures from experiments and simulation is given in Table 6.10. Experimentally, from 326 to 403 K, an unknown liquid crystalline phase is observed, which is different to the phase discussed. From 403 to 417 K the phase presented in the work is observed and the LC-isotropic phase transition occurs at 417 K. In this work, a crystal to LC phase

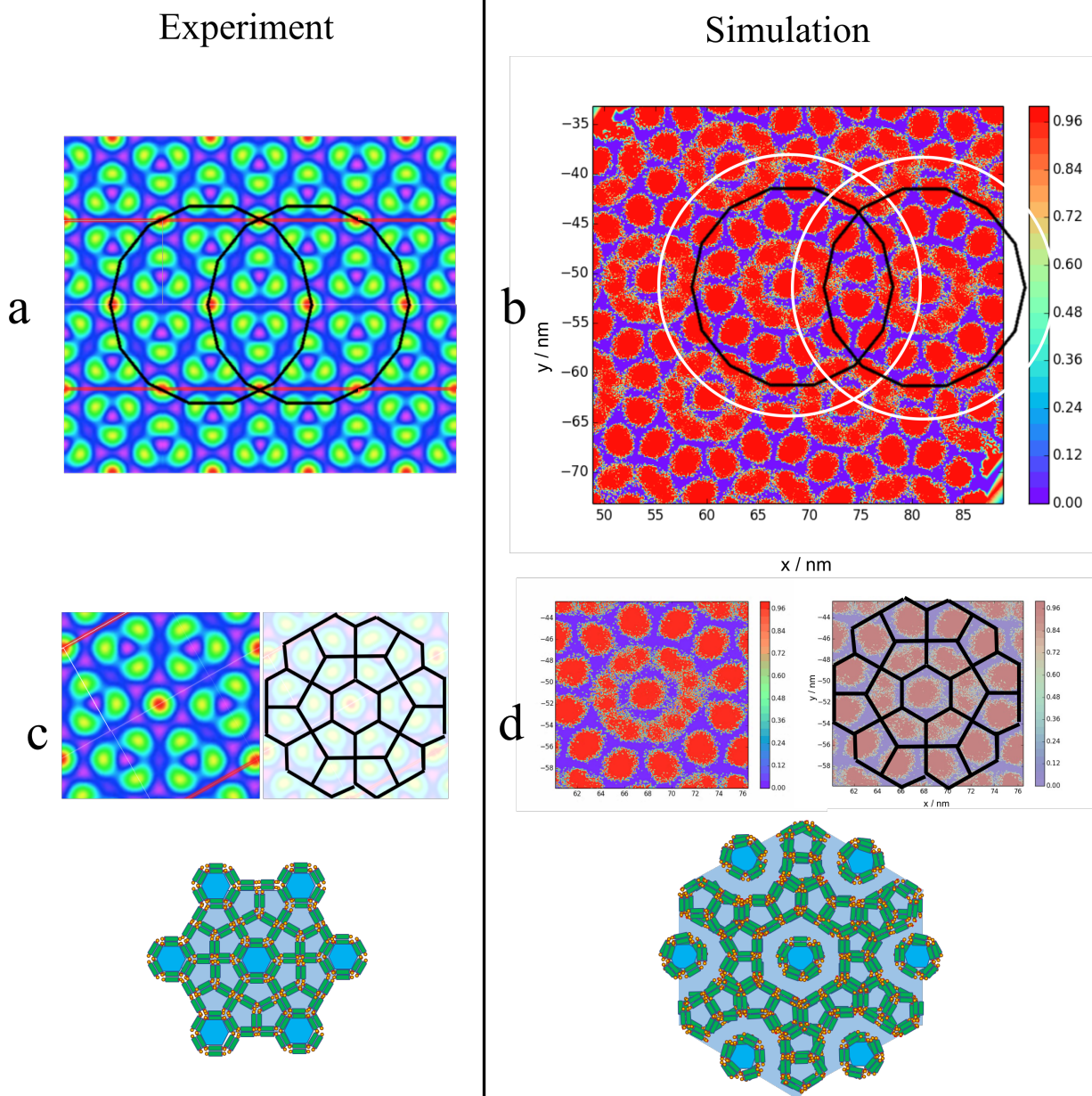


FIGURE 6.26: Comparison between structures obtained experimentally and in simulation for the asymmetric BA ($m = 5$, $n = 1$): **a** Electron density map taken from ref [301], with colours explained in Figure 6.19. **b** Heatmap of local mole fraction of alkyl moieties on the plane perpendicular to the director observed in simulations at $T = 340$ K, with the colours explained in Figure 6.19. **a** and **b** have the same scale, with the black and white rings being the distance between the central columns observed experimentally and in simulation respectively. In both cases a hexagonal superlattice is observed with a central hexagonal surrounded by layers of pentagons as clearly highlighted by **c** and **d**.

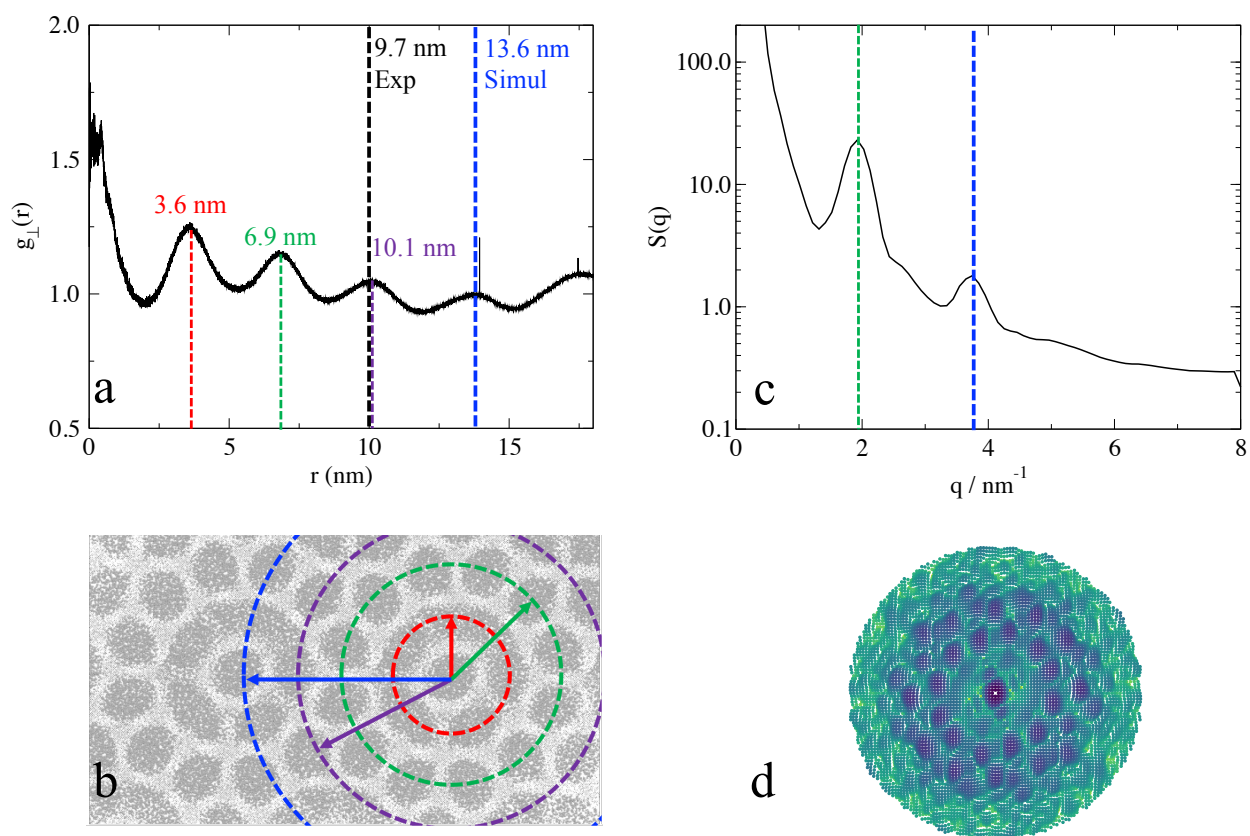


FIGURE 6.27: *a* planar radial distribution function, $g_{\perp}$, of the alkyl moieties on the plane orthogonal to the director, with the peaks highlighted with different colours corresponding to distances shown in *b*. The unit cell distance is 13.1 nm *c* Structure factor of the alkyl group in the same system, with two peaks with a ratio of 2 : 1 clearly visible, with *d* showing the 2D diffraction pattern of the same system clearly showing 12 peaks.

TABLE 6.10: Comparison of the phase transitions of the asymmetric swallow-tail BA ($m = 5$, $n = 1$) as observed experimentally [301] and predicted with simulations in this work.

Phase Transition	$T_{Trans, Exp} / K$	$T_{Trans, Sim} / K$
Crystalline Solid to Unknown LC	326	-
Crystalline Solid to p6mm LC	-	320
Unknown LC to p6mm LC	403	-
p6mm LC to isotropic	417	400

transition is observed at around 320 K and the p6mm to isotropic phase is observed at 400 K, again the solid-liquid crystal transition temperatures are in quantitative agreement, however, just like the previous case, the LC-isotropic phase transition is underestimated with simulations. It is not discussed in literature what the unknown liquid crystalline phase that is observed in simulations are, however, the quantitative agreement between simulation and experiments is very striking. It is also interesting that in this work, just like experiments, the isotropic transition temperature for BAs is lower than that predicted for the T-shaped BA, signifying that the liquid crystalline phase is less stable. This could potentially be explained in Figure 6.25, where in the LC phase the shorter side chain is confined to the interface between the alkyl groups and the other moieties. In an isotropic system this side chain could interact with more alkyl groups.

So far, it has been shown that the model developed for BAs in this work can predict the self-assembly of T-shaped as well as asymmetric swallow-tail BAs, with both the sizes and the transition temperatures being in quantitatively similar. The next molecule that will be studied is the symmetric BA ($m = 3$, $n = 3$).

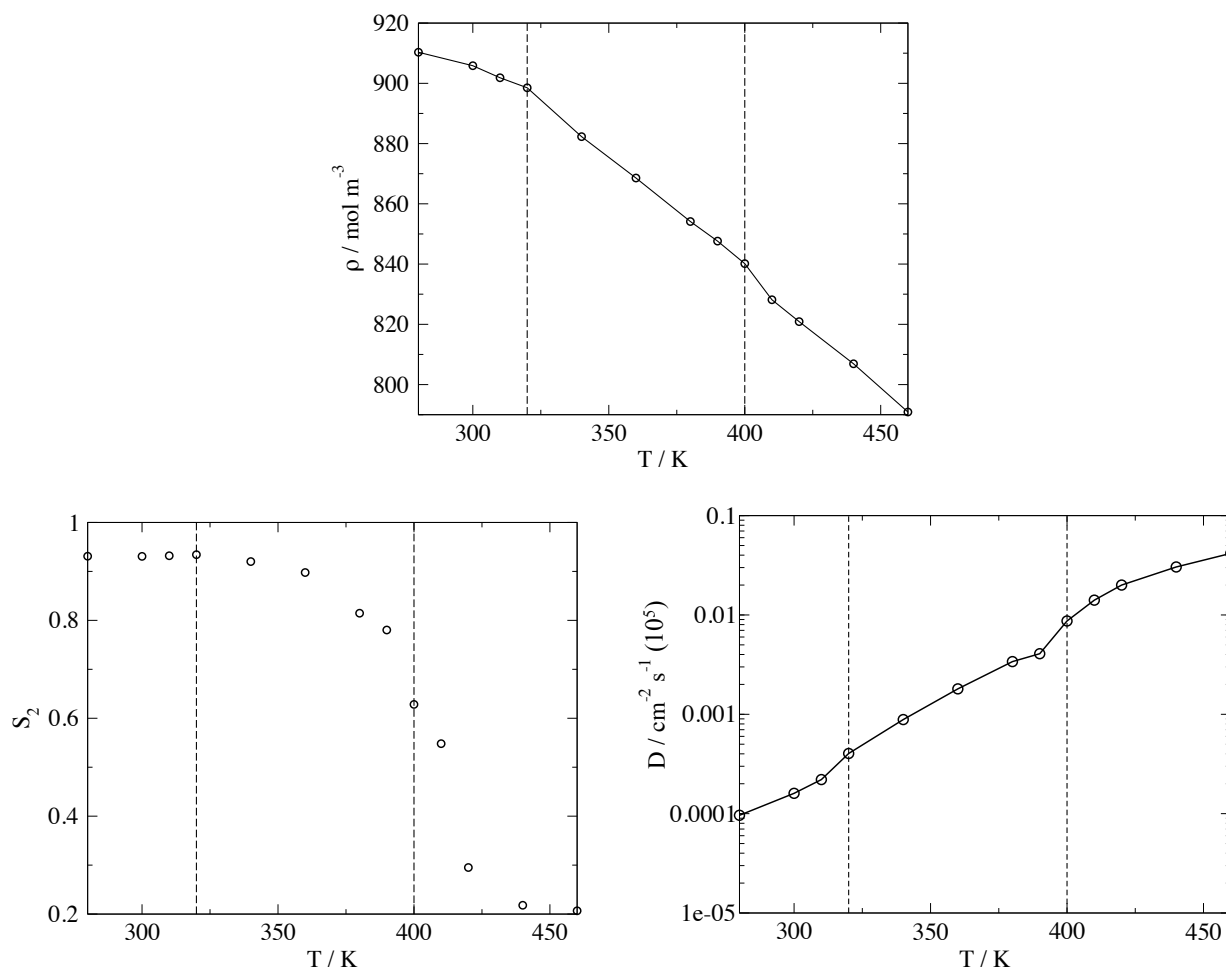


FIGURE 6.28: Plots of parameters vs temperature for the swallow-tail BA (m=5, n=1), used to calculate the transition temperature, T_{trans} . **Top** Density vs T, **Bottom Left** Nematic order parameter, S_2 , and the hexagonal orientational planar order parameter, Ψ_6 , of the principal axis of the rigid backbone vs T, **Bottom Right** Diffusion coefficient of all CG segments vs T. The dashed lines indicate the transition temperatures.

Study III: Symmetric Swallow-tail ($m_{CG} = 3$, $n_{CG} = 3$)

The next molecule studied is the symmetric BA, with 3 segments in each tail of the swallow-tail side chain, corresponding to ten united atom carbons each. Figure 6.29 shows the difference between the symmetric swallow-tail and the T-shaped BA. For this system, more than 20 simulations were run with different number of molecules and different system sizes. In all but one system, it was not possible to find any pentagonal + octagonal columnar phases, with real periodicity. The only system where octagonal and pentagonal columnar phases were observed is presented in Figure 6.30. The simulation was set up, with a box containing 400 symmetric swallow-tail BAs compressed at a high pressure of 100 bar until a liquid phase was observed. The box was allowed to relax at 1 bar for 100,000 times steps, after which the box was replicated 3 times, once in the x direction, once in y and once in the x and y direction. The system containing 1,600 molecules was then simulated in the N σ T ensemble at $T = 340$ K and $\sigma = 1$ bar. As presented in Figure 6.30, it is possible to observe a liquid crystalline phase composed of a combination of octagonal and pentagonal columns with a rectangular unit cell. Just like the previous case of the asymmetric swallow-tail BA, to the best of our knowledge, this c2mm phase of columnar pentagons and octagons has never been observed in simulations. As can be seen in the snapshots, the alkyl moiety clearly demonstrates the existence of octagonal and pentagonal phases. Each octagonal super-structure is made up of two pentagons and a square (superimposed yellow sketches on the simulation snapshots) with each edge being composed of the rigid backbone. This means that in the centre of the octagon, there is a single column of glycerol type group, where the backbones of the square column and the two pentagonal columns meet. Experimentally, Poppe et al. were not able to determine the exact reason why a region of high electron density was observed in the centre of the octagon, and simulations carried out in this work clearly indicate the existence of a single column of glycerol in the centre of the octagon. The existence of the square columnar along with pentagonal columns indicates that the volume occupied by the side-chains in the columns is not constant and the swallow-tail morphology significantly frustrates columnar organisation of these systems.

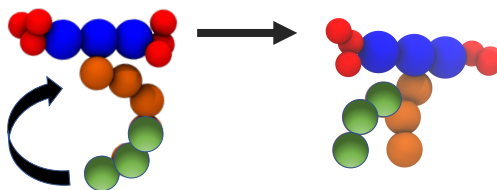


FIGURE 6.29: The structure of the symmetric BA as it compares to the T-shaped BA.

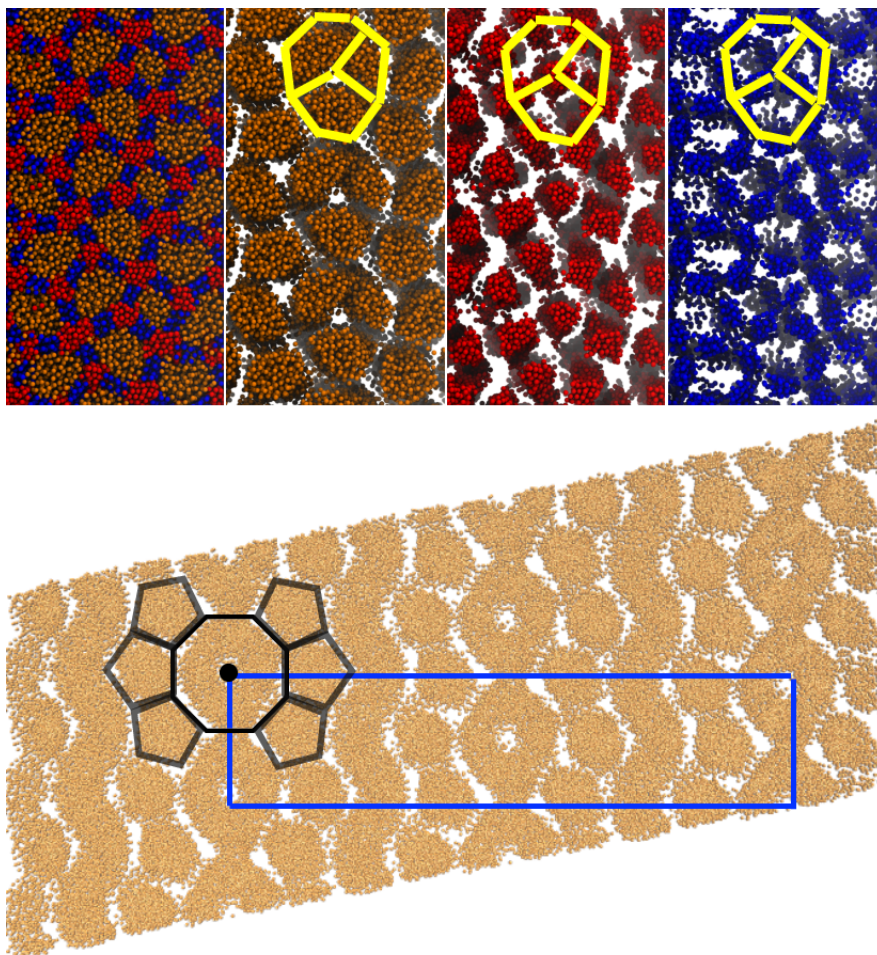


FIGURE 6.30: **Top** The snapshots of different functional groups in the final frame of simulations of 1,600 swallow-tail BAs with $m = 3$, $n = 3$. Colors are as those as in Figure 6.17. The yellow sketch superimposed on the snapshots shows the arrangement of the backbones in the octagonal columnar phase. **Bottom** snapshot of the alkyl group with added periodicity to clearly show the $c2mm$ rectangular unit cell, as well as the structure of the octagonal and pentagonal columns.

TABLE 6.11: Comparison of the lattice units defining the rectangular unit cell for the symmetric ST BA.

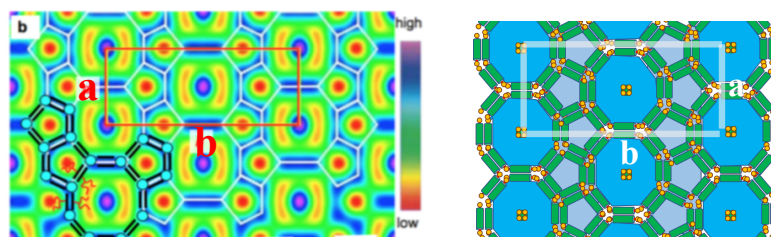
Lattice unit	length _{exp} / nm	length _{sim} / nm
a	6.2	6.2
b	15.5	30.5

Comparison between simulations and experimental results is presented in Figure 6.31. Sketches are also used to highlight the key difference between the experimentally observed phase and that seen in simulations. In both simulations and experiments there is a row of octagons, surrounded by a row of pentagons on each side. Additionally in simulations there is a zigzag shaped region formed of the alkyl group, with no apparent columnar structure inside the region (i.e. isotropic). This region could be an artefact of the simulation, as previously mentioned, the phase observed here was obtained only once in 20 different simulations with different sizes and box lengths. The phase behaviour of this symmetric swallow-tail is highly susceptible to system size effects. Therefore, unless the system equilibrates to the correct box dimensions, commensurate with the lattice lengths, it would be impossible to observe the correct phase behaviour of this system. The difference between the two phases can be most clearly seen in the sketches.

To calculate the lattice lengths and compare it to experiments, the mole fraction of the alkyl group on the plane perpendicular to the director was calculated at different points along the director. The mole fractions were then averaged to give a heat map as previously presented for the other mentioned molecules. The lattice lengths were then calculated using the heat map (Figure 6.31). Due to the extra disordered alkyl regions present in the simulations, the long side of the unit-cell (denoted as b) was expected to be overestimated. However, the short side (denote as a) is expected to be the same as the experiments. The comparison between the repeat units is given in Table 6.11. As could be seen, both simulations and experiments give the same lattice length a, at around 6.2 nm. However, the length of the last unit b was predicted to be almost twice that of the experimental results.

Finally, the thermotropic properties of the BAs were calculated using the nematic order, the density, and the diffusion coefficient, with the summary of the transition temperatures given in table 6.12, with the value of the parameters vs temperature

Experiment



Simulation

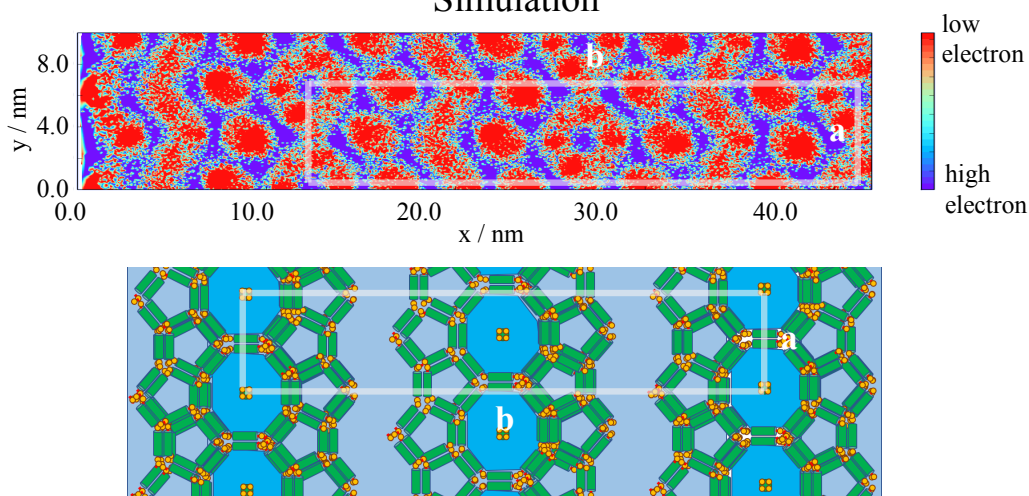


FIGURE 6.31: Comparison between the self-assembly of symmetric swallow-tail BA ($m = 3$, $n = 3$) as observed from experiments and simulations. Both experiments and simulation predict a rectangular unit cell columnar phase (c2mm).

TABLE 6.12: Comparison of the phase transitions of the symmetric swallow-tail BA ($m = 3$, $n = 3$) as observed experimentally [301] and predicted with simulations in this work.

Phase Transition	$T_{Trans, Exp} / K$	$T_{Trans, Sim} / K$
Crystalline Solid to c2mm	348	315
c2mm to isotropic	420	420

plotted in Figure 6.32. In this work, a crystalline solid phase to a liquid crystalline phase is characterised by the change in the diffusion coefficient and the drop in the density, which occurs around 315 K. The simulations underestimate this transition temperature by almost 30 K. However, the LC-isotropic transition temperature is predicted correctly using the nematic S_2 order parameter.

Comment on the Simulations of Bolaamphiphiles with SAFT- γ Mie Forcefield

In this work, it has been demonstrated that the methodology proposed here is predictive and robust in predicting the self-assembly of BAs. For the first time, a structurally and thermodynamically robust coarse-grained model is proposed, which can predict the structures with accurate dimensions and transition temperatures. All structures observed here have dimensions consistent with those predicted in experiments without fitting any of the parameters to experimental data of BAs. Moreover, not only have we predicted structures never observed in simulations before, additional insights have been gained as to the arrangement of the liquid crystals. Particularly, it was not known why there is a region of high electron density in the centre of the octagonal columnar phase, and how the molecules were arranging themselves. Here, it was shown that this central column is composed of the glycerol group, which can give help experimentalists in understanding phase behaviour of these BAs. The arrangement of the regions of high electron density allows for the design of ordered electricity conducting nano-structures, and can therefore have industrial applications.

Given that the model presented here is validated against experimental data, now it is possible to do a systematic study of the phases of swallow-tails, and other T-shaped BAs by changing the side-chain lengths and the degree of branching.

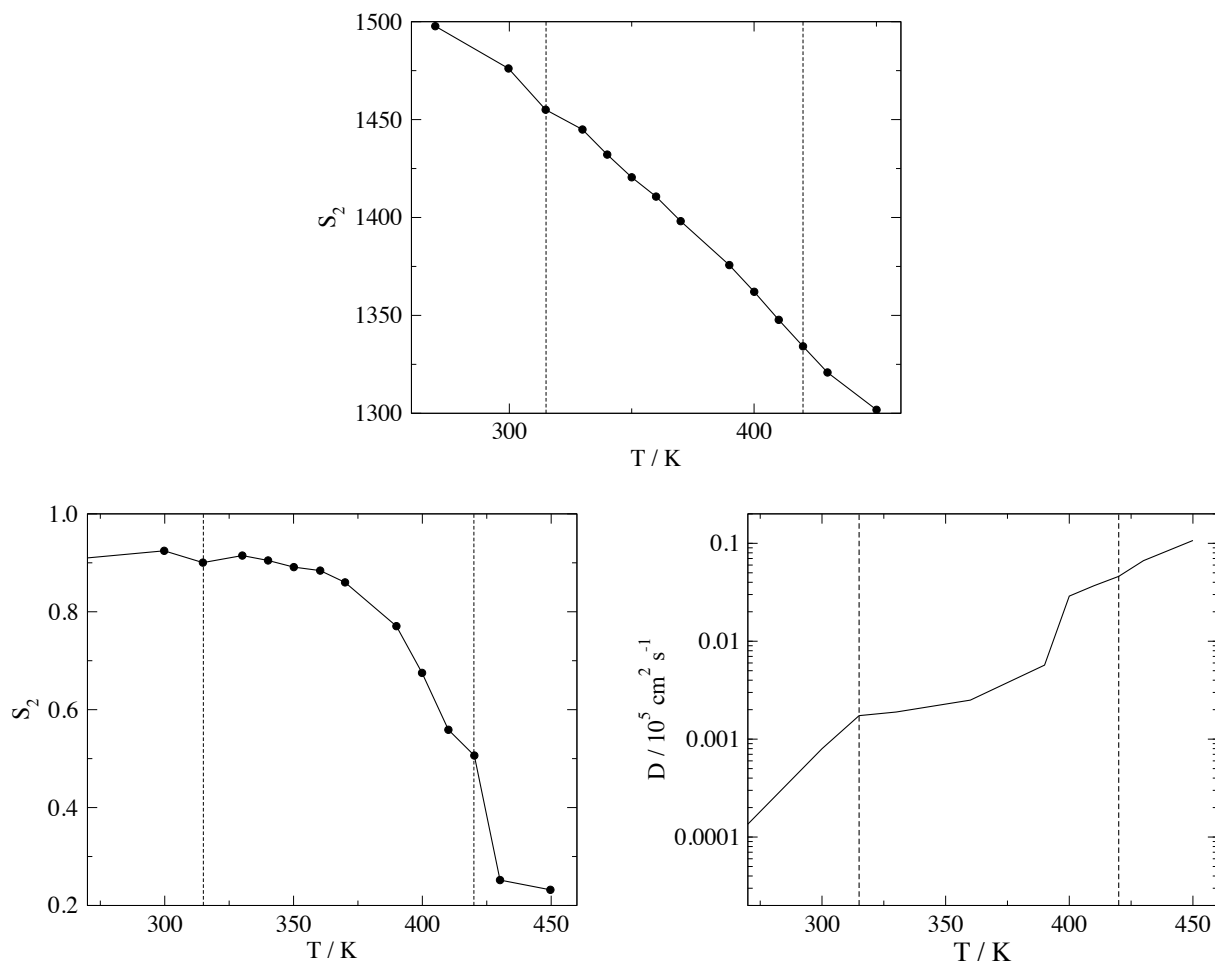


FIGURE 6.32: Plots of parameters vs temperature for the swallow-tail BA ($m=3$, $n=3$), used to calculate the transition temperature, T_{trans} . **Top** Density vs T , **Bottom Left** Nematic order parameter, S_2 , and the hexagonal orientational planar order parameter, Ψ_6 , of the principal axis of the rigid backbone vs T , **Bottom Right** Diffusion coefficient of all CG segments vs T . The dashed lines indicate the transition temperatures.

6.3.3 Phase Map Exploration

In this section, the aim was to quickly discover LC phases of swallow-tail and T-shaped BAs. Simulations were run in the $N\sigma T$ ensemble at a fixed temperature well within the crystalline or the liquid crystalline region and no attempts was made to investigate the transition temperatures. This could certainly be further investigated in the future.

Square Columnar Phases: $m = 3, n = 0, 1, 2$ & $m = 4, n = 0, 1$

The first exploration was carried out for BAs with at least one side chain containing 3 beads at $T = 340$. By increasing the length of the swallow tail, it would be possible to understand why the octagonal+pentagonal phase forms at $m = 3, n = 3$. Simulations were run with 1,600 molecules, just like the case of $m = 3, n = 3$, to ensure consistency. All three cases studied here give rise to a square columnar phase. The snapshots, the angular distribution of the backbones and the RDF of the alkyl moiety for the different side chain morphologies is given in Figure 6.33. It could be seen from the RDF that by increasing the length of the second tail of the BA, the intercolumnar distances are reduced. This is due to some of the square columns being occupied by the shorter side chain which occupy less space. This leads to smaller columns which could be entropically unfavourable for the larger chain. Upon further increasing the length of the second tail from 2 to 3, the system undergoes a drastic change. However as discussed previously, it is not possible to definitely comment on this as there is no access to the free energy.

The same trends observed for BAs of $m = 3$ was also observed for $m = 4, n = 0, 1$. Only square columnar phases were observed. For the T-shaped BA with $m = 3, 4$ the intercolumnar distance was found to be 3.4 nm.

Pentagonal Columnar Phases: $m = 5, n = 0$

To investigate the reason why the hexagonal superlattice discovered in this work was observed, a system containing 1,600 T-shaped BA with $m = 5, n = 0$ was simulated at $T = 340$ K. A p2gg phase composed only of pentagonal columns was predicted as can be seen in Figure 6.34. Although this phase has been investigated

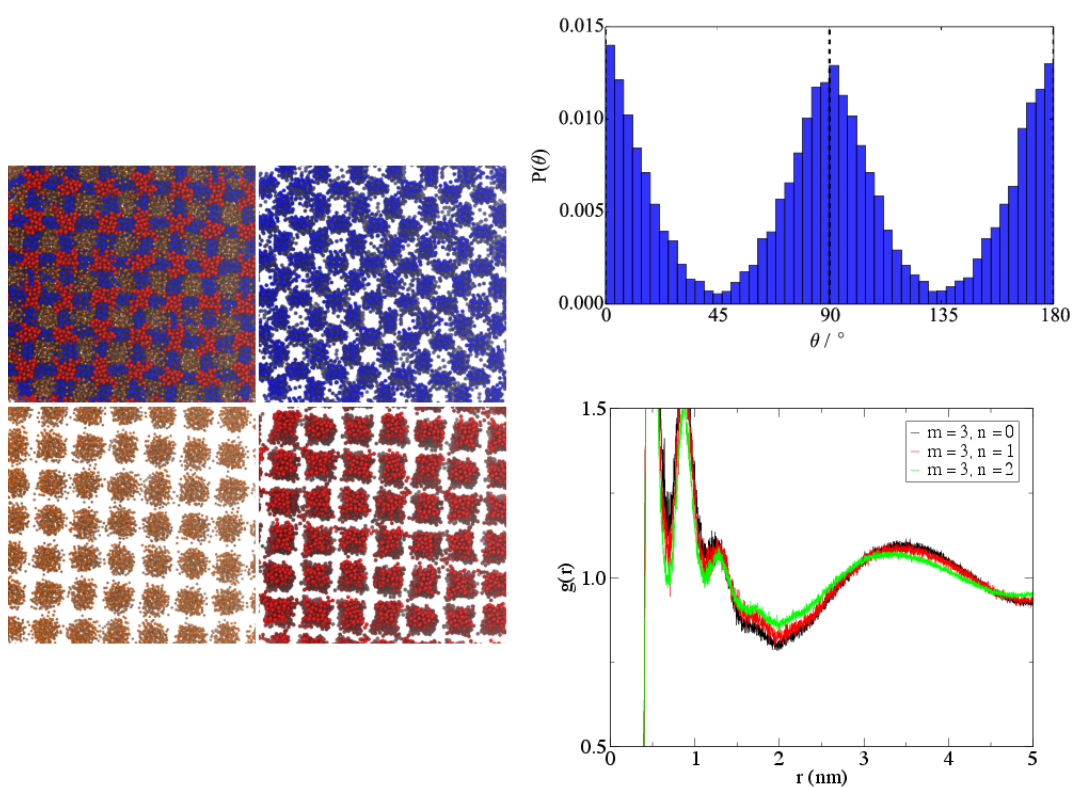


FIGURE 6.33: Square columnar phases of BAs with $m = 3$, $n = 0, 1, 2$. *Left* Simulation snapshots at $T = 340$ K. *Right Top* Angular distributions of the backbones on the plane perpendicular to the director. *Right Bottom* RDFs of the alkyl moiety for the three different molecules.

in simulations, the interesting difference between this work and previous cases is that previously it was not possible to obtain ordered pentagonal columnar with the unit cell clearly visible from the simulations. Bates and Walker [298] simulated this phase, however, they had to modify the potential parameters significantly, making the structure of the backbone of the BA asymmetric (excluding the side-chain), which rendered the model as not fully representative of the experimental molecules. Here, the representability of the molecules is intact and the simulations are fully. The angular distribution of the backbones has peaks of factors of 45 and not 108 degrees of the regular pentagon. This clearly highlights the fact that these pentagonal columns are not regular. The intercolumnar distances was calculated using the planar RDF. The intercolumnar distance at 3.8 nm is slightly higher than 3.4 nm calculated for the square columnar phase, and is in the same order of magnitude as the σ of one alkyl bead. This value of 3.8 nm is slightly larger than the first peak (3.6 nm) of the planar RDF for the case of $m = 5$, $n = 1$ (Figure 6.27). The addition of an extra tail reduces the column sizes, making the packing of long chains in the systems less favourable. This causes a shift in the morphology of these mesophases.

The peaks of the angular distribution of the backbones in the plane perpendicular to the director, as presented in Figure 6.34, are much broader than the cases of the hexagonal and the square columnar phases shown previously. However, it can be seen that there are peaks at 0° , 90° , 135° and 180° . This is in agreement with previous studies on pentagonal columnar phases [298], as the backbones meeting at the 4-fold vertices form angles of 90° . This is visually presented in Figure 6.35

Symmetric Swallow-Tails: $m-n = 8-8$, $12-12$

Recently it has been discovered in experiments [286] and simulation [302] that swallow-tail BAs with long lateral side chains form 3D periodic structures such as skeletal cubic and gyroid phases. Whereas the focus of this work has been on shorter side chains of maximum 20 united atom carbons, it has been shown that for a symmetric BA with two tails of 20 united atom carbons each, gyroid phases exist. Here attempts were made to observe gyroid phases with $m = 8$, $n = 8$. This corresponds to each tail

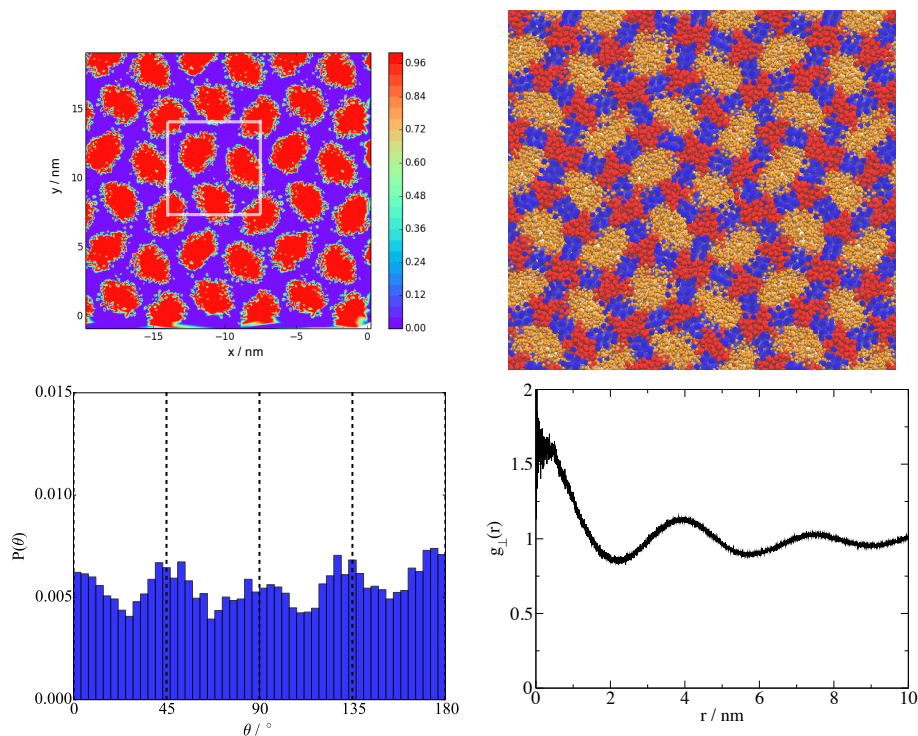


FIGURE 6.34: The pentagonal columnar phase with square symmetry predicted for $m = 5$, $n = 0$. **Top Left** The heat map of the mole fraction of the alkyl group. The white lines indicate the unit cell **Top Right** Simulation snapshot of the final frame. **Bottom Left** Angular distribution of the backbones in the plane perpendicular to the director. **Bottom Right** Planar RDFs of the alkyl moiety, with the first peak indicating the intercolumnar distances.

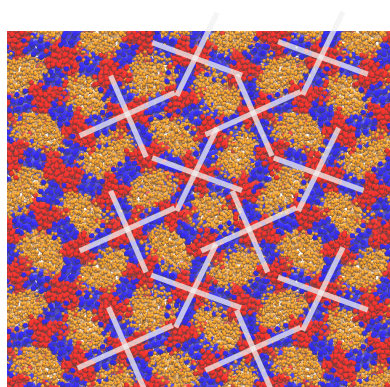


FIGURE 6.35: Backbones meeting at the 4-fold vertices form angles of 90° .

having a side chain length of approximately 30 carbons. Only a disordered bicontinuous phase was observed. This could certainly be the focus of future studied.

A diamond phase has been observed for the the case of $m, n = 12, 12$ (40, 40 UA carbons) where a 3D structure with hexagonal symmetry is observed. For the case of a single lateral side-chain of length 12, Crane et al. [293] observed lamellar phases where the backbone and the end groups of the BA formed one layer and the lateral side chain formed the other layer in the lamellar phase. However, when a swallow-tail is used with two tails of size 12, skeletal structures are formed with 3D periodicity. The second tail disrupts the lamellar phase and diamond like structures are formed. This phase has only been seen in simulations of swallowtails BAs and our results add to the evidence of the existence of such phases. The snapshots of the box is presented in Figure 6.36, where it could be seen that the glycerol groups are organised into regular layers and the rigid backbone has a 3D hexagonal geometry. Upon separating one of the layers formed of the glycerol groups, it is possible to observe a hexagonal geometry more clearly. The structure factor calculated for the glycerol groups again indicate three peaks corresponding to a hexagonal symmetry, even though the nematic order parameter is 15%.

Further simulations of symmetric ST BAs with each chain containing more than 20 beads were simulated, all indicating the existence of a diamond phase.

6.4 Conclusions

In this chapter, a robust method of coarse-graining complex polyphilic bolaamphiphiles was presented in order to improve upon previous phenomenological simulation studies of these molecules. The key highlight of this chapter are the forcefield parameters derived using the SAFT- γ Mie methodology explained in this thesis. It was shown that the forcefield parameters are robust and it was possible to predict all of the recently discovered structures for short chain swallow chains. These phases have never been studied or predicted in simulation studies previously and are therefore novel. From the experimental point of view, these simulations can help experimentalists in better understanding the structure of the mesophases, as has been demonstrated for the case of the octagonal and pentagonal columns. Experimentally, it

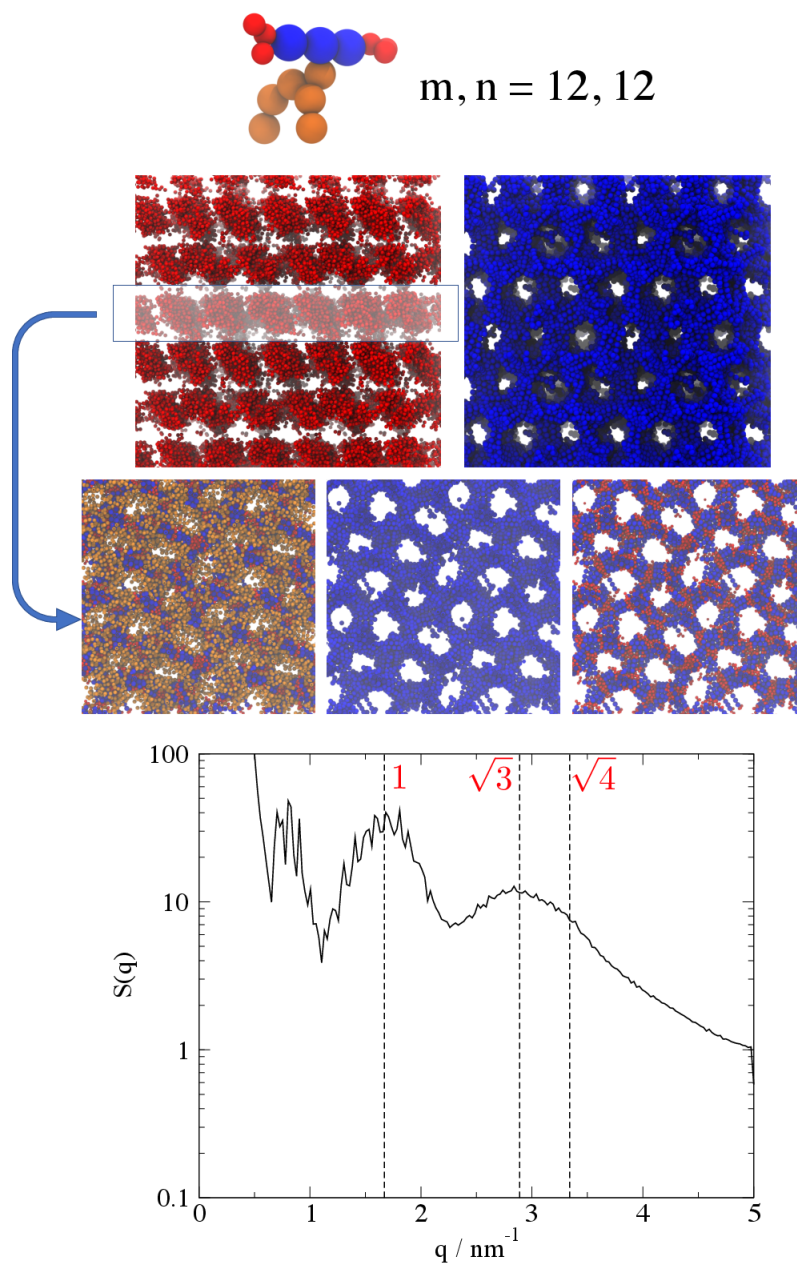


FIGURE 6.36: Snapshots of the single diamond phase observed in this work for $m = 12$, $n = 12$ as well as the structure factor of the glycerol groups indicating a hexagonal geometry. The colors correspond to the moieties described at the top of the Figure. The top row shows the ordered 3D structure and the bottom row of snapshots shows the hexagonal geometry within one of the layers.

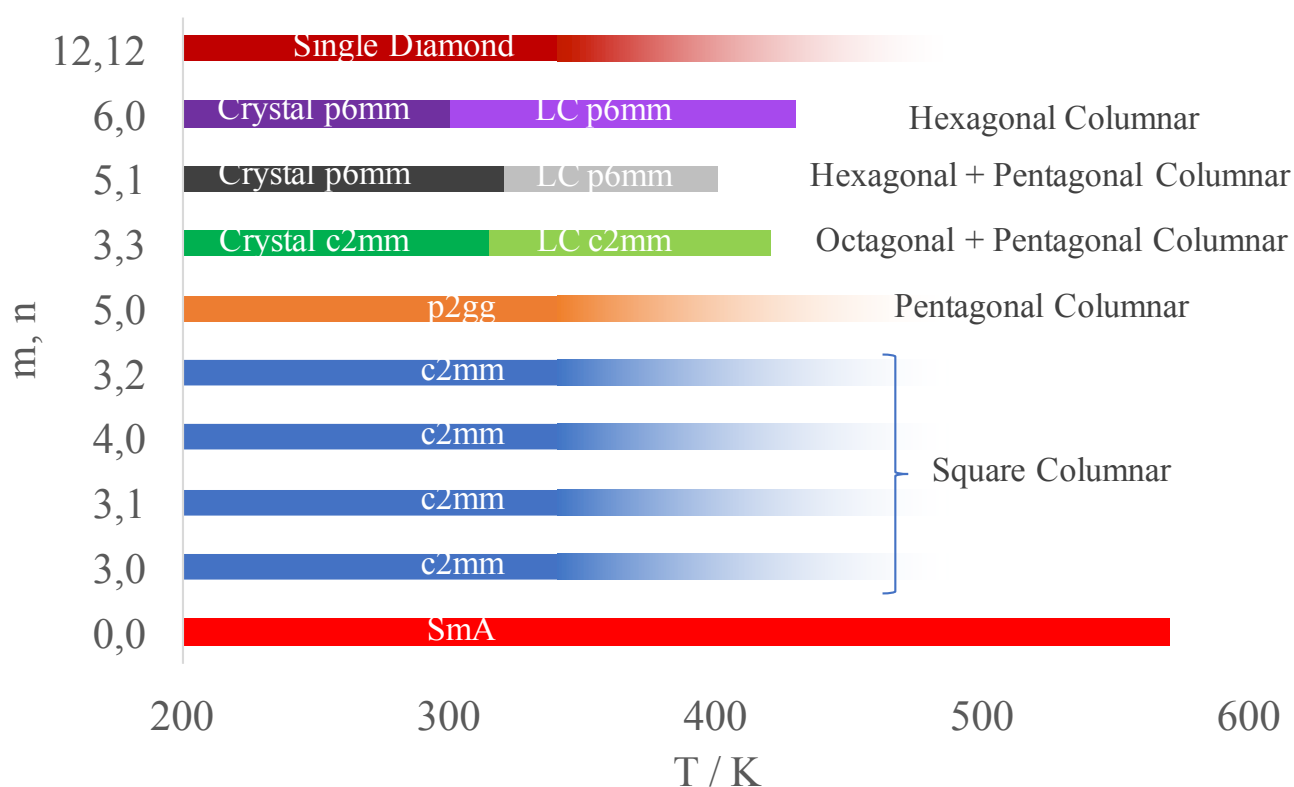


FIGURE 6.37: Summary of all the results in this work. Bars with Colour gradients are cases for which simulations were run only at $T = 340 K$

has not been possible to determine exactly the arrangement of the BA molecules in the c2mm phase (octagonal and pentagonal columns) and here an attempt has been made to explain this.

More importantly from a simulation point of view, the forcefield here has the ability to predict the correct dimensions as well as the transition temperatures for the system studied, something which is not possible with other simulations. Moreover, the regular p2gg phase simulated in this work has been very challenging to simulate with previous models, and this forcefield improves even the phenomenological study of these BAs.

A phase map of all the phases observed in this work is presented in Figure 6.37. This certainly lays the foundations for a systematic study of all bolaamphiphiles with swallow-tail lateral side-chains in the future, especially systems containing 7 or 8 segments in the side chain. Moreover, it has been shown that for longer lateral side chains ($m, n = 12, 12$) three dimensional periodic structures start to form. This can be further extended to investigate the gyroid phases observed experimentally.

Chapter 7

Conclusions & Final Remarks

7.1 Conclusions

In this thesis, the SAFT- γ Mie CG methodology was applied to obtain accurate force-fields for two different types of complex fluids: polymers and liquid crystals. The methodology is top-down, with molecular interaction parameters fitted to thermophysical properties using a molecular based equation of state, SAFT- γ Mie. In this EoS, molecules are modelled as chains of tangentially bonded spheres interacting with the Mie potential. Fitting the Mie interaction parameters to thermodynamic properties allows the prediction of complex phase behaviour of the mentioned fluids with quantitative accuracy. All interaction parameters obtained in this work are state independent, and could be used for a wide range of temperatures, pressures, molecular weight of the molecules and the chemical structures.

Previous coarse-grained simulations using the EoS have focused on small molecules, where it is known that the equation of state works remarkably well. However, the viability of this EoS in modelling long chain molecules, particularly polymers, has not been extensively explored. To assess the viability, in Chapter 4, six common polymers presented in Table 4.1 were parametrised using small molecules that contained the monomer units. It was shown that the EoS could model melt and mixture phase behaviour well. It has been shown that again with the correct cross interaction parameters the EoS could predict the correct phase behaviour of polymers.

Given the success of the EoS in modelling polymers, the viability of using the same Mie interaction parameters used in the EoS to model polymers in molecular

simulations was assessed. This is the advantage of this methodology as other molecular based equations of state do not have interaction parameters that could be used directly in simulations. This approach has never been used in modelling polymers, and therefore the focus of this work was to reproduce thermodynamic behaviour of polymer-solvent mixtures as predicted by the EoS. In the theory of SAFT, no assumptions are made about the structure of the molecules, and therefore intramolecular potentials (particularly angle potentials) were fitted to underlying atomistic representation of the polymers to ensure a structurally robust representation of the polymers. The results presented in Chapter 5 clearly indicate the robustness of the parameters obtained to model polymers. LCST, UCST, pressure induced phase separation and other complex phase behaviour of all 6 different polymers were observed with quantitative accuracy. The success of this methodology in modelling polymer solvent mixtures comes from the accurate state-independent parametrisation of the cross-species interactions, something which other coarse-graining models of polymers lack.

Therefore, one of the main highlights of the two chapters mentioned has been developing a framework where experiments, theory and simulations can be used altogether to study polymeric systems, with the theory and simulations representing exactly the same systems.

Polymers in this work were modelled as chains of spherical segments of the same type, i.e. *homonuclear*. The next chapter focused on complex self-assembly of *heteronuclear* molecules with complex molecular architecture and multiple functional groups within the same molecule. Polyphilic liquid crystals are molecules that can have very complex microphases at the mesoscale. The tiling patterns produced by these molecules cannot be predicted accurately by theory given the complexity of their molecular architecture and the variety of the functional groups in each molecule. Therefore, coarse-grained molecular simulations are the only way to investigate the phase behaviour of such systems. Given the complexity of these molecules, all previous simulation studied have only investigated the phase behaviour of these molecules phenomenologically. Here for the first time a CG force

field was obtained that could predict all complex self-assembly structures of swallow-tail bolaamphiphiles. Moreover, the lattice lengths predicted in this work match remarkably well with the experimental observations. More impressive is the transition temperatures which are in quantitative agreement with experiments without fitting any of the parameters to the liquid crystalline systems. Structure of other phases were then predicted.

Thus it has been shown that the SAFT- γ Mie methodology presented in this is a robust way of obtaining coarse-grained models of molecules for applications at the mesoscale.

7.1.1 Comparison Between the Original Objectives and Achievements

It is imperative in any work of research to reflect upon the achievements and failures and compare it to the original objectives set at the inception of the work. In this subsection, for each of the objectives, the successes and failures are assessed. There were three main objectives as highlighted previously in Chapter 1.

1. The development of reliable and robust coarse-grained models.

- **Polymers:** Prediction and estimation of pure component properties (PVT data), phase behaviour of polymers in solution and blends, and microphase separation, with one set of unadjusted monomer interaction parameters, transferable to any system size (from oligomers to high Mw polymers) for all ranges of temperature and pressure,

- **Achieved:**

For systems composed of pure component polymers, both theory and simulations give the correct PVT data, with pure component parameters being predicted from small molecules, and parameters were transferable for the a wide range of conditions. It is possible to correctly predict densities and thermodynamic properties such as isothermal compressibilities for pure components.

Perhaps the key highlight of this work has been the modelling of polymer solvent mixtures. The advantage of SAFT- γ Mie methodology proposed here is the robust **state independent** cross interaction parameters obtained from the theory, which can be used directly in simulations without adjustments to observe the same phase behaviour in simulations. In this way, it is possible to simulate LCST, UCST, pressure induced phase separation and other phase behaviour of polymer mixtures with quantitative accuracy. Obtaining reliable cross interaction parameters for these systems has been a major simulation challenge. Moreover, it has been shown that the parameters are independent of temperature, pressure, polymer Mw and composition.

– **Unachieved:**

For pure components polymers, it was not possible for some cases (PE and PBD) to predict the radius of gyration and end-to-end distances correctly by fitting the angle potentials to underlying atomistic models, and the harmonic constant for the angle potential had to be modified. Moreover, glass transition temperatures were severely underpredicted for the polystyrene models. Improving this requires using dynamic properties in the objective function for parameter estimation.

One of the potential drawbacks of using the SAFT models for polymers is that distances between monomer units might be different to actual bond distances, affecting structural properties. Developing fused sphere models can ameliorate the problem. However, the connection to the theory is lost, as fused spheres are represented differently in SAFT- γ EoS and in molecular simulations. An improvement to the theory is required.

For polymer blends there was a discrepancy between the two polystyrene

models for both pure component properties (densities) and mixture properties. The shape of the phase envelopes for mixtures the PS-CG2 model was more commensurate to that of experimental data, however, critical points (UCST and LCST) were captured more accurately with the PS-CG1 model. Moreover, for the mixtures of polymers, the shape of the phase enveloped for the PS-CG1 model was different in simulations and in theory. This could be due to the effect of branching in simulations which is not captured in the theory.

It was not possible to observe microphase separation in block copolymer systems, as the system sizes were too large for this level of coarse-graining.

- **Rod-like Liquid Crystals:** Predicting the previously unobserved complex morphologies of bolaamphiphilic liquid crystals by employing an accurate molecular based methodology of coarse-graining,

- **Achieved:**

A model for swallow-tail bolaamphiphiles was developed to simulate recently discovered liquid crystalline mesophases.

The model is predictive, and can predict the correct mesophase structures, lattice lengths and transition temperatures.

Major improvement on previous simulation models.

- **Unachieved:**

The model could not be used to study liquid crystalline phase behaviour of the rigid backbone. However, by adding polar end groups to the rigid backbone, it was possible to observe mesophase separation for bolaamphiphiles, with smectic phases forming at temperature ranges measured in experiments.

A problem with the model presented in this work is the very long

equilibration times. Each system requires many μ s of simulation time (or 100s of millions of time-steps). This is due to the very small k_{ij} values predicted. This makes phase map exploration slow. This can be improved by making the cross-interactions among different moieties less favourable. However, this significantly affects the transition temperatures.

- **Disk-like Liquid Crystals:** Providing the initial foundations for a robust coarse-graining methodology to model polycyclic aromatics,
 - **Achieved:** Accurate models for polycyclic aromatics molecules.

Preliminary work has been carried out as explained in the next section, with lamellar and hexagonal columnar phases predicted for polyphilic discotic liquid crystals.

- **Unachieved:**

This work is still in its early stages, and it was not possible to finalise the results within this thesis. Importantly, cross interaction parameters need to be optimised.

2. Direct link between experiments, theoretical models and *in silico* simulations:

- Both theory (EoS) and simulations will provide a full phase diagram from different moieties studied in this thesis, with simulations testing the validity of interaction parameters used in the EoS for complex systems, with predictions from both methods compared to experimental data

- **Achieved:**

It has been successfully demonstrated that in terms of thermodynamic properties, with a few exceptions (such as branched polymer blends), the theory and simulation results agree remarkably well. This coarse-graining methodology is thermodynamically robust for a wide range of systems. Given that the theory uses experimental results as input data for parameter estimation, experiments, theory and simulation all provide very similar results for a wide range of thermodynamic properties, with some exceptions.

– **Unachieved:**

Some thermodynamic properties cannot be accurately modelled with the proposed method. For associating molecules, such as those that form hydrogen bonding (e.g. glycerol), it is not possible to calculate surface tension accurately, which for mesoscopic systems is an important property.

Moreover, accurate modelling of thermodynamic properties affects other properties such as structural properties and dynamic properties. For example, as mentioned before, distances between monomer units can be drastically different to actual distances.

Dynamic properties have not been investigated extensively, but as seen for the case of transition temperatures of pure polymer melts, it can be seen that predictions of those properties is still a challenge.

3. Capturing phase equilibrium properties as well as structural and dynamic properties of complex systems

- Both theory (EoS) and simulations will provide a full phase diagram from different moieties studied in this thesis, with simulations testing the validity of interaction parameters used in the EoS for complex systems, with predictions from both methods compared to experimental data

– **Achieved:**

In terms of phase equilibrium properties, the proposed coarse-graining methodology is a very powerful tool to study phase equilibrium at the mesoscale. In this thesis a lot of results have been presented to support the usefulness of the method.

By adding the correct intramolecular potentials, it is possible to observe the correct structural properties too, as can be seen by the predictions of the self-assembly of bolaamphiphiles.

– **Unachieved:**

Unfortunately, dynamic properties have not been extensively studied in this work, and a major focus has to be on assessing the predictions of dynamic properties.

7.2 Model Improvements & Future Work

7.2.1 Polymers

For polymers, although it has been highlighted that correct thermodynamic behaviour could be predicted in simulations, transport properties were not investigated. This should be the main focus of future research in this work. For melts, dynamic and structural properties, e.g. monomer diffusion and entanglement length, significantly affect the macroscopic properties of these materials such as elasticity. It is not known whether the models presented here can correctly predict dynamic properties such as the monomer diffusion and the transition from Rouse to entanglement regimes. In terms of intramolecular interactions, dihedrals and torsions should also be added to the models presented here. For polyethylene, torsions are known not be significant for the level of mapping presented here, however for polystyrene, this should certainly be investigated as the level of coarse-graining is much smaller than the Kuhn lengths.

For mixtures of polymers, other properties could also be investigated, such as the diffusion of gases or liquids in the polymer matrix, the intrinsic viscosity of polymer-solvent mixtures and the surface tension of liquid with added polymer. Preliminary results show that for linear alkanes (C_{16} , C_{20} and C_{142}) it is possible to predict the correct surface tensions of polymer melts compared with the correlations of Poser and Sanchez [322]. However, surface tensions of short-length polystyrene melts are significantly lower than the correlations of Poser and Sanchez.

Moreover, microphase separation of block copolymers should be investigated. As mentioned before, attempts have been made to simulate block copolymers using the parameters for polystyrene and polyisoprene. However, experimentally phase separation in these block copolymers occurs at $M_W > 30$ kDa, or around 400 segments per molecules. Attempts were made to simulate block copolymer melts.

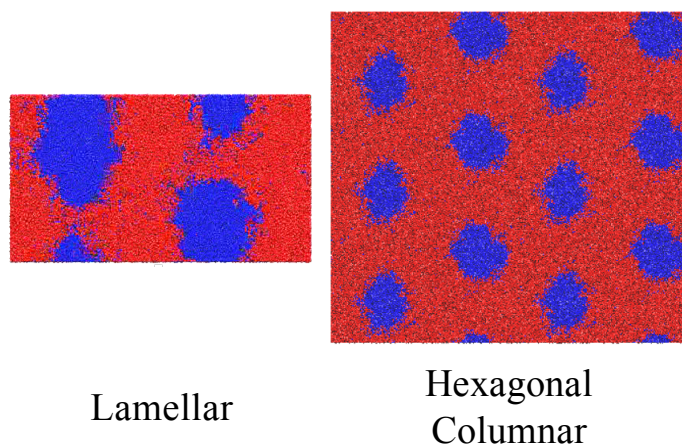


FIGURE 7.1: Hexagonal and lamellar phases observe in this work for a PS-PBD block copolymer of 500 chain, with different weight fractions of PS. Blue is PS and red is PBD. The like interactions were unchanged by the k_{ij} was significantly increased $k_{ij} = 0.6$. With the k_{ij} fitted to thermophysical properties, it was not possible to observe ordered mesophases.

However, with the k_{ij} fitted to thermophysical properties, equilibration times were extremely long and it was not possible to observe microphase separation given the computational capacities. By having very large k_{ij} parameters between the unlike species, it was possible to observe block copolymer self-assembly, observing hexagonal columnar and lamellar phases for different volume fractions. These are shown in Figure 7.1. However, this means that it was not possible to model these systems with quantitative accuracy using molecular dynamics simulations.

7.2.2 Polyphilic Liquid Crystals

Before starting the study into swallow-tail BAs, it was not expected to be able to predict the phase behaviour of these molecules with such quantitative agreement. Having said that, the model presented in this thesis for these group of molecules could certainly be improved. Firstly, the key focus should be on improving the representation of the rigid backbone. Attempts were made to investigate the nematic-isotropic and the nematic-smectic phase behaviour of the 3 segment p-terphenyl modelled in this work. However, it was not possible to observe nematic ordering and smectic phases as the spheres did not like side to side packing. Consequently at high pressures (and packing fractions) a solid fcc lattice was observed, which highlights the

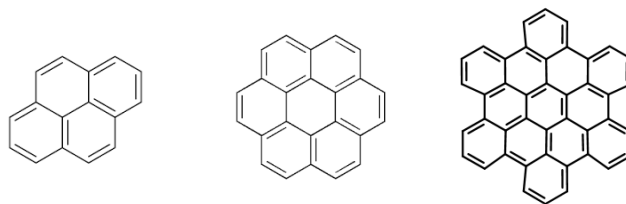


FIGURE 7.2: Polycyclic aromatics that can be used as discotic liquid crystals. From left to right: pyrene, coronene and hexabenzocoronene.

fact that the 3-segment model of p-terphenyl could be improved. Secondly, it was highlighted that the surface tension of glycerol is considerably overestimated with the model proposed. This could also be improved in the future by fitting intermolecular parameters to experimental data.

Moreover, an interesting area of future work with BAs is the study of the gyroid phases observed experimentally. This is because typically gyroid phases are observed for polymeric systems with large molecular weight. Therefore, the lattice lengths of these phases are quite large. These BAs provide a pathway to designing 3D periodic systems with charge carrying abilities with wide applications in the electronics industry, given the π -conjugation of the rigid backbones. Creating bicontinuous 3D structures with small lattice lengths can have extensive applications and *in silico* prediction of these structures can help in structure discovery.

Developing Realistic Potentials for Discotic Liquid Crystals

Given the success of the work on calamitic liquid crystals, a direction of future research could be the study of self-assembly of polyphilic discotic liquid crystals. The first step in modelling polyphilic discotics with realist potentials is the development of a robust CG modelling of the disc-like moiety. Recently, Müller and Mejía have come up with a novel corresponding states method to obtain Mie potentials for ring-like molecules. [323] This has been implemented to investigate three disc-like molecules shown in Figure 7.2: pyrene, coronene and hexabenzocoronene. The model for pyrene has been validated and published in recently [324].

Figure 7.3 clearly shows that it is possible to have thermodynamically consistent models of discotic molecules. Structurally, the correct centre of mass-centre of mass

TABLE 7.1: Polymers studied in this work, with parameters estimated in the previous chapter

Polymer	$M_{W, CG seg}$	m	λ_r	ε [K]	σ Å
Pyrene	50.56	4	15.79	459.04	4.134
Coronene	42.91	7	14.83	370.86	3.69
Hexabenzocoronene	46.21	13	14.83	370.86	3.69

RDF can be predicted for this CG model of pyrene, when compared with OPLS-AA simulations at 450 K. This is presented in Figure 7.4. In ref [324], it has also been shown that it is possible to predict solubilities of pyrene in n-hexane, n-heptane and toluene, again indicating a robust set of parameters that can be used in studying discotic liquid crystals.

Parameters published by Müller and Mejia for coronene were used to model both coronene and hexabenzocoronene. It is also possible to observe the correct structures for them as shown in Figure 7.4.

The first case of amphiphilic discotic LC studies was that of the alkyl substituted hexabenzocoronene (C12-HBC), where at the end of each side a n-dodecane alkyl chain, previously studied by Ziogos and Theodorou [325] using atomistic simulations. Dodecane was modelled using the parameters from ref [241] and cross-interaction parameters were calculated using combining rules. Starting with a perfect square columnar structure, if the system is in a liquid phase it would change into a hexagonal columnar structure. This could be used to predict the melting temperature, which is 380 K. Preliminary results show that the melting point of C12-HBC is correctly predicted. This could be seen in Figure 7.5

For polyphilic liquid crystals, a hexabenzocoronene molecule with two side chains of ethoxylated chains and two side chains of alkanes were modelled in tetrahydrofuran. Given that it is preliminary results, the potential parameters are not presented. However, just to demonstrate the complex phase behaviour of discotic liquid crystals, the snapshots of the structures formed by polyphilic LC are presented in Figure 7.6. It is possible to observe lamellar phases at high molecular concentrations of the polymer, hexagonal columnar phases at intermediate concentrations and chiral nanowires at low concentrations. Jin et al. [326] have observed self-assembled nanotubes with the molecules presented in Figure 7.6 and it would be interesting to see

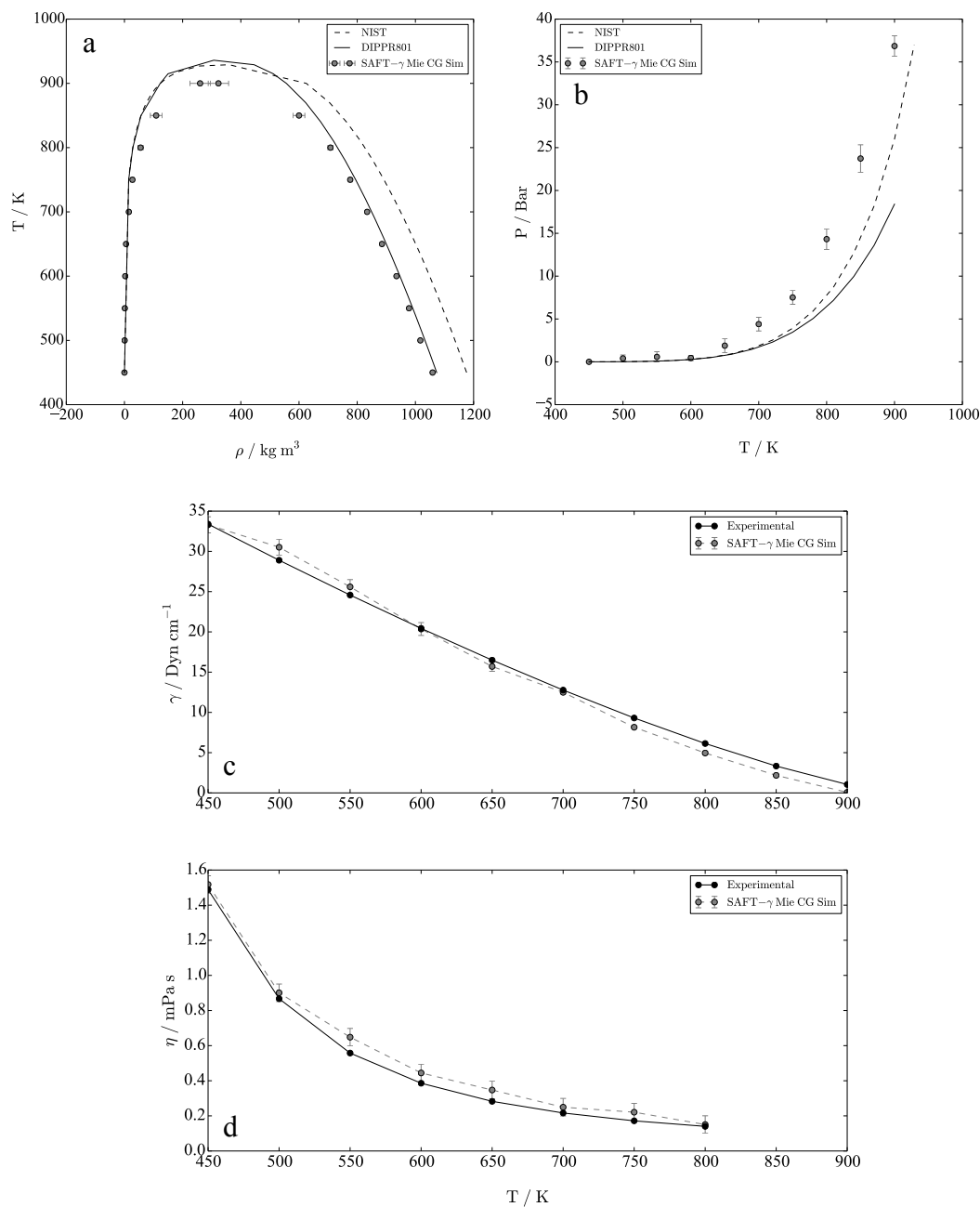


FIGURE 7.3: Thermophysical properties of pyrene: *a* saturation densities, *b* vapour pressures, *c* surface tension and *d* viscosity. *c* and *d* are predictions.

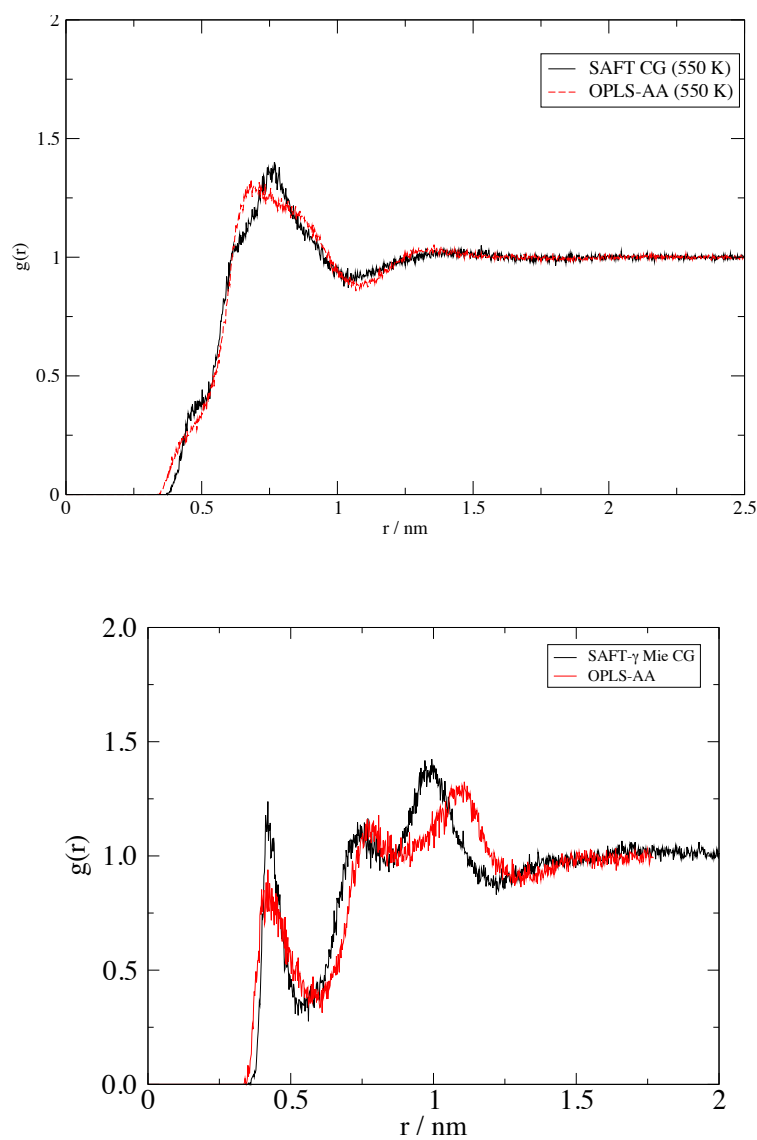


FIGURE 7.4: *Top* CoM-CoM RDF of pyrene at 450 K, *Bottom* CoM-CoM RDF of corone at 500 K. Red represents atomistic simulations and black the SAFT CG simulations in this work.

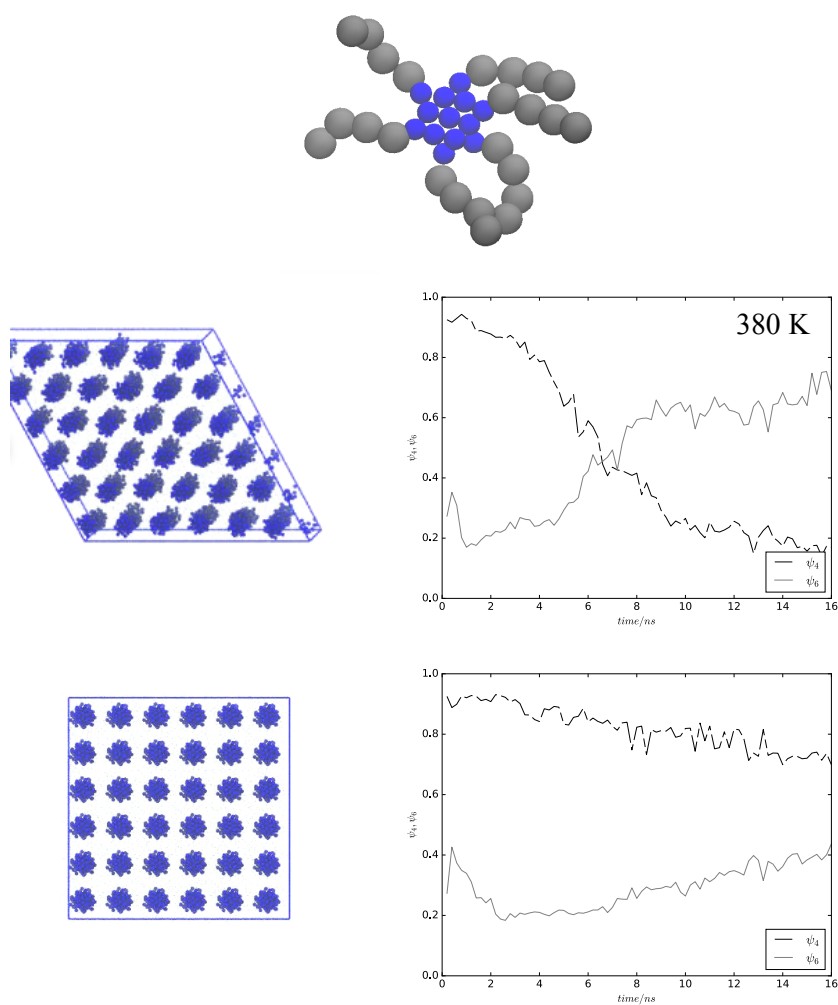


FIGURE 7.5: *Top* Melting of dodecane substituted hexabenzocorone, where starting with a square columnar configuration at 380 K a hexagonal phase is observed, whereas at 350 K the structure is square columnar.

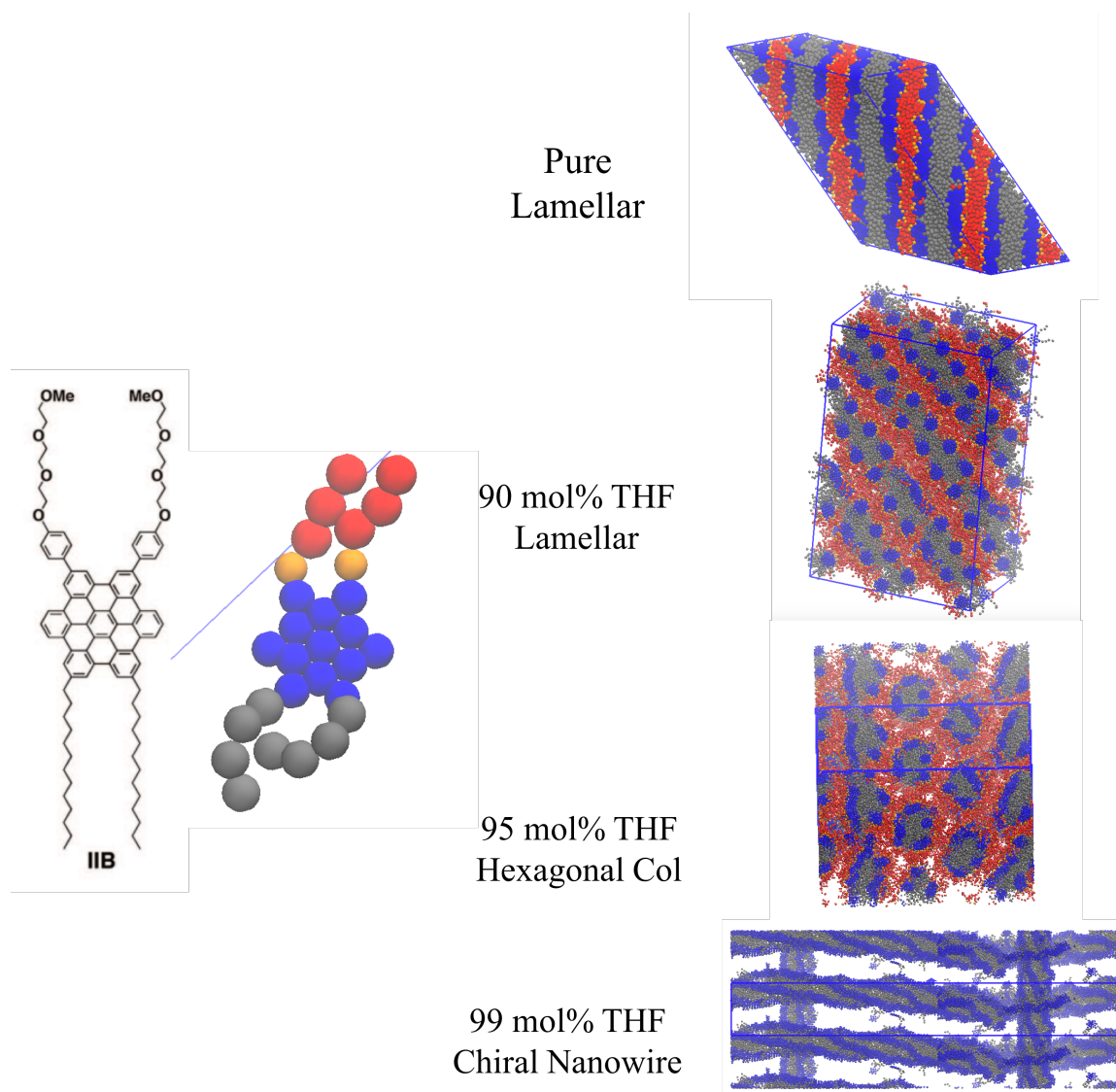


FIGURE 7.6: *Top* Structures observed at different solvent concentrations for the polyphilic discotic (HBC) liquid crystal

if this could be predicted with the models proposed in this thesis.

7.3 Bridging the Gap Between Polyphilic Liquid Crystals and Polymers: Study of Solution Phase Behaviour of Amphiphilic Oligomers

Given that the proposed CG methodology presented here is robust in modelling both polymers and polyphilic molecules it would be useful to try and use simulations as tools for materials discovery. Toy-models with Lennard-Jones type potentials of

molecules can be used to find interesting phase behaviour, and SAFT- γ could be used to find real molecules that have similar potentials as the models used to find interesting phase behaviour. In this regard, preliminary work has been carried out to identify interesting phase behaviour of polyphilic oligomers that are pentablock oligomers.

Simulation Details

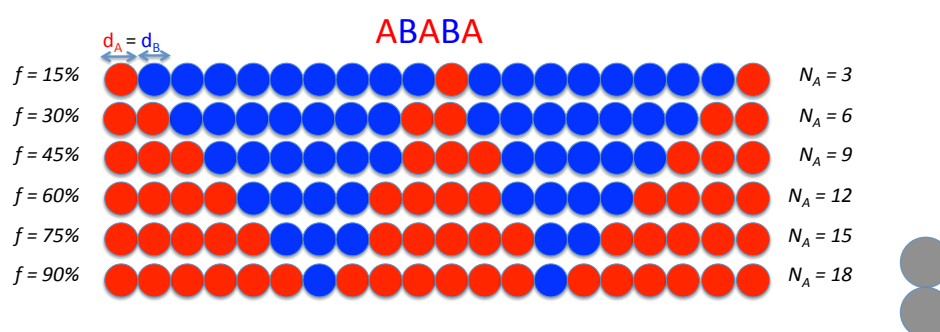


FIGURE 7.7: The schematic of the molecules used in this investigation, the polymers are shown as long chains of beads, the solvent is shown as a grey on the right

We define our polymers/oligomers as molecules with 20 beads, with two types of beads 'A' beads represented as red in Fig 7.7, and 'B' beads represented as blue. This in reverse engineering term corresponds to a polymer with a molecular weight of $2,000 - 4,000 \text{ g mol}^{-1}$ with each bead having a molecular weight of around $40 - 80 \text{ g mol}^{-1}$. The solvent is represented as a two bead model, because the most common representation of common solvents using SAFT is with two beads, for example cases of hexane, heptane and benzene are best represented using two or three beads. Moreover, this model offers the flexibility in future investigations. For example the same solvent could be used to model an amphiphilic solvent, with one side liking a particular polymer and one side being self-attractive. Fig 7.7 shows the five types of pentablocks studied. Each simulation box contains 50,000 beads to ensure system size effects do not affect the results of the simulations and periodic boundary conditions are implemented.

There are three parameters that define each set of simulations:

- The pair interaction of different beads, ϵ_{ij}

- The fraction of polymer occupied by A beads, $f_A = \frac{N_{Beads, A} + N_{Beads, B}}{N_{Beads, Polymer}}$,
- The number concentration of polymer, $\phi = \frac{N_{Polymers} N_{Beads, Polymer}}{N_{Beads, Total}}$,

The pair interaction of different beads, ϵ_{ij}

All interactions are Lennard-Jones interactions (12-6 exponents).

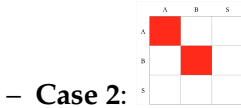
$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (7.1)$$

Here we will describe everything in reduced units of $\sigma = 1$. The ϵ values are also defined in reduced units. There are two sets of epsilons in this study: $\epsilon_{unattract} = 1$ for cases where the interactions are of comparable to $k_B T$, which corresponds to a case of no attractions, and $\epsilon_{unattract} = 2$ case where interactions are twice as attractive as the former case. For the simulations in the previous section with glycerol and icosane, the glycerol groups have an ϵ that is 1.8 times more attractive than the side chains, and so an attractive energy of $\epsilon_{attract} = 2$ is reasonable for these simulations to induce strong segregation in these systems.

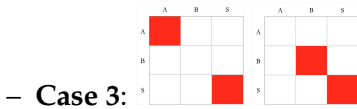
There will be 5 types of interactions that can lead to different morphologies:



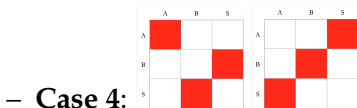
A segment of polymer is self-attracting: ($\epsilon_{A,A} = 2$ and $\epsilon_{B,B} = \epsilon_{S,S} = 1$) or ($\epsilon_{B,B} = 2$ and $\epsilon_{A,A} = \epsilon_{S,S} = 1$)



Both segments of polymer are self-attracting: ($\epsilon_{A,A} = \epsilon_{B,B} = 2$ and $\epsilon_{S,S} = 1$)



A segment of polymer is self-attracting and the solvent is self-attracting: ($\epsilon_{A,A} = \epsilon_{S,S} = 2$ and $\epsilon_{B,B} = 1$) or ($\epsilon_{B,B} = \epsilon_{S,S} = 2$ and $\epsilon_{A,A} = 1$)



Amphiphilic case, A segment of polymer is self-attracting and the other segment likes the solvent: ($\epsilon_{A,A} = 2$ and $\epsilon_{B,S} = 2$) or ($\epsilon_{B,B} = 2$ and $\epsilon_{A,S} = 1$)

	A	B	S
A	Red	White	White
B	White	Red	White
S	White	White	Red

– **Case 5:**

Every type of bead is self-attractive ($\epsilon_{A,A} = \epsilon_{B,B} = \epsilon_{S,S} = 2$)

For all these cases Pressure, $P / (\epsilon / \sigma^3) \approx 0.001$, and temperature is $T / (\epsilon / k_B) = 1.5$, a midway between strong attractive energies and the unattractive energies. Each simulation is run for 10 million time steps to ensure equilibration and then morphologies are investigated.

The fraction of polymer occupied by A beads, f_A

A range of f_A are investigated as shown in Fig 7.7. The f_A ranges from 15% to 90%.

The number concentration of polymer, ϕ_{Poly}

Concentrations are defined as the number of polymer beads divided by the total number of beads in the system. A range of concentrations, ϕ_{Poly} , will be investigated, namely 10%, 30%, 50%, 70% concentration. which is from dilute to very concentrated systems.

Progress & Achievements

160 simulations at the conditions specified in the previous section have been run. For all cases shown, the A type segments are shown as red beads, B segments are shown as blue and solvents as grey. These morphologies can be divided into a few categories:

- Isotropic phases: when f_A is small (15%) and A-A interactions are attractive, independent of ϕ ,
- Micellar phases: $\phi < 30\%$,
- Worm-like and Polymer columnar phases: $\phi \approx 30\%$,
- Lamellar and perforated lamellar Phases: $\phi \approx 30\text{-}50\%$,
- Solvent Columnar phases: $\phi \approx 75\%$,

- Vesicles: Localised high concentration

Low Concentration, $\phi < 30\%$: Micellar Phases

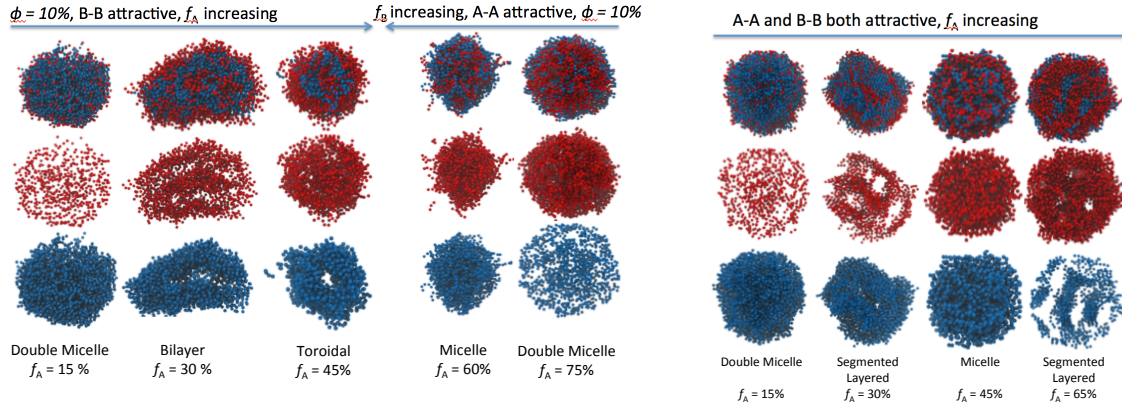


FIGURE 7.8: **Left** Micelles observed for Case 1 type of interactions, **Right** Micelles observed for Case 2 type of interactions, segmentation can be seen with increasing f_A

For different interactions, different morphologies of micelles are observed as shown in Fig 7.8 and Fig 7.9. The main morphologies of micelles formed through the Case 1 interactions described before (i.e. only one segment of the polymer is self-attractive) are highlighted in Fig 7.8 Left. At low f_A or f_B , the micelles have a double micelle structure, meaning there is a small core within a larger shell. As f_A is increased, this double micelle structure changes to a bilayer structure.

If both segments types of the polymer (A and B) become self-attractive (Case 2), segmentation starts to appear and micelles become 'lamellar' (Fig 7.8 Right), if the solvent also becomes self-attractive, then helical micelles start to appear (Fig 7.9).

Worm-like and polymer columnar phases: $\phi \approx 30\%$

Increasing ϕ from 15% to $\approx 30\%$, it could be seen that micelles start coalescing and growing into columns to form worm-like micelles or columns that have high aspect ratios ($\frac{Length}{Diameter} \gg 1$). There is a distinction between polymer columns and worm-like micelles. Worm-like micelles have an inner solvophobic core surrounded by an

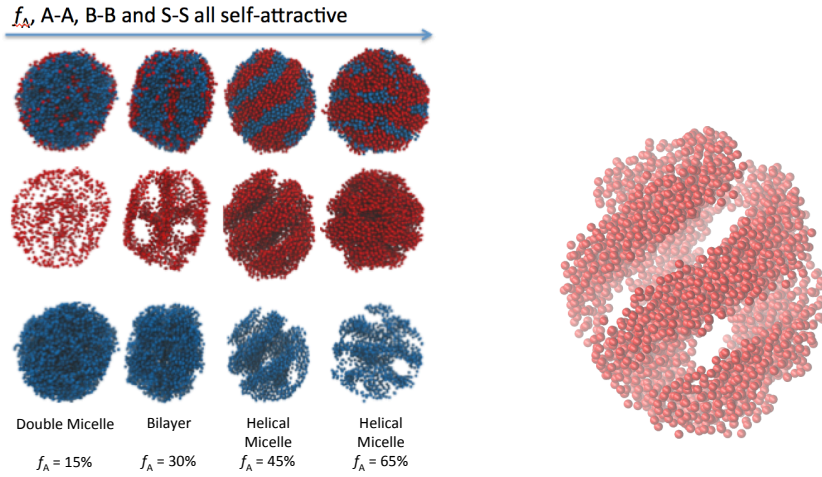


FIGURE 7.9: Micelles observed for Case 5 type of interactions, segmentation can be seen with the latter cases, with higher f_A

outer shell of solvophilic shell which acts as a border between the core and the solvent, reducing the interfacial tension of the interface. Polymer columns are different to worm-like micelles in that there is no outer shell protecting the inner core. Fig 7.10 shows examples of worm-like and polymer columnar phases observed in this case study. The two examples on the left are for the cases where A-A head groups are attractive, and the two cases on the right are for cases where B-B chains are attractive. When $f_A \approx f_B$ and A – A is attractive, a segmented phase (Fig 7.10 Top Left) is preferred to a worm-like micellar phase, whereas increasing the fraction of the attractive beads leads to formation of worm-like phases (Bottom Left). This is in contrast for the cases when B – B is attractive and the phases formed are all worm-like micellar phases (Top/Bottom Right). Interesting observation is the reduction of the persistence length of the worm-like chains for the case of B-B attractive when the A groups become more attractive. This is shown in the two right figures in Fig 7.10. All simulation boxes are similar in size.

Intermediate concentrations, $\phi \approx 30\text{-}50\%$: Lamellar and perforated lamellar Phases

Case 1: A-A attractive

Fig 7.11 shows the most common morphology for this set of attractions, shown from two different views with A blocks shown in red and B blocks shown in blue.

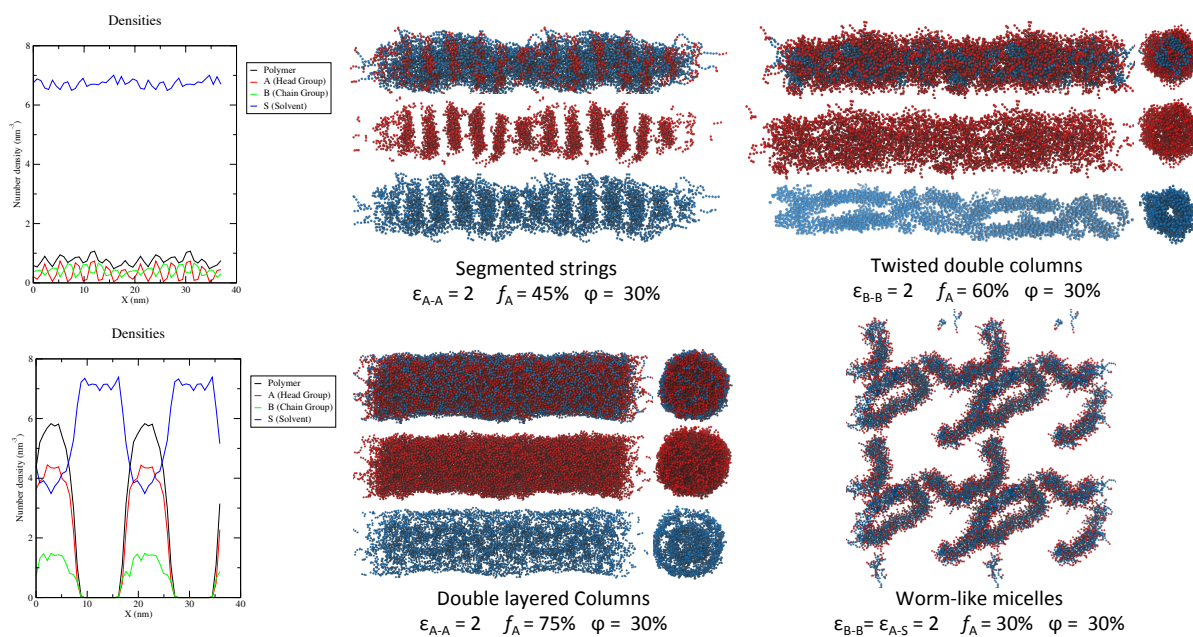


FIGURE 7.10: Different types of columns and worm-like chains observed in these simulations

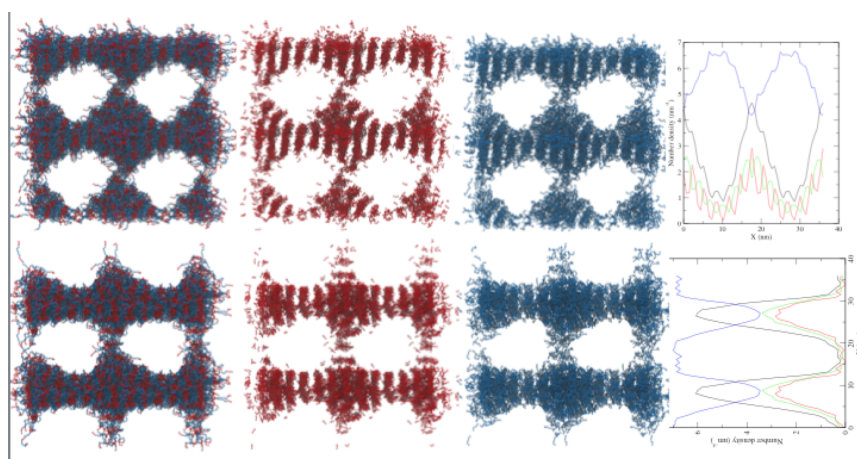


FIGURE 7.11: Perforated sheets occurring for Case 1 (A-A Attractive), top and bottom figures are for the same state but from two different angles

The morphology most common for this type of interaction is a perforated and segmented sheet. In typical diblock copolymer phases, perforated phases are metastable and are precursors to gyroid phases, however since this is observed frequently in many of the simulations of these pentablocks, these perforated sheets are thought to be stable given these conditions of concentration and interaction energies. However simulation size effects on these morphologies need to be further investigated.

Case 1: B-B attractive

This set of simulations are of particular interest as both B-B interactions and f_A play a significant role in shaping the morphologies. Fig 7.12 demonstrates the effect of increasing f_A on the sheets. Increasing f_A reduces the stiffness of the polymers and the shape of the perforations become less regular and more asymmetric. The bottom figure in Fig 7.12 in particular shows very complex morphologies formed, which in this case is double diamond phase structure.

Case 2: A-A & B-B attractive

By making A-A and B-B self-attractive, one gets morphologies that at lower concentrations ($\phi = 30\%$) are perforated with chiral segmentation. Increasing the concentration ($\phi = 50\%$) induces a structural change from a chiral segmented perforated sheet into a 'fingerprint' bicontinuous microdomains within the lamellae. Fig 7.13 shows the morphologies of the systems mentioned.

Case 4: A-A & B-S attractive

Interesting domains are formed as shown in Fig 7.14 when the A blocks are solvophobic and the B blocks are solvophilic. Due to the fact each polymer is made up of multiple solvophobic domains, the micelles are bridged with each other forming clusters of interconnected micelles. With increasing f_A these micelles start coalescing forming interconnected worm micelles.

High Polymer Concentration, $\phi > 50\%$: Columnar and spherical solvent phases

At high ϕ , the solvent becomes trapped within the polymer system and depending on conditions, different types of morphologies can be formed. The most interesting morphologies observed are shown in Fig 7.15, and these are the following:

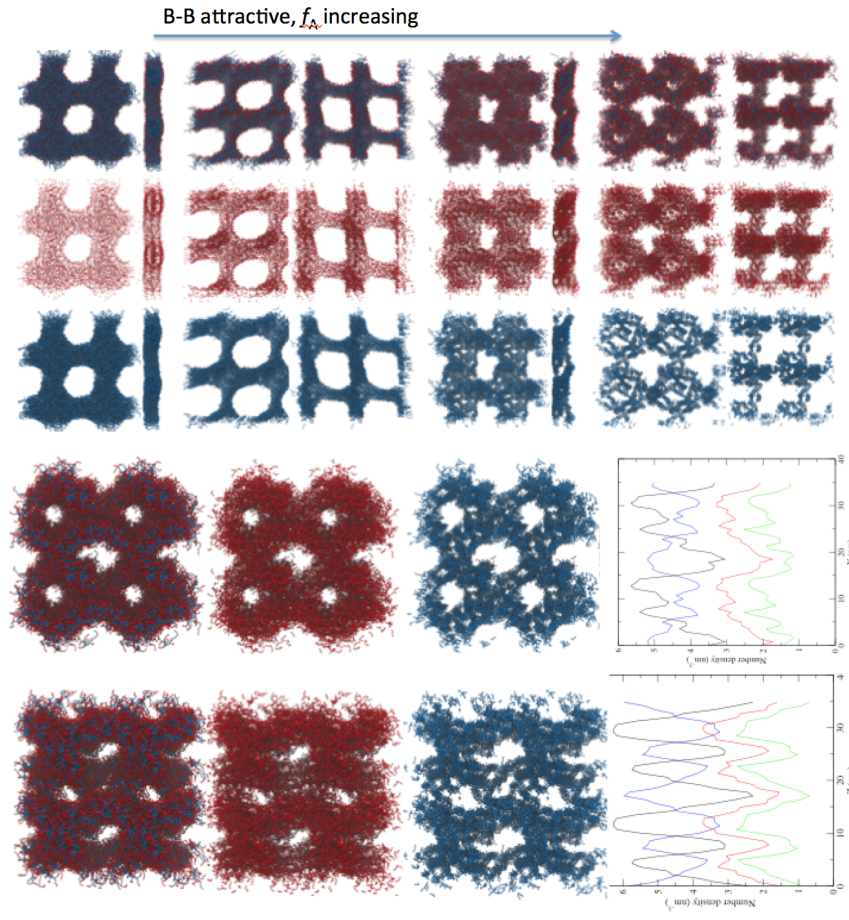


FIGURE 7.12: *Top*: Morphologies occurring for case of Case 1 (B-B Attractive) cases when $\phi = 30\%$, each pair of figures representing the same system from two different planes, *Bottom*: Double diamond

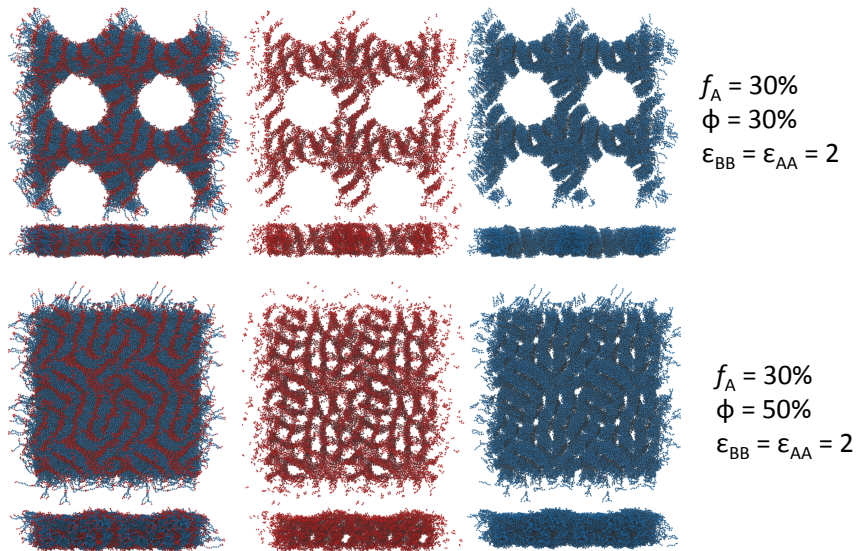


FIGURE 7.13: Morphologies of the lamellar structures formed when both (A-A and B-B are attractive, *Top*: Chiral segmented sheets are formed when $\phi = 30\%$), *Bottom*: Bicontinuous phases when $\phi = 50\%$)

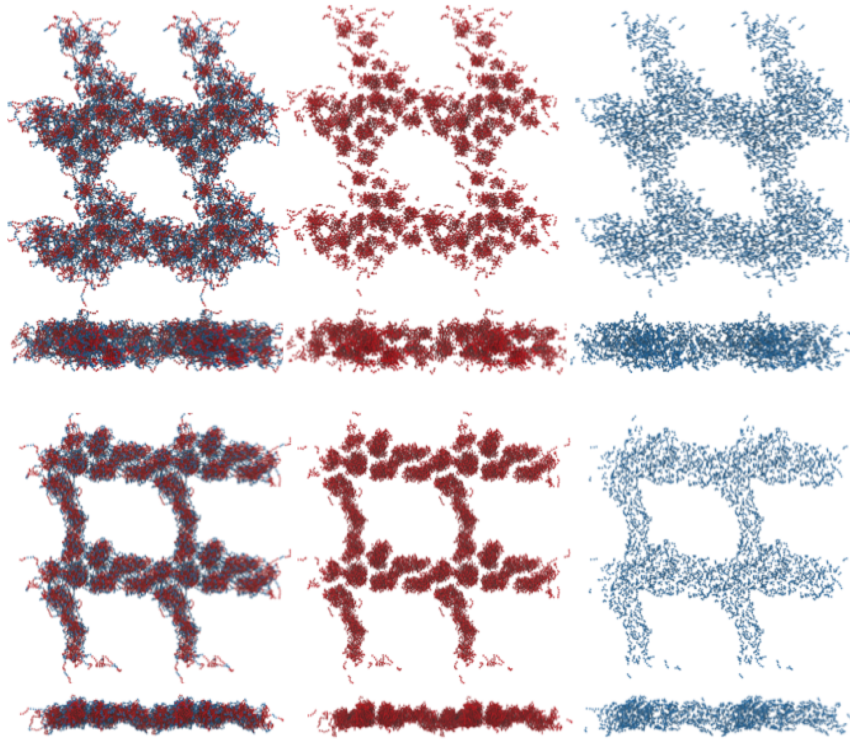


FIGURE 7.14: **Top** Clustering of micelles into perforated sheets when A (red) group is solvophobic and B (blue) groups are solvophilic, $f_A = 30\%$, $\phi = 10\%$, **Bottom** Increasing f_A leads to formation of interconnected worm-like micelles. $f_A = 45\%$, $\phi = 10\%$

- Spherical phases: solvents form spheres that arrange themselves into ordered face-centred cubic structures, occurring when the solvent is strongly self-attracting and a segment of the polymer is self-attracting too, resulting in a strong segregation between polymer and solvent, the attraction of the polymer offsets the attraction of the solvents and prevent the solvent from full phase separation,
- Circular columns: solvents form columns that have a circular base, with columnar phases preferred due to a low concentration of the solvent,
- Square columns: this occurs for the case when the B group, shielded from the solvent by the A groups, are attractive, forming bilayers at high concentrations, these bilayers join and form square shaped columns,
- Octagonal columns: the columns are circular with an octagonal outer layer, induced by the strong attraction of the B segments of the polymer as well as the solvent at small f_A ,
- Both spheres and columns: this phase requires further investigation, as this

type of phase behaviour has not been observed in literature and could be a metastable phase, at the conditions specified in Fig 7.15 spheres and columns coexist, forming a hexagonal structure,

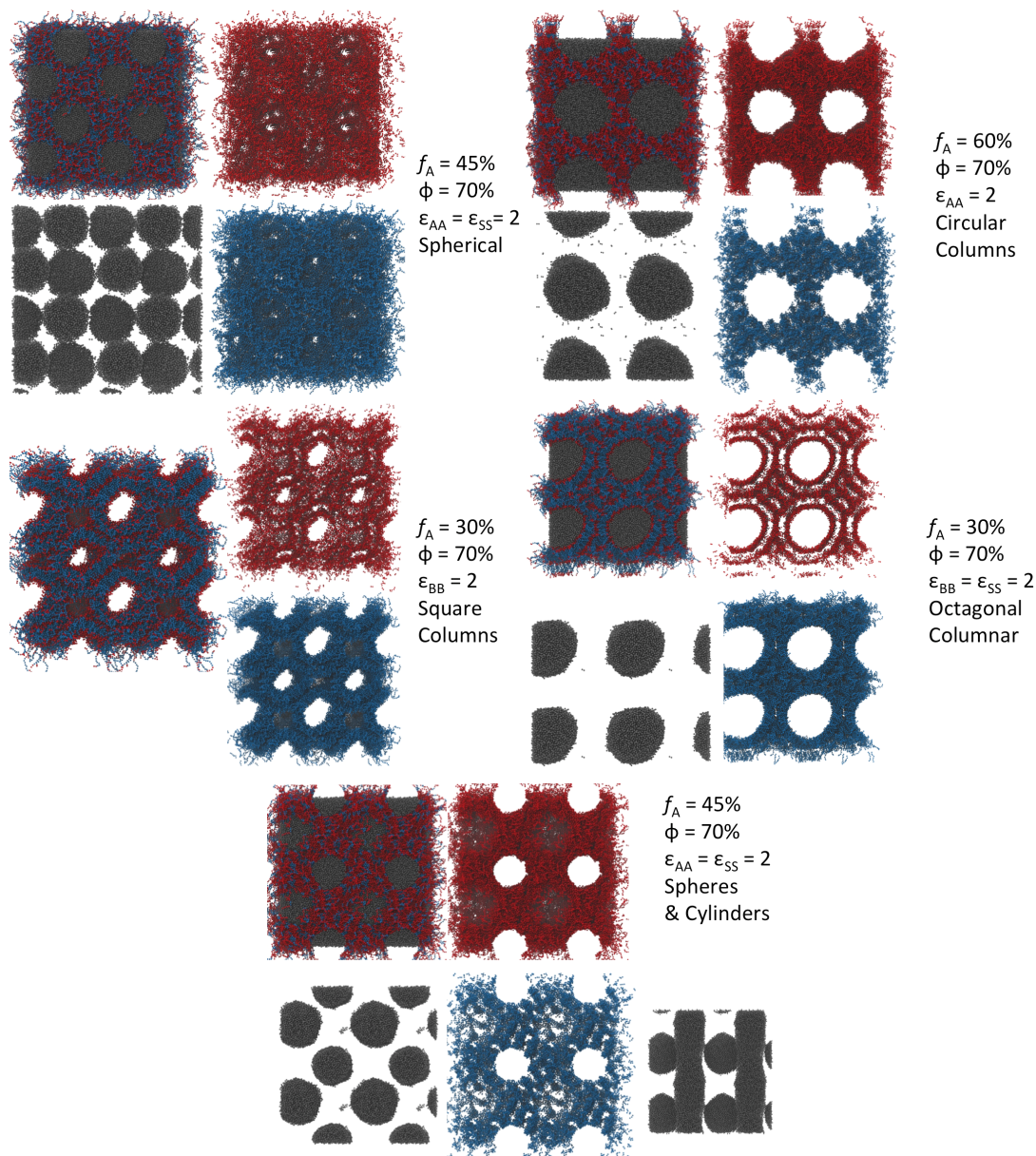


FIGURE 7.15: *Top* Phases observed at high ϕ

Localised High Concentration

For every simulation box, the length of each side was extended by 30% and the newly created empty volume is filled with solvent molecules, creating a localised high concentration of polymers surrounded by a pool of solvents. Vesicles are formed when the polymer is solvophobic and the polymer and solvent are immiscible. This

means that only Case 3 interactions lead to vesicle formation, as can be seen from Fig 7.16.

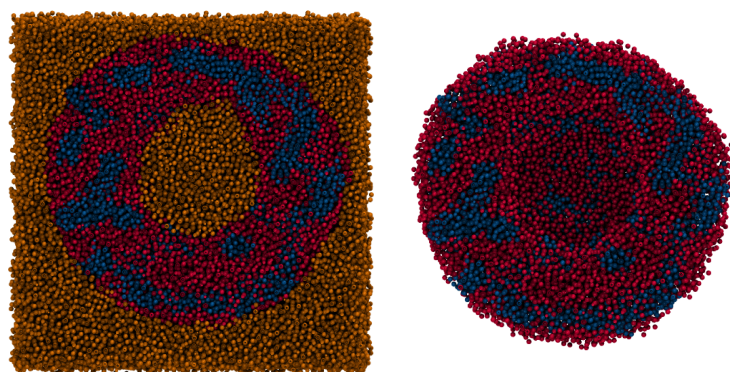


FIGURE 7.16: vesicles formed, with *Left* showing the solvent as orange for better distinction, and *Right* showing the system without the solvent, clearly indicating that the system shown is a vesicle

Here a range of different structures formed by pentablock oligomers are presented and in the next step SAFT- γ Mie could be used to find real moieties that can produce the structures seen here.

7.4 Final Words

No PhD thesis is ever complete and there is always additional material that could be developed upon the work that has been carried out. The key message that this manuscript conveys is that it is possible to develop quantitatively accurate coarse-grained models to study phase behaviour of complex fluids at the mesoscale.

Bibliography

1. Gompper, G, Dhont, J. K. & Richter, D. Editorial A unified view of soft matter systems? *The European Physical Journal E: Soft Matter and Biological Physics* **26**, 1–2 (2008).
2. Martin, B. R. *et al.* Orthogonal self-assembly on colloidal gold-platinum nanorods. *Advanced Materials* **11**, 1021–1025 (1999).
3. Glotzer, S., Solomon, M. & Kotov, N. A. Self-assembly: From nanoscale to microscale colloids. *AIChE Journal* **50**, 2978–2985 (2004).
4. Glotzer, S. C. & Solomon, M. J. Anisotropy of building blocks and their assembly into complex structures. *Nature Materials* **6**, 557 (2007).
5. Frenkel, D. & Wales, D. J. Colloidal self-assembly: designed to yield. *Nature Materials* **10**, 410 (2011).
6. Avendaño, C. & Escobedo, F. A. Packing, entropic patchiness, and self-assembly of non-convex colloidal particles: A simulation perspective. *Current Opinion in Colloid & Interface Science* **30**, 62–69 (2017).
7. Schönhöfer, P. W., Ellison, L. J., Marechal, M., Cleaver, D. J. & Schröder-Turk, G. E. Purely entropic self-assembly of the bicontinuous Ia3d gyroid phase in equilibrium hard-pear systems. *Interface focus* **7**, 20160161 (2017).
8. Bates, F. S. & Fredrickson, G. H. Block copolymer thermodynamics: theory and experiment. *Annual Review of Physical Chemistry* **41**, 525–557 (1990).
9. Foerster, S. *et al.* Complex phase behavior of polyisoprene-polystyrene diblock copolymers near the order-disorder transition. *Macromolecules* **27**, 6922–6935 (1994).
10. Binder, K. *Monte Carlo and molecular dynamics simulations in polymer science* (Oxford University Press, 1995).

11. Khandpur, A. K. *et al.* Polyisoprene-polystyrene diblock copolymer phase diagram near the order-disorder transition. *Macromolecules* **28**, 8796–8806 (1995).
12. Martínez-Veracoechea, F. J. & Escobedo, F. A. Lattice Monte Carlo simulations of the gyroid phase in monodisperse and bidisperse block copolymer systems. *Macromolecules* **38**, 8522–8531 (2005).
13. Anderson, J. A. & Travesset, A. Coarse-grained simulations of gels of nonionic multiblock copolymers with hydrophobic groups. *Macromolecules* **39**, 5143–5151 (2006).
14. Ouldridge, T. E., Johnston, I. G., Louis, A. A. & Doye, J. P. The self-assembly of DNA Holliday junctions studied with a minimal model. *The Journal of Chemical Physics* **130**, 02B603 (2009).
15. Reinhardt, A. & Frenkel, D. Numerical evidence for nucleated self-assembly of DNA brick structures. *Physical Review Letters* **112**, 238103 (2014).
16. Snodin, B. E. *et al.* Direct simulation of the self-assembly of a small DNA origami. *ACS Nano* **10**, 1724–1737 (2016).
17. Cygan, Z. T., Cabral, J. T., Beers, K. L. & Amis, E. J. Microfluidic platform for the generation of organic-phase microreactors. *Langmuir* **21**, 3629–3634 (2005).
18. Gompper, G., Ihle, T., Kroll, D. & Winkler, R. English. in *Advanced Computer Simulation Approaches for Soft Matter Sciences III* (eds Holm, C. & Kremer, K.) 1–87 (Springer Berlin Heidelberg, 2009). ISBN: 978-3-540-87705-9. doi:10.1007/978-3-540-87706-6_1. <http://dx.doi.org/10.1007/978-3-540-87706-6_1>.
19. Voth, G. A. *Coarse-graining of condensed phase and biomolecular systems* 1–4 (CRC press, 2008).
20. Niethammer, C. *et al.* ls1 mardyn: The Massively Parallel Molecular Dynamics Code for Large Systems. *Journal of Chemical Theory and Computation* **10**. PMID: 26588142, 4455–4464 (2014).
21. Klein, M. L. & Shinoda, W. Large-scale molecular dynamics simulations of self-assembling systems. *Science* **321**, 798–800 (2008).

22. Müller, E. A. & Jackson, G. Force-field parameters from the SAFT- γ equation of state for use in coarse-grained molecular simulations (2014).
23. Saunders, M. G. & Voth, G. A. Coarse-graining methods for computational biology. *Annual Review of Biophysics* **42**, 73–93 (2013).
24. Flory, P. J. *Principles of polymer chemistry* (Cornell University Press, 1953).
25. Fox Jr, T. G. & Flory, P. J. Second-order transition temperatures and related properties of polystyrene. I. Influence of molecular weight. *Journal of Applied Physics* **21**, 581–591 (1950).
26. Louis, A. Beware of density dependent pair potentials. *Journal of Physics: Condensed Matter* **14**, 9187 (2002).
27. Papaioannou, V. *et al.* Group contribution methodology based on the statistical associating fluid theory for heteronuclear molecules formed from Mie segments. *The Journal of Chemical Physics* **140**, 054107 (2014).
28. Mie, G. Zur kinetischen Theorie der einatomigen Körper. *Annalen der Physik* **316**, 657–697 (1903).
29. Avendaño, C. *et al.* SAFT- γ force field for the simulation of molecular fluids. 1. A single-site coarse grained model of carbon dioxide. *The Journal of Physical Chemistry B* **115**, 11154–11169 (2011).
30. Avendaño, C. *et al.* SAFT- γ force field for the simulation of molecular fluids: 2. Coarse-grained models of greenhouse gases, refrigerants, and long alkanes. *The Journal of Physical Chemistry B* **117**, 2717–2733 (2013).
31. Lafitte, T. *et al.* SAFT- γ force field for the simulation of molecular fluids: 3. Coarse-grained models of benzene and hetero-group models of n-decylbenzene. *Molecular Physics* **110**, 1189–1203 (2012).
32. Rahman, S. *et al.* SAFT- γ Force Field for the Simulation of Molecular Fluids. 5. Hetero-Group Coarse-Grained Models of Linear Alkanes and the Importance of Intramolecular Interactions. *The Journal of Physical Chemistry B*.

33. Morgado, P. *et al.* SAFT- γ force field for the simulation of molecular fluids: 8. Hetero-segmented coarse-grained models of perfluoroalkylalkanes assessed with new vapour-liquid interfacial tension data. *Molecular Physics* **114**, 2597–2614 (2016).
34. Ervik, Å., Mejía, A. & Müller, E. A. Bottled SAFT: a web app providing SAFT- γ Mie force field parameters for thousands of molecular fluids. *Journal of Chemical Information and Modeling* **56**, 1609–1614 (2016).
35. Lobanova, O. Development of coarse-grained force fields from a molecular based equation of state for thermodynamic and structural properties of complex fluids (2014).
36. Rahman, S. *et al.* Development of coarse-grained models of ionic and non-ionic surfactants for the molecular simulation of structural, thermodynamic and dynamical properties (2016).
37. Matsen, M. W. Self-consistent field theory and its applications. *Soft Matter* **1**, 87–178 (2006).
38. Schmid, F. Theory and Simulation of Multiphase Polymer Systems. *Handbook of Multiphase Polymer Systems*, 31–80 (2011).
39. De Gennes, P.-G. & Gennes, P.-G. *Scaling concepts in polymer physics* (Cornell university press, 1979).
40. Doi, M. & Edwards, S. F. *The theory of polymer dynamics* (oxford university press, 1988).
41. Teraoka, A. A. & Teraoka, I. *Polymer solutions: an introduction to physical properties* (John Wiley & Sons, 2002).
42. Kremer, K. & Grest, G. S. Dynamics of entangled linear polymer melts: A molecular-dynamics simulation. *The Journal of Chemical Physics* **92**, 5057–5086 (1990).
43. Domb, C. Excluded-Volume Effect for Two-and Three-Dimensional Lattice Models. *The Journal of Chemical Physics* **38**, 2957–2963 (1963).
44. Klapp, S. H., Diestler, D. J. & Schoen, M. Why are effective potentials ‘soft’? *Journal of Physics: Condensed Matter* **16**, 7331 (2004).

45. Flory, P. J. Thermodynamics of high polymer solutions. *The Journal of Chemical Physics* **10**, 51–61 (1942).
46. Huggins, M. L. Solutions of long chain compounds. *The Journal of Chemical Physics* **9**, 440–440 (1941).
47. Yang, Y., Qiu, F., Tang, P. & Zhang, H. Applications of self-consistent field theory in polymer systems. *Science in China Series B* **49**, 21–43 (2006).
48. Maranas, J. K. *et al.* Liquid structure, thermodynamics, and mixing behavior of saturated hydrocarbon polymers. 1. Cohesive energy density and internal pressure. *Macromolecules* **31**, 6991–6997 (1998).
49. Han, C. C. *et al.* Temperature, composition and molecular-weight dependence of the binary interaction parameter of polystyrene/poly (vinyl methyl ether) blends. *Polymer* **29**, 2002–2014 (1988).
50. Petri, H.-M. & Wolf, B. Composition-dependent Flory-Huggins parameters: molecular weight influences at high concentrations. *Macromolecular Chemistry and Physics* **196**, 2321–2333 (1995).
51. Dudowicz, J. & Freed, K. F. Pressure dependence of polymer fluids: application of the lattice cluster theory. *Macromolecules* **28**, 6625–6641 (1995).
52. Freed, K. F. & Dudowicz, J. Lattice cluster theory for pedestrians: The incompressible limit and the miscibility of polyolefin blends. *Macromolecules* **31**, 6681–6690 (1998).
53. Foreman, K. & Freed, K. F. Lattice cluster theory of multicomponent polymer systems: Chain semiflexibility and specific interactions. *Advances in Chemical Physics* **103**, 335–390 (1998).
54. Cho, J. & Sanchez, I. C. PVT relationships and equations of state of polymers. *The Wiley Database of Polymer Properties* (2003).
55. Rouse Jr, P. E. A theory of the linear viscoelastic properties of dilute solutions of coiling polymers. *The Journal of Chemical Physics* **21**, 1272–1280 (1953).
56. Zimm, B. H. Dynamics of polymer molecules in dilute solution: viscoelasticity, flow birefringence and dielectric loss. *The Journal of Chemical Physics* **24**, 269–278 (1956).

57. De Gennes, P.-G. Reptation of a polymer chain in the presence of fixed obstacles. *The Journal of Chemical Physics* **55**, 572–579 (1971).
58. Matsen, M. W. & Bates, F. S. Unifying weak-and strong-segregation block copolymer theories. *Macromolecules* **29**, 1091–1098 (1996).
59. Hadjichristidis, N., Iatroua, H., Pitsikalis, M., Pispas, S. & Avgeropoulos, A. Linear and non-linear triblock terpolymers. Synthesis, self-assembly in selective solvents and in bulk. *Prog. Polym. Sci* **30**, 725–782 (2005).
60. Gemma, T., Hatano, A. & Dotera, T. Monte Carlo simulations of the morphology of ABC star polymers using the diagonal bond method. *Macromolecules* **35**, 3225–3237 (2002).
61. Chremos, A. & Theodorakis, P. E. Morphologies of bottle-brush block copolymers. *ACS Macro Letters* **3**, 1096–1100 (2014).
62. Li, Y. *et al.* Hierarchical nanostructures self-assembled from a mixture system containing rod-coil block copolymers and rigid homopolymers. *Scientific Reports* **5**, 10137 (2015).
63. Van Konynenburg, P. & Scott, R. Critical lines and phase equilibria in binary van der Waals mixtures. *Phil. Trans. R. Soc. Lond. A* **298**, 495–540 (1980).
64. Shultz, A. & Flory, P. Phase Equilibria in Polymer—Solvent Systems^{1, 2}. *Journal of the American Chemical Society* **74**, 4760–4767 (1952).
65. Cabral, J. T. & Higgins, J. S. Spinodal nanostructures in polymer blends: On the validity of the Cahn-Hilliard length scale prediction. *Progress in Polymer Science* **81**, 1–21 (2018).
66. Paricaud, P., Galindo, A. & Jackson, G. Understanding liquid-liquid immiscibility and LCST behaviour in polymer solutions with a Wertheim TPT1 description. *Molecular Physics* **101**, 2575–2600 (2003).
67. Bae, Y., Lambert, S., Soane, D. & Prausnitz, J. M. Cloud-point curves of polymer solutions from thermo-optical measurements. *Macromolecules* **24**, 4403–4407 (1991).

68. Davies, L. A., Jackson, G. & Rull, L. F. Closed-loop phase equilibria of a symmetrical associating mixture of square-well molecules examined by Gibbs ensemble Monte Carlo simulation. *Physical Review E* **61**, 2245 (2000).
69. Sheng, Y. J., Panagiotopoulos, A. Z., Kumar, S. K. & Szleifer, I. Monte Carlo calculation of phase equilibria for a bead-spring polymeric model. *Macromolecules* **27**, 400–406 (1994).
70. Friedel, G. *Les états mésomorphes de la matière* in *Annales de physique* **9** (1922), 273–474.
71. Prost, J. & de Gennes, P. G. *The physics of liquid crystals* (Oxford university press, 1995).
72. Onsager, L. The effects of shape on the interaction of colloidal particles. *Annals of the New York Academy of Sciences* **51**, 627–659 (1949).
73. Eppenga, R & Frenkel, D. Monte Carlo study of the isotropic and nematic phases of infinitely thin hard platelets. *Molecular physics* **52**, 1303–1334 (1984).
74. Bolhuis, P. & Frenkel, D. Tracing the phase boundaries of hard spherocylinders. *The Journal of chemical physics* **106**, 666–687 (1997).
75. Wu, L., Malijevský, A., Jackson, G., Müller, E. A. & Avendaño, C. Orientational ordering and phase behaviour of binary mixtures of hard spheres and hard spherocylinders. *The Journal of chemical physics* **143**, 044906 (2015).
76. Wu, L, Wensink, H., Jackson, G & Müller, E. A generic equation of state for liquid crystalline phases of hard-oblate particles. *Molecular Physics* **110**, 1269–1288 (2012).
77. Wood, W. Monte carlo calculations for hard disks in the isothermal-isobaric ensemble. *The Journal of Chemical Physics* **48**, 415–434 (1968).
78. Avendaño, C., Jackson, G., Müller, E. A. & Escobedo, F. A. Assembly of porous smectic structures formed from interlocking high-symmetry planar nanorings. *PNAS* **113**, 9699–9703 (2016).
79. Maier, W. & Saupe, A. Eine einfache molekular-statistische Theorie der nematischen kristallinflüssigen Phase. Teil I1. *Zeitschrift für Naturforschung A* **14**, 882–889 (1959).

80. Majumdar, A. Equilibrium order parameters of nematic liquid crystals in the Landau-de Gennes theory. *European Journal of Applied Mathematics* **21**, 181–203 (2010).
81. Droulias, S., Vanakaras, A. G. & Photinos, D. J. Extending the Maier–Saupe theory to cybotactic nematics. *Liquid Crystals* **37**, 969–976 (2010).
82. Luckhurst, G. & Zannoni, C. Why is the Maier–Saupe theory of nematic liquid crystals so successful? *Nature* **267**, 412 (1977).
83. Percec, V. *et al.* Self-assembly of Janus dendrimers into uniform dendrimer-somes and other complex architectures. *Science* **328**, 1009–1014 (2010).
84. Israelachvili, J. & Findenegg, G. Intermolecular and Surface Forces (With Applications to Colloidal and Biological Systems). *Berichte der Bunsengesellschaft für physikalische Chemie* **90**, 1241–1242 (1986).
85. Kontogeorgis, G. M. & Folas, G. K. *Thermodynamic models for industrial applications: from classical and advanced mixing rules to association theories* (John Wiley & Sons, 2009).
86. Lafitte, T. *et al.* Accurate statistical associating fluid theory for chain molecules formed from Mie segments. *The Journal of Chemical Physics* **139**, 154504 (2013).
87. Allen, M. P. & Tildesley, D. J. *Computer simulation of liquids* (Oxford university press, 2017).
88. Alder, B. & Wainwright, T. Phase transition for a hard sphere system. *The Journal of Chemical Physics* **27**, 1208–1209 (1957).
89. Jones, J. E. On the determination of molecular fields.—I. From the variation of the viscosity of a gas with temperature. *Proc. R. Soc. Lond. A* **106**, 441–462 (1924).
90. Weeks, J. D., Chandler, D. & Andersen, H. C. Role of repulsive forces in determining the equilibrium structure of simple liquids. *The Journal of Chemical Physics* **54**, 5237–5247 (1971).
91. Gay, J. & Berne, B. Modification of the overlap potential to mimic a linear site–site potential. *The Journal of Chemical Physics* **74**, 3316–3319 (1981).

92. Bates, M. & Luckhurst, G. Computer simulation studies of anisotropic systems XXIX. Quadrupolar Gay-Berne discs and chemically induced liquid crystal phases. *Liquid Crystals* **24**, 229–241 (1998).
93. Bates, M. & Luckhurst, G. in *Liquid Crystals I* 65–137 (Springer, 1999).
94. Prybytak, P, Frith, W. & Cleaver, D. Hierarchical self-assembly of chiral fibres from achiral particles. *Interface Focus* **2**, 651–657 (2012).
95. Dastan, A., Matsumoto, E. A., Frith, W. J. & Cleaver, D. J. Self-assembly of twisted, multi-sheet aggregates. *Molecular Physics*, 1–13 (2018).
96. Kityk, A. V. *et al.* Molecular ordering of nematic liquid crystals in tubular nanopores: Tailoring of optical anisotropy at the nanoscale by polymer pore-surface grafting. *arXiv preprint arXiv:1806.05630* (2018).
97. Haslam, A. J. An introduction to statistical thermodynamics and its applications in equation of state modelling of fluids. *Department of Chemical Engineering* (2016).
98. Carnahan, N. F. & Starling, K. E. Equation of state for nonattracting rigid spheres. *The Journal of Chemical Physics* **51**, 635–636 (1969).
99. Peng, D.-Y. & Robinson, D. B. A new two-constant equation of state. *Industrial & Engineering Chemistry Fundamentals* **15**, 59–64 (1976).
100. Wertheim, M. Fluids with highly directional attractive forces. I. Statistical thermodynamics. *Journal of Statistical Physics* **35**, 19–34 (1984).
101. Wertheim, M. Fluids with highly directional attractive forces. II. Thermodynamic perturbation theory and integral equations. *Journal of Statistical Physics* **35**, 35–47 (1984).
102. Wertheim, M. Fluids with highly directional attractive forces. III. Multiple attraction sites. *Journal of Statistical Physics* **42**, 459–476 (1986).
103. Wertheim, M. Fluids with highly directional attractive forces. IV. Equilibrium polymerization. *Journal of Statistical Physics* **42**, 477–492 (1986).
104. Jackson, G., Chapman, W. G. & Gubbins, K. E. Phase equilibria of associating fluids: Spherical molecules with multiple bonding sites. *Molecular Physics* **65**, 1–31 (1988).

105. Chapman, W. G., Jackson, G. & Gubbins, K. E. Phase equilibria of associating fluids: chain molecules with multiple bonding sites. *Molecular Physics* **65**, 1057–1079 (1988).
106. Chapman, W. G., Gubbins, K. E., Jackson, G. & Radosz, M. New reference equation of state for associating liquids. *Industrial & Engineering Chemistry Research* **29**, 1709–1721 (1990).
107. Kontogeorgis, G. M. & von Solms, N. 11 Thermodynamics of Polymer Solutions. *Choice* **1**, 23 (2009).
108. Huang, S. H. & Radosz, M. Equation of state for small, large, polydisperse, and associating molecules. *Industrial & Engineering Chemistry Research* **29**, 2284–2294 (1990).
109. Fu, Y.-H. & Sandler, S. I. A simplified SAFT equation of state for associating compounds and mixtures. *Industrial & Engineering Chemistry Research* **34**, 1897–1909 (1995).
110. Kraska, T. & Gubbins, K. E. Phase equilibria calculations with a modified SAFT equation of state. 1. Pure alkanes, alkanols, and water. *Industrial & Engineering Chemistry Research* **35**, 4727–4737 (1996).
111. Kraska, T. & Gubbins, K. E. Phase equilibria calculations with a modified SAFT equation of state. 2. Binary mixtures of n-alkanes, 1-alkanols, and water. *Industrial & Engineering Chemistry Research* **35**, 4738–4746 (1996).
112. Gil-Villegas, A. *et al.* Statistical associating fluid theory for chain molecules with attractive potentials of variable range. *The Journal of Chemical Physics* **106**, 4168–4186 (1997).
113. Gross, J. & Sadowski, G. Perturbed-chain SAFT: An equation of state based on a perturbation theory for chain molecules. *Industrial & Engineering Chemistry Research* **40**, 1244–1260 (2001).
114. Barker, J. A. & Henderson, D. Perturbation theory and equation of state for fluids. II. A successful theory of liquids. *The Journal of Chemical Physics* **47**, 4714–4721 (1967).

115. Barker, J. A. & Henderson, D. What is "liquid"? Understanding the states of matter. *Reviews of Modern Physics* **48**, 587 (1976).
116. Zhang, B.-J. Calculating thermodynamic properties from perturbation theory: I. An analytic representation of square-well potential hard-sphere perturbation theory. *Fluid Phase Equilibria* **154**, 1–10 (1999).
117. Hutacharoen, P. *et al.* Predicting the solvation of organic compounds in aqueous environments: from alkanes and alcohols to pharmaceuticals. *Industrial & Engineering Chemistry Research* **56**, 10856–10876 (2017).
118. Shinoda, W., DeVane, R. & Klein, M. L. Multi-property fitting and parameterization of a coarse grained model for aqueous surfactants. *Molecular Simulation* **33**, 27–36 (2007).
119. Marrink, S. J., Risselada, H. J., Yefimov, S., Tieleman, D. P. & De Vries, A. H. The MARTINI force field: coarse grained model for biomolecular simulations. *The Journal of Physical Chemistry B* **111**, 7812–7824 (2007).
120. Peter, C. & Kremer, K. Multiscale simulation of soft matter systems - from the atomistic to the coarse-grained level and back. *Soft Matter* **5**, 4357–4366 (2009).
121. Crane, A. J. Coarse-Grained Simulations of the Self-Assembly and Mesophase Behaviour of Polyphilic Liquid Crystals (2010).
122. Bradley, R. & Radhakrishnan, R. Coarse-grained models for protein-cell membrane interactions (2013).
123. Noid, W. Perspective: coarse-grained models for biomolecular systems. *The Journal of Chemical Physics* **139**, 090901 (2013).
124. Reith, D., Pütz, M. & Müller-Plathe, F. Deriving effective mesoscale potentials from atomistic simulations. *Journal of Computational Chemistry* **24**, 1624–1636 (2003).
125. McQuarrie, D. A. Statistical thermodynamics (1973).
126. Wang, Z.-J. & Deserno, M. A systematically coarse-grained solvent-free model for quantitative phospholipid bilayer simulations. *The Journal of Physical Chemistry B* **114**, 11207–11220 (2010).

127. Moore, T. C., Iacovella, C. R. & McCabe, C. Derivation of coarse-grained potentials via multistate iterative Boltzmann inversion. *The Journal of Chemical Physics* **140**, 224104 (2014).
128. Fu, C.-C., Kulkarni, P. M., Shell, M. S. & Leal, L. G. A test of systematic coarse-graining of molecular dynamics simulations: Thermodynamic properties. *The Journal of Chemical Physics* **137**, 164106 (2012).
129. Milano, G. & Müller-Plathe, F. Mapping atomistic simulations to mesoscopic models: A systematic coarse-graining procedure for vinyl polymer chains. *The Journal of Physical Chemistry B* **109**, 18609–18619 (2005).
130. Harmandaris, V., Adhikari, N., van der Vegt, N. F. & Kremer, K. Hierarchical modeling of polystyrene: From atomistic to coarse-grained simulations. *Macromolecules* **39**, 6708–6719 (2006).
131. Carbone, P., Varzaneh, H. A. K., Chen, X. & Müller-Plathe, F. Transferability of coarse-grained force fields: The polymer case. *The Journal of Chemical Physics* **128**, 064904 (2008).
132. Spyriouni, T., Tzoumanekas, C., Theodorou, D., Müller-Plathe, F. & Milano, G. Coarse-grained and reverse-mapped united-atom simulations of long-chain atactic polystyrene melts: Structure, thermodynamic properties, chain conformation, and entanglements. *Macromolecules* **40**, 3876–3885 (2007).
133. Karimi-Varzaneh, H. A., van der Vegt, N. F., Müller-Plathe, F. & Carbone, P. How good are coarse-grained polymer models? A comparison for atactic polystyrene. *ChemPhysChem* **13**, 3428–3439 (2012).
134. Bayramoglu, B. & Faller, R. Coarse-grained modeling of polystyrene in various environments by iterative Boltzmann inversion. *Macromolecules* **45**, 9205–9219 (2012).
135. Izvekov, S. & Voth, G. A. A multiscale coarse-graining method for biomolecular systems. *The Journal of Physical Chemistry B* **109**, 2469–2473 (2005).
136. Ruhle, V., Junghans, C., Lukyanov, A., Kremer, K. & Andrienko, D. Versatile object-oriented toolkit for coarse-graining applications. *Journal of Chemical Theory and Computation* **5**, 3211–3223 (2009).

137. Monticelli, L. *et al.* The MARTINI coarse-grained force field: extension to proteins. *Journal of Chemical Theory and Computation* **4**, 819–834 (2008).
138. Uusitalo, J. J., Ingolfsson, H. I., Akhshi, P., Tieleman, D. P. & Marrink, S. J. Martini coarse-grained force field: extension to DNA. *Journal of Chemical Theory and Computation* **11**, 3932–3945 (2015).
139. Panizon, E., Bochicchio, D., Monticelli, L. & Rossi, G. MARTINI coarse-grained models of polyethylene and polypropylene. *The Journal of Physical Chemistry B* **119**, 8209–8216 (2015).
140. Rossi, G., Monticelli, L., Puisto, S. R., Vattulainen, I. & Ala-Nissila, T. Coarse-graining polymers with the MARTINI force-field: polystyrene as a benchmark case. *Soft Matter* **7**, 698–708 (2011).
141. Shelley, J. C., Shelley, M. Y., Reeder, R. C., Bandyopadhyay, S. & Klein, M. L. A coarse grain model for phospholipid simulations. *The Journal of Physical Chemistry B* **105**, 4464–4470 (2001).
142. DeVane, R., Shinoda, W., Moore, P. B. & Klein, M. L. Transferable coarse grain nonbonded interaction model for amino acids. *Journal of chemical Theory and Computation* **5**, 2115–2124 (2009).
143. Parrinello, M. & Rahman, A. Crystal structure and pair potentials: A molecular-dynamics study. *Physical Review Letters* **45**, 1196 (1980).
144. Glotzer, S. C. & Paul, W. Molecular and mesoscale simulation methods for polymer materials. *Annual Review of Materials Research* **32**, 401–436 (2002).
145. Groot, R. D. & Warren, P. B. Dissipative particle dynamics: Bridging the gap between atomistic and mesoscopic simulation. *Journal of Chemical Physics* **107**, 4423 (1997).
146. Pivkin, I. V. & Caswell, B. Dissipative particle dynamics. *Reviews in Computational Chemistry* **27** (2010).
147. Pastorino, C, Kreer, T, Müller, M & Binder, K. Comparison of dissipative particle dynamics and Langevin thermostats for out-of-equilibrium simulations of polymeric systems. *Physical Review E* **76**, 026706 (2007).

148. Moeendarbary, E, Ng, T. & Zangeneh, M. Dissipative particle dynamics: introduction, methodology and complex fluid applications—a review. *International Journal of Applied Mechanics* **1**, 737–763 (2009).
149. Espanol, P. & Warren, P. Statistical mechanics of dissipative particle dynamics. *EPL (Europhysics Letters)* **30**, 191 (1995).
150. Español, P. & Warren, P. B. Perspective: Dissipative particle dynamics. *The Journal of Chemical Physics* **146**, 150901 (2017).
151. Van Vliet, R. E., Hoefsloot, H. C., Hamersma, P. J. & Iedema, P. D. Pressure-induced phase separation of polymer-solvent systems with dissipative particle dynamics. *Macromolecular Theory and Simulations* **9**, 698–702 (2000).
152. Wijmans, C., Smit, B & Groot, R. Phase behavior of monomeric mixtures and polymer solutions with soft interaction potentials. *The Journal of Chemical Physics* **114**, 7644–7654 (2001).
153. Frenkel, D. & Smit, B. *Understanding molecular simulation: from algorithms to applications* (Academic press, 2001).
154. Chen, S. & Doolen, G. D. Lattice Boltzmann method for fluid flows. *Annual Review of Fluid Mechanics* **30**, 329–364 (1998).
155. Benzi, R., Succi, S. & Vergassola, M. The lattice Boltzmann equation: theory and applications. *Physics Reports* **222**, 145–197 (1992).
156. Gonnella, G, Orlandini, E & Yeomans, J. Lattice-Boltzmann simulations of complex fluids. *International Journal of Modern Physics C* **8**, 783–792 (1997).
157. Wu, J. & Li, Z. Density-functional theory for complex fluids. *Annu. Rev. Phys. Chem.* **58**, 85–112 (2007).
158. Bates, F. S. Polymer-polymer phase behavior. *Science* **251**, 898–905 (1991).
159. Bertuccio, A. & Vetter, G. *High pressure process technology: fundamentals and applications* (Elsevier, 2001).
160. Jonuzaj, S., Akula, P. T., Kleniati, P.-M. & Adjiman, C. S. The formulation of optimal mixtures with generalized disjunctive programming: A solvent design case study. *AIChE Journal* **62**, 1616–1633 (2016).

161. Black, C. T. *et al.* Polymer self assembly in semiconductor microelectronics. *IBM Journal of Research and Development* **51**, 605–633 (2007).
162. Darling, S. B. Block copolymers for photovoltaics. *Energy & Environmental Science* **2**, 1266–1273 (2009).
163. Sary, N. *et al.* A New Supramolecular Route for Using Rod-Coil Block Copolymers in Photovoltaic Applications. *Advanced Materials* **22**, 763–768 (2010).
164. Allen, C., Maysinger, D. & Eisenberg, A. Nano-engineering block copolymer aggregates for drug delivery. *Colloids and Surfaces B: Biointerfaces* **16**, 3–27 (1999).
165. Flory, P., Orwoll, R. & Vrij, A. Statistical thermodynamics of chain molecule liquids. I. An equation of state for normal paraffin hydrocarbons. *Journal of the American Chemical Society* **86**, 3507–3514 (1964).
166. Sako, T., Wu, A. H. & Prausnitz, J. M. A cubic equation of state for high-pressure phase equilibria of mixtures containing polymers and volatile fluids. *Journal of Applied Polymer Science* **38**, 1839–1858 (1989).
167. Kontogeorgis, G. M., Harismiadis, V. I., Fredenslund, A. & Tassios, D. P. Application of the van der Waals equation of state to polymers: I. Correlation. *Fluid Phase Equilibria* **96**, 65–92 (1994).
168. Boukouvalas, C., Spiliotis, N, Coutisikos, P., Tzouvaras, N & Tassios, D. Prediction of vapor-liquid equilibrium with the LCVm model: a linear combination of the Vidal and Michelsen mixing rules coupled with the original UNIF. *Fluid Phase Equilibria* **92**, 75–106 (1994).
169. Kontogeorgis, G. M., Fredenslund, A. & Tassios, D. P. Simple activity coefficient model for the prediction of solvent activities in polymer solutions. *Industrial & Engineering Chemistry Research* **32**, 362–372 (1993).
170. Elbro, H., Fredenslund, A. & Rasmussen, P. A new simple equation for the prediction of solvent activities in polymer solutions. *Macromolecules* **23**, 4707–4714 (1990).
171. Oishi, T. & Prausnitz, J. M. Estimation of solvent activities in polymer solutions using a group-contribution method. *Industrial & Engineering Chemistry Process Design and Development* **17**, 333–339 (1978).

172. Sanchez, I. C. & Lacombe, R. H. Statistical thermodynamics of polymer solutions. *Macromolecules* **11**, 1145–1156 (1978).
173. Kiran, E., Xiong, Y. & Zhuang, W. Modeling polyethylene solutions in near and supercritical fluids using the Sanchez-Lacombe model. *The Journal of Supercritical Fluids* **6**, 193–203 (1993).
174. Wang, W., Tree, D. & High, M. A comparison of lattice-fluid models for the calculation of the liquid-liquid equilibria of polymer solutions. *Fluid Phase Equilibria* **114**, 47–62 (1996).
175. Orbey, H., Bokis, C. P. & Chen, C.-C. Polymer- solvent vapor- liquid equilibrium: Equations of state versus activity coefficient models. *Industrial & Engineering Chemistry Research* **37**, 1567–1573 (1998).
176. Trumpi, H., De Loos, T. W., Krenz, R. & Heidemann, R. High pressure phase equilibria in the system linear low density polyethylene+ ethylene: experimental results and modelling. *The Journal of Supercritical Fluids* **27**, 205–214 (2003).
177. Gross, J. & Sadowski, G. Modeling polymer systems using the perturbed-chain statistical associating fluid theory equation of state. *Industrial & Engineering Chemistry Research* **41**, 1084–1093 (2002).
178. Gross, J., Spuhl, O., Tumakaka, F. & Sadowski, G. Modeling copolymer systems using the perturbed-chain SAFT equation of state. *Industrial & Engineering Chemistry Research* **42**, 1266–1274 (2003).
179. Von Solms, N., Kouskoumvekaki, I. A., Lindvig, T., Michelsen, M. L. & Kontogeorgis, G. M. A novel approach to liquid–liquid equilibrium in polymer systems with application to simplified PC-SAFT. *Fluid Phase Equilibria* **222**, 87–93 (2004).
180. Tihic, A., Kontogeorgis, G. M., von Solms, N., Michelsen, M. L. & Constantinou, L. A predictive group-contribution simplified PC-SAFT equation of state: Application to polymer systems. *Industrial & Engineering Chemistry Research* **47**, 5092–5101 (2007).

181. Guerrieri, Y., Pontes, K. V., Costa, G. M. N. & Embirucu, M. in *Polymerization* (InTech, 2012).
182. Lobanova, O., Mejía, A., Jackson, G. & Müller, E. A. SAFT- γ force field for the simulation of molecular fluids 6: Binary and ternary mixtures comprising water, carbon dioxide, and n-alkanes. *The Journal of Chemical Thermodynamics* **93**, 320–336 (2016).
183. Mastny, E. A. & de Pablo, J. J. Melting line of the Lennard-Jones system, infinite size, and full potential. *The Journal of Chemical Physics* **127**, 104504 (2007).
184. Auaullee, L *et al.* Gsaft: Application of the SAFT- γ mie group contribution EoS in the Oil/Gas Industry - From academic research to industrial deployment. *AIChE 2012 - 2012 AIChE Annual Meeting, Conference Proceedings* (2012).
185. Rodgers, P. A. Pressure–volume–temperature relationships for polymeric liquids: a review of equations of state and their characteristic parameters for 56 polymers. *Journal of Applied Polymer Science* **48**, 1061–1080 (1993).
186. Sanchez, I. C. & Lacombe, R. H. An elementary molecular theory of classical fluids. Pure fluids. *The Journal of Physical Chemistry* **80**, 2352–2362 (1976).
187. Sanchez, I. C. & Lacombe, R. H. An elementary equation of state for polymer liquids. *Journal of Polymer Science: Polymer Letters Edition* **15**, 71–75 (1977).
188. LINSTORM, P. NIST Chemistry WebBook, NIST Standard Reference Database Number 69. *J. Phys. Chem. Ref. Data, Monograph* **9**, 1–1951 (1998).
189. Mejía, A., Herdes, C. & Müller, E. A. Force Fields for Coarse-Grained Molecular Simulations from a Corresponding States Correlation. *Industrial & Engineering Chemistry Research* **53**, 4131–4141 (2014).
190. De Loos, T. W., Poot, W & Lichtenthaler, R. Fluid Phase Equilibria in Binary Ethylene+ n-Alkane Systems. *Berichte der Bunsengesellschaft für physikalische Chemie* **88**, 855–859 (1984).
191. Tourino, A, Hervello, M, Moreno, V, Iglesias, M & Marino, G. Thermodynamics of binary mixtures of aliphatic linear alkanes (C6–C12) at 298.15 K. *Physics and Chemistry of Liquids* **42**, 37–51 (2004).

192. Surana, R. K., Danner, R. P., de Haan, A. & Beckers, N. New technique to measure high-pressure and high-temperature polymer-solvent vapor-liquid equilibrium. *Fluid Phase Equilibria* **139**, 361–370 (1997).
193. Schwarz, C. & Nieuwoudt, I. Phase equilibrium of propane and alkanes part II: hexatriacontane through hexacontane. *The Journal of Supercritical Fluids* **27**, 145–156 (2003).
194. Xiong, Y. & Kiran, E. Comparison of Sanchez–Lacombe and SAFT model in predicting solubility of polyethylene in high-pressure fluids. *Journal of Applied Polymer Science* **55**, 1805–1818 (1995).
195. Liu, D. D. & Prausnitz, J. M. Solubilities of gases and volatile liquids in polyethylene and in ethylene-vinyl acetate copolymers in the region 125–225 C. *Industrial & Engineering Chemistry Fundamentals* **15**, 330–335 (1976).
196. De Loos, T. W., Poot, W & Diepen, G. Fluid phase equilibria in the system polyethylene+ ethylene. 1. Systems of linear polyethylene+ ethylene at high pressure. *Macromolecules* **16**, 111–117 (1983).
197. Kwei, T. & Wang, T. in *Polymer Blends, Volume 1* 141–184 (Elsevier, 1978).
198. Martin, T. M., Lateef, A. A. & Roberts, C. B. Measurements and modeling of cloud point behavior for polypropylene/n-pentane and polypropylene/n-pentane/carbon dioxide mixtures at high pressure. *Fluid Phase Equilibria* **154**, 241–259 (1999).
199. Besserer, G. J. & Robinson, D. B. Equilibrium-phase properties of n-pentane-carbon dioxide system. *Journal of Chemical and Engineering Data* **18**, 416–419 (1973).
200. Whaley, P., Winter, H. & Ehrlich, P. Phase equilibria of polypropylene with compressed propane and related systems. 1. Isotactic and atactic polypropylene with propane and propylene. *Macromolecules* **30**, 4882–4886 (1997).
201. Sandler, S. I. *Models for thermodynamic and phase equilibria calculations* (Dekker, 1994).

202. Delmas, G. & De Saint-Romain, P. Upper and lower critical solution temperatures in polybutadiene-alkane systems: Effect of the surface-to-volume ratio of the polymer. *European Polymer Journal* **10**, 1133–1140 (1974).
203. Kouskoumvekaki, I. A., von Solms, N., Lindvig, T., Michelsen, M. L. & Kontogeorgis, G. M. Novel method for estimating pure-component parameters for polymers: application to the PC-SAFT equation of state. *Industrial & Engineering Chemistry Research* **43**, 2830–2838 (2004).
204. Zeman, L & Patterson, D. Pressure effects in polymer solution phase equilibria. II. Systems showing upper and low critical solution temperatures. *The Journal of Physical Chemistry* **76**, 1214–1219 (1972).
205. Sadeqzadeh, M. *et al.* The development of unlike induced association-site models to study the phase behaviour of aqueous mixtures comprising acetone, alkanes and alkyl carboxylic acids with the SAFT- γ Mie group contribution methodology. *Fluid Phase Equilibria* **407**, 39–57 (2016).
206. Cowie, J. & McEwen, I. Polymer-cosolvent systems: 5. Upper and lower critical solution temperatures of polystyrene in n-alkanes. *Polymer* **24**, 1445–1448 (1983).
207. Krichevskii, I. & Sorina, G. Liquid-gas phase equilibria in the cyclohexane-carbon dioxide and cyclohexane-nitrous oxide systems. *Russ. J. Phys. Chem* **34**, 679 (1960).
208. Al-Sahhaf, T. A., Al-Ameeri, R. S. & Hamam, S. E. Bubble point measurements for the ternary system: carbon dioxide, cyclohexane and naphthalene. *Fluid Phase Equilibria* **53**, 31–37 (1989).
209. Barrick, M. W., Anderson, J. M. & Robinson Jr, R. L. Solubilities of carbon dioxide in cyclohexane and trans-decalin at pressures to 10.7 MPa and temperatures from 323 to 423 K. *Journal of Chemical and Engineering Data* **31**, 172–175 (1986).
210. Saeki, S, Kuwahara, N, Konno, S & Kaneko', M. Upper and lower critical solution temperatures in polystyrene solutions. *Macromolecules* **6**, 246–250 (1973).
211. Bungert, B. Komplexe Phasengleichgewichte von Polymerlösungen. *Ph.D. Dissertation* (1998).

212. Jeon, H., Nakatani, A., Han, C. C. & Colby, R. Melt rheology of lower critical solution temperature polybutadiene/polyisoprene blends. *Macromolecules* **33**, 9732–9739 (2000).
213. Voutsas, E. C., Pappa, G. D., Boukouvalas, C. J., Magoulas, K. & Tassios, D. P. Miscibility in binary polymer blends: correlation and prediction. *Industrial & Engineering Chemistry Research* **43**, 1312–1321 (2004).
214. Theodorou, D. N. & Suter, U. W. Atomistic modeling of mechanical properties of polymeric glasses. *Macromolecules* **19**, 139–154 (1986).
215. Mavrantzas, V. G., Boone, T. D., Zervopoulou, E. & Theodorou, D. N. End-bridging Monte Carlo: A fast algorithm for atomistic simulation of condensed phases of long polymer chains. *Macromolecules* **32**, 5072–5096 (1999).
216. Harmandaris, V. *et al.* Crossover from the rouse to the entangled polymer melt regime: signals from long, detailed atomistic molecular dynamics simulations, supported by rheological experiments. *Macromolecules* **36**, 1376–1387 (2003).
217. Tsolou, G., Mavrantzas, V. G. & Theodorou, D. N. Detailed atomistic molecular dynamics simulation of cis-1, 4-poly (butadiene). *Macromolecules* **38**, 1478–1492 (2005).
218. Harmandaris, V. A., Mavrantzas, V. G. & Theodorou, D. N. Atomistic molecular dynamics simulation of polydisperse linear polyethylene melts. *Macromolecules* **31**, 7934–7943 (1998).
219. Karanikas, S. & Economou, I. G. Molecular simulation of structure, thermodynamic and transport properties of polyacrylonitrile, polystyrene and their alternating copolymers in high temperatures. *European Polymer Journal* **47**, 735–745 (2011).
220. Moore, J., Cui, S., Cochran, H. & Cummings, P. A molecular dynamics study of a short-chain polyethylene melt.: I. steady-state shear. *Journal of Non-Newtonian Fluid Mechanics* **93**, 83–99 (2000).

221. Milano, G., Goudeau, S. & Müller-Plathe, F. Multicentered Gaussian-based potentials for coarse-grained polymer simulations: Linking atomistic and mesoscopic scales. *Journal of Polymer Science Part B: Polymer Physics* **43**, 871–885 (2005).
222. Tschöp, W., Kremer, K., Batoulis, J., Bürger, T. & Hahn, O. Simulation of polymer melts. I. Coarse-graining procedure for polycarbonates. *Acta Polymerica* **49**, 61–74 (1998).
223. Praprotnik, M., Site, L. D. & Kremer, K. Multiscale simulation of soft matter: From scale bridging to adaptive resolution. *Annu. Rev. Phys. Chem.* **59**, 545–571 (2008).
224. Qian, H.-J. *et al.* Temperature-transferable coarse-grained potentials for ethylbenzene, polystyrene, and their mixtures. *Macromolecules* **41**, 9919–9929 (2008).
225. Peter, C. & Kremer, K. Multiscale simulation of soft matter systems—from the atomistic to the coarse-grained level and back. *Soft Matter* **5**, 4357–4366 (2009).
226. Sun, Q. & Faller, R. Systematic coarse-graining of atomistic models for simulation of polymeric systems. *Computers & Chemical Engineering* **29**, 2380–2385 (2005).
227. Meyer, H., Biermann, O., Faller, R., Reith, D. & Müller-Plathe, F. Coarse grain-ing of nonbonded inter-particle potentials using automatic simplex optimization to fit structural properties. *The Journal of Chemical Physics* **113**, 6264–6275 (2000).
228. Hahn, O., Site, L. D. & Kremer, K. Simulation of polymer melts: From spherical to ellipsoidal beads. *Macromolecular Theory and Simulations* **10**, 288–303 (2001).
229. Sun, Q. & Faller, R. Systematic coarse-graining of a polymer blend: Polyisoprene and polystyrene. *Journal of Chemical Theory and Computation* **2**, 607–615 (2006).
230. Megariotis, G., Vyrkou, A., Leygue, A. & Theodorou, D. N. Systematic coarse graining of 4-cyano-4-pentylbiphenyl. *Industrial & Engineering Chemistry Research* **50**, 546–556 (2010).

231. Fischer, J., Paschek, D., Geiger, A. & Sadowski, G. Modeling of aqueous poly (oxyethylene) solutions. 2. Mesoscale simulations. *The Journal of Physical Chemistry B* **112**, 13561–13571 (2008).
232. Wu, C. Phase Morphologies of Binary Polymer Blends Predicted by Systematically Coarse-Grained Models. *Macromolecular Theory and Simulations* **25**, 336–347 (2016).
233. Rossi, G, Fuchs, P., Barnoud, J & Monticelli, L. A coarse-grained MARTINI model of polyethylene glycol and of polyoxyethylene alkyl ether surfactants. *The Journal of Physical Chemistry B* **116**, 14353–14362 (2012).
234. Nawaz, S. & Carbone, P. Coarse-graining poly (ethylene oxide)–poly (propylene oxide)–poly (ethylene oxide)(PEO–PPO–PEO) block copolymers using the MARTINI force field. *The Journal of Physical Chemistry B* **118**, 1648–1659 (2014).
235. Gromov, D. G., de Pablo, J. J., Luna-Bárcenas, G., Sanchez, I. C. & Johnston, K. P. Simulation of phase equilibria for polymer–supercritical solvent mixtures. *The Journal of Chemical Physics* **108**, 4647–4653 (1998).
236. Jiménez-Serratos, G., Herdes, C., Haslam, A. J., Jackson, G. & Müller, E. A. Group Contribution Coarse-Grained Molecular Simulations of Polystyrene Melts and Polystyrene Solutions in Alkanes Using the SAFT- γ Force Field. *Macromolecules* **50**, 4840–4853 (2017).
237. Jorgensen, W. L., Maxwell, D. S. & Tirado-Rives, J. Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids. *Journal of the American Chemical Society* **118**, 11225–11236 (1996).
238. Pronk, S. *et al.* GROMACS 4.5: a high-throughput and highly parallel open source molecular simulation toolkit. *Bioinformatics* **29**, 845–854 (2013).
239. Hess, B., Kutzner, C., Van Der Spoel, D. & Lindahl, E. GROMACS 4: algorithms for highly efficient, load-balanced, and scalable molecular simulation. *Journal of Chemical Theory and Computation* **4**, 435–447 (2008).

240. Abraham, M. J. *et al.* GROMACS: High performance molecular simulations through multi-level parallelism from laptops to supercomputers. *SoftwareX* **1**, 19–25 (2015).
241. Herdes, C., Totton, T. S. & Müller, E. A. Coarse grained force field for the molecular simulation of natural gases and condensates. *Fluid Phase Equilibria* **406**, 91–100 (2015).
242. Nosé, S. A molecular dynamics method for simulations in the canonical ensemble. *Molecular Physics* **52**, 255–268 (1984).
243. Hoover, W. G. Canonical dynamics: equilibrium phase-space distributions. *Physical Review A* **31**, 1695 (1985).
244. Parrinello, M. & Rahman, A. Polymorphic transitions in single crystals: A new molecular dynamics method. *Journal of Applied physics* **52**, 7182–7190 (1981).
245. Nosé, S. & Klein, M. Constant pressure molecular dynamics for molecular systems. *Molecular Physics* **50**, 1055–1076 (1983).
246. Gelb, L. D. & Müller, E. A. Location of phase equilibria by temperature-quench molecular dynamics simulations. *Fluid Phase Equilibria* **203**, 1–14 (2002).
247. Foteinopoulou, K., Karayiannis, N. C., Laso, M. & Kröger, M. Structure, dimensions, and entanglement statistics of long linear polyethylene chains. *The Journal of Physical Chemistry B* **113**, 442–455 (2008).
248. Tzounis, P.-N., Anogiannakis, S. D. & Theodorou, D. N. General Methodology for Estimating the Stiffness of Polymer Chains from Their Chemical Constitution: A Single Unperturbed Chain Monte Carlo Algorithm. *Macromolecules* **50**, 4575–4587 (2017).
249. Smit, B., Karaborni, S. & Siepmann, J. I. Computer simulations of vapor–liquid phase equilibria of n-alkanes. *The Journal of Chemical Physics* **102**, 2126–2140 (1995).
250. Paul, W., Yoon, D. Y. & Smith, G. D. An optimized united atom model for simulations of polymethylene melts. *The Journal of Chemical Physics* **103**, 1702–1709 (1995).

251. Logotheti, G. E. & Theodorou, D. N. Segmental and chain dynamics of isotactic polypropylene melts. *Macromolecules* **40**, 2235–2245 (2007).
252. Heine, D., Wu, D. T., Curro, J. G. & Grest, G. S. Role of intramolecular energy on polyolefin miscibility: Isotactic polypropylene/polyethylene blends. *The Journal of Chemical Physics* **118**, 914–924 (2003).
253. Hadjichristidis, N., Zhongde, X., Fetters, L. & Roovers, J. The characteristic ratios of stereoirregular polybutadiene and polyisoprene. *Journal of Polymer Science: Polymer Physics Edition* **20**, 743–750 (1982).
254. Gestoso, P., Nicol, E., Doxastakis, M. & Theodorou, D. Atomistic Monte Carlo simulation of polybutadiene isomers: cis-1,4-polybutadiene and 1,2-polybutadiene. *Macromolecules* **36**, 6925–6938 (2003).
255. Mark, J. E. *et al.* Polymer data handbook (2009).
256. Chen, S.-j., Banaszak, M. & Radosz, M. Phase behavior of poly (ethylene-1-butene) in subcritical and supercritical propane: ethyl branches reduce segment energy and enhance miscibility. *Macromolecules* **28**, 1812–1817 (1995).
257. De Loos, T. W., Poot, W. & Lichtenthaler, R. The influence of branching on high-pressure vapor-liquid equilibria in systems of ethylene and polyethylene. *The Journal of Supercritical Fluids* **8**, 282–286 (1995).
258. Han, S., Lohse, D., Radosz, M. & Sperling, L. Short chain branching effect on the cloud-point pressures of ethylene copolymers in subcritical and supercritical propane. *Macromolecules* **31**, 2533–2538 (1998).
259. Van Vliet, R. E., Hoefsloot, H. C. & Iedema, P. D. Mesoscopic simulation of polymer-solvent phase separation: linear chain behaviour and branching effects. *Polymer* **44**, 1757–1763 (2003).
260. Cheng, H. *et al.* Effect of degree of branching on the thermoresponsive phase transition behaviors of hyperbranched multiarm copolymers: comparison of systems with lcst transition based on coil-to-globule transition or hydrophilic-hydrophobic balance. *The Journal of Physical Chemistry B* **114**, 6291–6299 (2010).

261. Walker, C. C., Genzer, J. & Santiso, E. E. Development of a fused-sphere SAFT- γ Mie force field for poly (vinyl alcohol) and poly (ethylene). *The Journal of chemical physics* **150**, 034901 (2019).
262. Fakirov, S & Krasteva, B. On the glass transition temperature of polyethylene as revealed by microhardness measurements. *Journal of Macromolecular Science, Part B* **39**, 297–301 (2000).
263. Stehling, F. C. & Mandelkern, L. The glass temperature of linear polyethylene. *Macromolecules* **3**, 242–252 (1970).
264. Nies, C. & Messing, G. L. Effect of glass-transition temperature of polyethylene glycol-plasticized polyvinyl alcohol on granule compaction. *Journal of the American Ceramic Society* **67**, 301–304 (1984).
265. Bu, H.-S., Cheng, S. Z. & Wunderlich, B. Addendum to the thermal properties of polypropylene. *Die Makromolekulare Chemie, Rapid Communications* **9**, 75–77 (1988).
266. Zemke, K, Chmelka, B., Schmidt-Rohr, K & Spiess, H. Conformational exchange near the glass transition: two-dimensional carbon-13 NMR study of atactic polypropylene. *Macromolecules* **24**, 6874–6876 (1991).
267. Richter, D, Frick, B & Farago, B. Neutron-spin-echo investigation on the dynamics of polybutadiene near the glass transition. *Physical review letters* **61**, 2465 (1988).
268. Frick, B, Farago, B & Richter, D. Temperature dependence of the nonergodicity parameter in polybutadiene in the neighborhood of the glass transition. *Physical Review Letters* **64**, 2921 (1990).
269. Rieger, J. The glass transition temperature of polystyrene. *Journal of Thermal Analysis* **46**, 965–972 (1996).
270. Whitesides, G. M., Mathias, J. P. & Seto, C. T. *Molecular self-assembly and nanochemistry: a chemical strategy for the synthesis of nanostructures* tech. rep. (DTIC Document, 1991).
271. Lindoy, L. F. & Atkinson, I. M. *Self-assembly in supramolecular systems* **7** (Royal Society of Chemistry, 2000).

272. Damasceno, P. F., Engel, M. & Glotzer, S. C. Predictive self-assembly of polyhedra into complex structures. *Science* **337**, 453–457 (2012).
273. Polshettiwar, V., Baruwati, B. & Varma, R. S. Self-assembly of metal oxides into three-dimensional nanostructures: synthesis and application in catalysis. *ACS nano* **3**, 728–736 (2009).
274. Pluth, M. D., Bergman, R. G. & Raymond, K. N. Proton-mediated chemistry and catalysis in a self-assembled supramolecular host. *Accounts of Chemical Research* **42**, 1650–1659 (2009).
275. Van Haaren, J & Broer, D. In search of the perfect image. *Chemistry and Industry* **24**, 1017–1021 (1998).
276. De Miguel, E. & Vega, C. The global phase diagram of the Gay–Berne model. *The Journal of Chemical Physics* **117**, 6313–6322 (2002).
277. Van Westen, T., Oyarzún, B., Vlugt, T. J. & Gross, J. An analytical equation of state for describing isotropic-nematic phase equilibria of Lennard-Jones chain fluids with variable degree of molecular flexibility. *The Journal of Chemical Physics* **142**, 244903 (2015).
278. Oyarzún, B., van Westen, T. & Vlugt, T. J. The phase behavior of linear and partially flexible hard-sphere chain fluids and the solubility of hard spheres in hard-sphere chain fluids. *The Journal of Chemical Physics* **138**, 204905 (2013).
279. Kölbel, M. *et al.* Design of liquid crystalline block molecules with nonconventional mesophase morphologies: calamitic bolaamphiphiles with lateral alkyl chains. *Journal of the American Chemical Society* **123**, 6809–6818 (2001).
280. Prehm, M. *et al.* Distinct columnar and lamellar liquid crystalline phases formed by new bolaamphiphiles with linear and branched lateral hydrocarbon chains. *Chemistry—A European Journal* **14**, 6352–6368 (2008).
281. Cheng, X. *et al.* Calamitic bolaamphiphiles with (semi) perfluorinated lateral chains: polyphilic block molecules with new liquid crystalline phase structures. *Journal of the American Chemical Society* **125**, 10977–10996 (2003).

282. Cheng, X., Das, M. K., Baumeister, U., Diele, S. & Tschierske, C. Liquid crystalline bolaamphiphiles with semiperfluorinated lateral chains: competition between layerlike and honeycomb-like organization. *Journal of the American Chemical Society* **126**, 12930–12940 (2004).
283. Cheng, X. *et al.* Influence of flexible spacers on liquid-crystalline self-assembly of T-shaped bolaamphiphiles. *Journal of the American Chemical Society* **133**, 7872–7881 (2011).
284. Glettner, B. *et al.* Liquid-Crystal Engineering with Anchor-Shaped Molecules: Honeycombs with Hexagonal and Trigonal Symmetries Formed by Polyphilic Bent-Core Molecules. *Angewandte Chemie International Edition* **47**, 6080–6083 (2008).
285. Prehm, M. *et al.* The Giant-Hexagon Cylinder Network—A Liquid-Crystalline Organization Formed by a T-Shaped Quaternary Amphiphile. *Angewandte Chemie International Edition* **46**, 7972–7975 (2007).
286. Liu, F., Prehm, M., Zeng, X., Tschierske, C. & Ungar, G. Skeletal cubic, lamellar, and ribbon phases of bundled thermotropic bolapolyphiles. *Journal of the American Chemical Society* **136**, 6846–6849 (2014).
287. Zeng, X., Prehm, M., Ungar, G., Tschierske, C. & Liu, F. Formation of a Double Diamond Cubic Phase by Thermotropic Liquid Crystalline Self-Assembly of Bundled Bolaamphiphiles. *Angewandte Chemie* **128**, 8464–8467 (2016).
288. Chen, B., Zeng, X., Baumeister, U., Ungar, G. & Tschierske, C. Liquid crystalline networks composed of pentagonal, square, and triangular cylinders. *Science* **307**, 96–99 (2005).
289. Kieffer, R. *et al.* Siloxanes and carbosilanes as new building blocks for T-shaped bolaamphiphilic LC molecules. *Soft Matter* **5**, 1214–1227 (2009).
290. Ungar, G. *et al.* Self-Assembly at Different Length Scales: Polyphilic Star-Branched Liquid Crystals and Miktoarm Star Copolymers. *Advanced Functional Materials* **21**, 1296–1323 (2011).
291. Tschierske, C. *et al.* Complex tiling patterns in liquid crystals. *Interface Focus* **2**, 669–680 (2012).

292. Zeng, X. *et al.* Complex multicolor tilings and critical phenomena in tetraphilic liquid crystals. *Science* **331**, 1302–1306 (2011).
293. Crane, A. J., Martínez-Veracoechea, F. J., Escobedo, F. A. & Müller, E. A. Molecular dynamics simulation of the mesophase behaviour of a model bolaamphiphilic liquid crystal with a lateral flexible chain. *Soft Matter* **4**, 1820–1829 (2008).
294. Crane, A. J. & Müller, E. A. Self-assembly of T-shaped polyphilic molecules in solvent mixtures. *The Journal of Physical Chemistry B* **115**, 4592–4605 (2011).
295. Bates, M. A. & Walker, M. Dissipative particle dynamics simulation of quaternary bolaamphiphiles: multi-colour tiling in hexagonal columnar phases. *Physical Chemistry Chemical Physics* **11**, 1893–1900 (2009).
296. Bates, M. & Walker, M. Dissipative particle dynamics simulation of T-and X-shaped polyphilic molecules exhibiting honeycomb columnar phases. *Soft Matter* **5**, 346–353 (2009).
297. Bates, M. A. & Walker, M. Computer simulation of the columnar phases of liquid crystalline bolaamphiphiles. *Liquid Crystals* **38**, 1749–1757 (2011).
298. Bates, M. A. & Walker, M. Computer simulation of the pentagonal columnar phase of liquid crystalline bolaamphiphiles. *Molecular Crystals and Liquid Crystals* **525**, 204–211 (2010).
299. Liu, X., Yang, K. & Guo, H. Dissipative Particle dynamics simulation of the phase behavior of T-Shaped ternary amphiphiles possessing rodlike mesogens. *The Journal of Physical Chemistry B* **117**, 9106–9120 (2013).
300. Liu, F., Tang, P., Zhang, H. & Yang, Y. Archimedean Tiling Patterns Self-Assembled from X-Shaped Rod-Coil Copolymers with Hydrogen Bonds. *Macromolecules* **51**, 7807–7816 (2018).
301. Poppe, S. *et al.* Zeolite-like liquid crystals. *Nature communications* **6**, 8637 (2015).
302. Sun, Y., Padmanabhan, P., Misra, M. & Escobedo, F. A. Molecular dynamics simulation of thermotropic bolaamphiphiles with a swallow-tail lateral chain: formation of cubic network phases. *Soft Matter* **13**, 8542–8555 (2017).

303. Stubbs, J. M., Potoff, J. J. & Siepmann, J. I. Transferable potentials for phase equilibria. 6. United-atom description for ethers, glycols, ketones, and aldehydes. *The Journal of Physical Chemistry B* **108**, 17596–17605 (2004).
304. Avendaño, C. & Müller, E. A. Liquid crystalline behavior of a coarse-grained model of shape-persistent macrocycles with flexible attractive chains. *Soft Matter* **7**, 1694–1701 (2011).
305. Saupe, A. Recent results in the field of liquid crystals. *Angewandte Chemie International Edition in English* **7**, 97–112 (1968).
306. Allen, M. P., Evans, G. T., Frenkel, D. & Mulder, B. Hard convex body fluids. *Advances in Chemical Physics* **86**, 1–166 (1993).
307. Low, R. J. Measuring order and biaxiality. *European Journal of Physics* **23**, 111 (2002).
308. Humphrey, W., Dalke, A. & Schulten, K. VMD: visual molecular dynamics. *Journal of Molecular Graphics* **14**, 33–38 (1996).
309. Linstrom, P. J. & Mallard, W. G. The NIST Chemistry WebBook: A chemical data resource on the internet. *Journal of Chemical & Engineering Data* **46**, 1059–1063 (2001).
310. Pierotti, G., Deal, C. & Derr, E. Activity coefficients and molecular structure. *Industrial & Engineering Chemistry* **51**, 95–102 (1959).
311. Staveley, L. & Milward, G. 874. Solutions of alcohols in non-polar solvents. Part IV. Some thermodynamic properties of glycols in benzene, heptane, and cyclohexane. *Journal of the Chemical Society (Resumed)*, 4369–4375 (1957).
312. Prausnitz, J. M., Lichtenthaler, R. N. & de Azevedo, E. G. *Molecular thermodynamics of fluid-phase equilibria* (Pearson Education, 1998).
313. Rowley, R. *et al.* DIPPR data compilation of pure chemical properties. *Design Institute for Physical Properties* (2006).
314. Papaioannou, V. *et al.* Application of the SAFT- γ Mie group contribution equation of state to fluids of relevance to the oil and gas industry. *Fluid Phase Equilibria* **416**, 104–119 (2016).

315. Lecat, M. M. A. *Tables azéotropiques: Azéotropes binaires orthobares* (chez l'auteur, 1949).
316. NguyenHuynh, D. Correlation and prediction of liquid–liquid equilibria for alcohol/hydrocarbon mixtures using PC-SAFT equation of state at high pressure up to 150 MPa. *Fluid Phase Equilibria* **425**, 206–214 (2016).
317. Petersen, J. E. *Azeotropic distillation* US Patent 2,360,685. Oct. 1944.
318. Martin, M. G. & Siepmann, J. I. Transferable potentials for phase equilibria. 1. United-atom description of n-alkanes. *The Journal of Physical Chemistry B* **102**, 2569–2577 (1998).
319. Lobanova, O., Avendaño, C., Lafitte, T., Müller, E. A. & Jackson, G. SAFT- γ force field for the simulation of molecular fluids: 4. A single-site coarse-grained model of water applicable over a wide temperature range. *Molecular Physics* **113**, 1228–1249 (2015).
320. Vega, C., McBride, C. & MacDowell, L. G. Liquid crystal phase formation for the linear tangent hard sphere model from Monte Carlo simulations. *The Journal of Chemical Physics* **115**, 4203–4211 (2001).
321. Van Westen, T. Development of an equation of state for nematic liquid crystals (2015).
322. Poser, C. I. & Sanchez, I. C. Surface tension theory of pure liquids and polymer melts. *Journal of Colloid and Interface Science* **69**, 539–548 (1979).
323. Müller, E. A. & Mejía, A. Extension of the SAFT-VR Mie EoS to model homonuclear rings and its parameterization based on the principle of corresponding states. *Langmuir* (2017).
324. Wand, C., Fayaz-Torshizi, M, Jimenez-Serratos, G, Müller, E. & Frenkel, D. Solubilities of pyrene in organic solvents: Comparison between chemical potential calculations using a cavity-based method and direct coexistence simulations. *The Journal of Chemical Thermodynamics* **131**, 620–629 (2019).
325. Ziogos, O. G. & Theodorou, D. N. Molecular dynamics simulations of alkyl substituted nanographene crystals. *Molecular Physics* **113**, 2776–2790 (2015).

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326. Jin, W. *et al.* Systematic studies on structural parameters for nanotubular assembly of hexa-peri-hexabenzocoronenes. *Journal of the American Chemical Society* **130**, 9434–9440 (2008).