

Molecular Physics

An International Journal at the Interface Between Chemistry and Physics

ISSN: (Print) (Online) Journal homepage: www.tandfonline.com/journals/tmph20

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To cite this article: Andrew J. Crane & Erich A. Müller (2024) Phase diagram of a rigid rod system with attractive end groups, Molecular Physics, 122:21-22, e2327528, DOI: 10.1080/00268976.2024.2327528

To link to this article: <https://doi.org/10.1080/00268976.2024.2327528>



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Phase diagram of a rigid rod system with attractive end groups

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ABSTRACT

We present a molecular dynamics study into the thermotropic liquid crystalline phase behaviour of a coarse-grained model of a rigid bolaamphiphilic molecule. The model consists of 11 spherical beads held in a fixed linear arrangement, where the two opposing terminal beads are self-attracting, mimicking hydrophilic segments and the remaining internal beads, as well as cross-bead interactions, are softly repulsive, mimicking hydrophobic organic segments. The effect of the model's end bead self-attraction strength on liquid crystalline phase behaviour is studied. Coexistence points between the smectic A, nematic and isotropic phases exhibited by the model are determined following a thermodynamic integration pathway, using equations of state constructed by multiple histogram reweighting of simulation data. Variants of Gibbs–Duhem integration are used to trace pressure–temperature coexistence curves. Under isobaric conditions, the effect of increasing the end-group self-attraction on the nematic–isotropic coexistence temperature is relatively small; however, the nematic phase stability is reduced at the expense of a significant increase in the smectic A–nematic coexistence temperature. Lower temperature simulations show the approximate smectic A–crystalline transition temperature to be only weakly dependent on the strength of the end-group self-attraction.

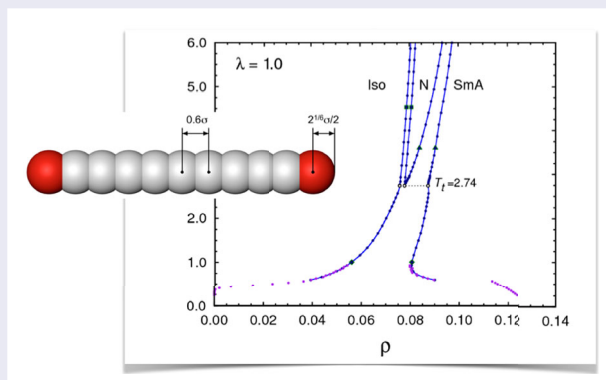
ARTICLE HISTORY

Received 22 January 2024

Accepted 3 March 2024

KEYWORDS

Liquid crystals;
bolaamphiphiles; coarse
graining



1. Introduction

Since the discovery of thermotropic liquid crystalline (LC) materials towards the end of the nineteenth century, a longstanding interest has been held in the physical origins of phases that possess structural symmetry intermediate to crystalline solids and isotropic liquids. The theoretical description of these fluids has proved challenging, hampered in part by the marked anisotropy characteristic of LC-forming fluids. Experiments suggest that most of the unusual phenomena associated with

these ordered phases have non-specific roots that relate to general overbearing, and, most often, conflicting, steric and energetic effects. Equations of state for these unique fluids are unavailable in the way they are for isotropic fluids; hence, it is in this context that molecular simulation becomes a useful tool to describe LC behaviour of model systems. While fully-atomistic molecular modelling of these fluids turns out to be computationally challenging due to the large molecule size, system sizes and time scales needed for phase self-organisation, simplified

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 Supplemental data for this article can be accessed online at <https://doi.org/10.1080/00268976.2024.2327528>.

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and coarse-grained models have been able to provide the computational speed-up necessary to study the self-assembly and complex phase behaviour of LC. The reader is referred to Wilson [1] or Care and Cleaver [2] for pertinent reviews.

Liquid crystals have been studied with angular and separation-dependent pair potentials, dramatically reducing system variables and retaining the most relevant physical features [3]. Most primitive LC models are athermal, i.e. based on hard repulsive intermolecular potentials. This proves to be a sensible approach that parallels the development of successful perturbation theories for molecular liquids [4]. For a distinct class of prolate symmetry mesogen, namely the calamitic mesogen, these coarse-grained model potentials are predominantly based around the ellipsoidal and spherocylinder geometries. Studies by Frenkel et al. were amongst the first to establish the existence of an LC phase with a hard ellipsoid model, discovering a transition from an isotropic (Iso) phase to an orientationally ordered nematic (Nem) liquid state [5,6]. Subsequent investigations into the hard ellipsoidal model proved that this model was not only capable of forming the Nem phase, but also the smectic A (SmA) phase, where the mesogens align into liquid-like layers. Another example of an LC coarse-grained model is the hard spherocylinder, uniquely defined by its length-to-diameter ratio. McGrother et al. investigated the dependence of the LC phase stability on this ratio [7] and demonstrated why early simulations by Vieillard-Baron could not detect LC phases by an unfortunately low choice of this parameter [8]. The manuscripts by Frenkel et al. explored the global phases diagram for the hard-spherocylinder [9], implementing novel techniques to study large length-to-diameter ratios and rotor solid phases that occur close to the hard-sphere limit [10]. Importantly, for large aspect ratios, the Nem–Iso transition was observed to approach the limit predicted by Onsager theory [11]. Camp et al. also found good theoretical agreement for simulations of hard ellipsoid in this limit [12–15]. One form of extension to hard potential models has been the incorporation of multiple moments, in essence representing an additional level of fundamental chemical detail. Studies into dipolar hard spherocylinders have shown LC phase stability to be highly dependent on both the position of the dipole in the hard particles, as well as the orientation of the dipole with respect to calamitic principle axis [16–18].

Examining the influence of attractions in anisotropic pair potentials has also been important towards understanding prolate mesogen phase behaviour. The Gay–Berne (GB) potential [19], has proven one of the most popular soft ellipsoidal potential since it was first proposed in the early 1970s. This potential was based on an

earlier Gaussian overlap model of Berne and Pechukas [20], adapted to replicate the resultant potential between two linear 4-site Lennard–Jones molecules. Initial simulations revealed the original GB parameterisation to form stable Nem phases under certain conditions [21–23]. Subsequent use of free energy methods allowed its global phase behaviour to be mapped through tracing the phase coexistence curves [24,25]. Whilst the GB potential has principally been a tool for understanding LC phase phenomena, it was noted that most calamitic mesogens have a larger aspect ratio than the original GB parameterisation [26]. By varying the GB parameters that control the ellipsoidal length to width ratio, the SmA phase was additionally found for longer aspect ratios [27,28]. Gay–Berne model simulations along with perturbation theory studies have clarified the role that attractive interactions play in stabilising the SmA phase for ellipsoidal geometry mesogens relative to hard ellipsoid models [29,30]. As with hard potential models, incorporation of electrostatic moments into softly repulsive models also influences LC phase stability. The influence of dipoles of various strength, relative orientation and position have been studied with the GB model. For longitudinal dipoles, SmA phase stability is enhanced when the dipole is centrally positioned [31,32], whilst Nem phase stability is enhanced when in a terminal position [33]. There has also been work into the addition of quadrupoles. For example, the smectic C phase, where the average molecular orientation is tilted with respect to the smectic layer axis, was observed by addition of a longitudinal quadrupole into the standard GB model [34]. In a similar vein, spherocylinders will exhibit a range of LC phases upon the inclusion of attractions. For an unabridged review of the current understanding the reader is referred to ref. [35].

One of the limitations of single-site asymmetric potential models is the ease at which increased molecular detail may be added to models. One approach to circumvent this, at the cost of increasing system degrees of freedom, has been a move back to using mesogen models composed of multiple spherically symmetric interaction sites. This is a curious turn of events, as in the 1970s, the GB potential was hailed as the potential of choice since it would effectively map 4 (or more) linear rigidly connected interaction sites into a single central site, thus reducing the computational by an order of magnitude. The exponential increase in computational power in the following decades has rendered this argument irrelevant, thus the trend to revert to more detailed, but still heavily coarse-grained models. This route permits the use of systematic coarse-graining techniques to parameterise the potentials using all-atom simulation [36,37] or thermodynamic data [38], thus providing a means to

more realistic mesogen models, without the computational expense of performing full all-atom simulations [39]. Like asymmetric single-site potential studies, early multiple-site mesogen models focused mainly on capturing LC phenomenology. Wilson et al. investigated the effect of mesogen flexibility for a hard-sphere chain model. Here chains of 7 sites tangentially bonded were found to exhibit Nem and smectic LC phases, whilst the 5-site chain gave rise to a metastable SmA phase only [40–42] reiterating the importance of mesogen aspect ratio towards relative LC phase stability. The reference rigid hard-sphere chain of this flexible model was subsequently studied by Williamson and Jackson [43], who overcame a previously found problem of entrapment in non-equilibrium glassy states close to the Nem-Iso transition, that resulted from non-convexity in molecular shape preventing efficient parallel rod movements [44]. They found that flexibility destabilised Nem stability and shifted the packing fraction of coexistent Nem and Iso phases to higher values. McBride and Vega extended these studies to fused hard sphere systems with partial flexibility, where they observed partial flexibility to have a noticeable influence on smectic-type phase stability [45]. Work has also been performed on analogous soft potentials rod systems. Ciccotti and coworkers found the presence of both SmA and Nem mesophases for an 11-site linear rod model interacting through the repulsive part of a Lennard-Jones potential [46]. Using the combined approach of TI and Gibbs-Duhem integration, similar to that of Frenkel and Bolhuis [10], the Nem-Iso and SmA-Nem coexistence curves were mapped for this system by Tian et al. [47]. Based on this, it was suggested that the system exhibited crystalline-SmA-Nem and crystalline-Nem-Iso triple points. A subsequent study showed that turning on the attractive part of the Lennard-Jones interaction stabilised the more ordered phases, thus isobarically shifting the coexistence curves to higher temperatures [48]. This behaviour was noted to be in accord with actual LC behaviour. The effect of flexibility on a similar model has also been explored and was found to suppress the Nem phase [49]. Other models have explored shorter Lennard-Jones linear chains [50,51]. In the same way as single local attractive sites may significantly alter mesogenic phase behaviour of repulsive rod systems, the presence of pairs of attractive sites also imparts significant changes in the overall phase diagram.

This manuscript concerns to bolaamphiphiles, LC molecules with two hydrophilic heads and a hydrophobic linker. This unique structure allows them to self-assemble into various nanostructures, including micelles, vesicles and liquid crystals [52–54]. They are an emerging class of molecules with recent applications as templates for

the formation of nanomaterials [55] and in biomedicine [56]. In particular, we focus here on a rigid linear mesogen model, an otherwise repulsive rigid rod, decorated with self-attractive sites at both ends of the molecule. The two terminal beads interact by a variable-strength pair potential similar in form to the Lennard-Jones potential, whilst all remaining internal beads and cross-pair interactions are softly repulsive. Such a model represents the underlying core of more complex polyphilic liquid crystals composed of a rigid bolaamphiphile decorated with a side chain [57–62]. These polyphilic molecules have been studied using molecular simulations and shown to exhibit a very rich self-assembly of motifs including columnar phases with cross-sections having different 2D patterns depending on the size of the lateral chains and ordered bi- and co-continuous phases, giant honeycomb phases and lamellar phases [63–71].

2. Molecular model

To achieve LC phase behaviour, even in the absence of attractions, a mesogen model is chosen as a rigid linear configuration of 11 beads, with a 0.6σ inter-bead distance, with σ being a model characteristic length, roughly a bead diameter. This separation, or bond distance, represented a balance between being sufficiently short as to prevent unphysical crossing of rods, whilst being adequately long, to obtain the required aspect ratio with a minimal number of rod beads. The resulting mesogenic core had an aspect ratio of 7; mesophases would be expected for this ratio [46], and this was confirmed by simulation, with the SmA and Nem phases found for the purely repulsive system. To mimic bolaamphiphilic behaviour, the two end beads of the rigid unit were defined as self-attractive, mimicking strongly interacting hydrogen-bonding sites, whilst the remaining pair interactions were modelled as softly repulsive, allowing the internal beads to represent weakly interacting sites typical of polyphenyl cores. A schematic of the molecular model is given in Figure 1. The bead pair potential energies, W_{AB} are defined by mixing two Lennard-Jones cut and shifted potential, W_{AB}^{LJCS} through the expressions.

$$W_{AB}(r, C_{AB}, \lambda) = \lambda W_{AB}^{LJCS}(r, C_{AB}) + (1 - \lambda) W_{AB}^{LJCS}(r, 2^{1/6}\sigma) \quad (1)$$

Where

$$W_{AB}^{LJCS}(r, C_{AB}) = \begin{cases} W_{AB}^{LJ}(r) - W_{AB}^{LJ}(C_{AB}) & \text{for } r < C_{AB} \\ 0 & \text{for } r \geq C_{AB} \end{cases} \quad (2)$$

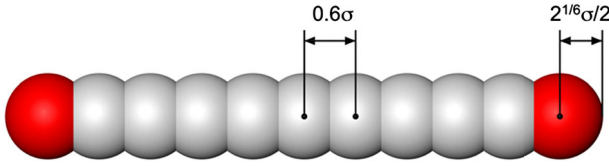


Figure 1. Schematic of the model used to describe a bolaamphiphilic type molecule. Beads are represented using the characteristic σ length. End spheres may be self-attracting.

Table 1. Table defining force field parameters used for each non-bonded pair potential, parameters listed as $(C_{AB}, \lambda_{AB}, \sigma_{AB}, \varepsilon_{AB})$.

	End bead	Internal bead
End bead	$2\sigma, 0-1, \sigma, \varepsilon$	$2^{1/6}\sigma, 1, \sigma, \varepsilon$
Internal bead	$2^{1/6}\sigma, 1, \sigma, \varepsilon$	$2^{1/6}\sigma, 1, \sigma, \varepsilon$

with W_{AB}^{LJ} being the common Lennard Jones potential.

$$W_{AB}^{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3)$$

where, the subscripts A and B define bead type, r is the bead separation, ε is the energy parameter defining the potential well depth, σ is the length parameter defining the range of the potential, C_{AB} is the cut and shifted distance, and λ is a mixing parameter that takes a value between 0 and 1. If the cut-off radius, C_{AB} , is chosen at the minimum of the potential well – i.e. $C_{AB} = 2^{1/6}\sigma$ – then W_{AB}^{LJCS} becomes a soft repulsive potential. Otherwise, the cut-off is fixed at $C_{AB} = 2\sigma$. For the internal/internal bead and end/internal bead pair interactions, λ_{AB} is fixed to 0, making these softly repulsive. For end/end bead pair interactions, the parameter, λ_{AB} , takes values between 0 and 1. When $\lambda = 0$, these pair interactions are the same as the remaining pair interactions, and the rods are softly repulsive. When $\lambda = 1$, the pair interaction is a cut and shifted Lennard–Jones potential, and the particles are self-attractive at separation between $2^{1/6}\sigma$ and C_{AB} . An illustration of the potential model used is given in Figure 2 (Table 1).

The model parameterisation is expressed in terms of a single length scale, σ , and energy scales, ε ; consequently, all properties can be presented in reduced form. To that end, the temperature is given by, $T^* = Tk_b/\varepsilon$, with k_b being the Boltzmann constant, pressure by $P^* = P\sigma^3/\varepsilon$, volume by $V^* = V/\sigma^3$, and field strength, to be defined later, by $\chi^* = \chi/\varepsilon$. For clarity, in this manuscript superscripts will be removed and all variables assumed appropriately reduced.

3. Determination of coexistence curves

To obtain the model's LC coexistence curves, individual coexistence points were initially found for the Nem–Iso

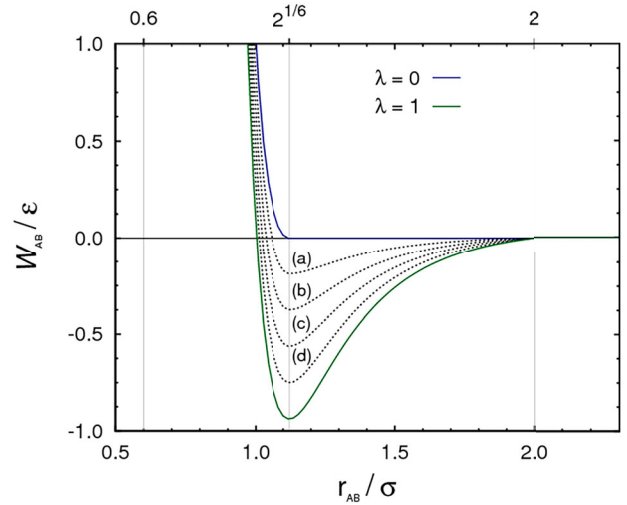


Figure 2. Plot of the bead-bead pair potentials used for the model bolaamphiphile for various interaction strengths; blue line $\lambda = 0.0$, grey dashed lines (a) $\lambda = 0.2$, (b) $\lambda = 0.4$, (c) $\lambda = 0.6$ and (d) $\lambda = 0.8$, and green line $\lambda = 1.0$. All other bead interactions (internal/internal and internal/end) correspond to $\lambda = 0.0$ (blue line).

and SmA–Nem transitions, for a specific end bead self-attraction, λ , and used as initial values for integration of the Clapeyron differential equation along TP coexistence curves [72,73]. Using a modified Clapeyron equation, the coexistence curve for varying λ was also traced, allowing the calculation of phase diagrams at varying end bead self-attraction strengths. In the sub-sections below we detail, exemplifying the nematic–Isotropic transition, the procedure and simulations techniques to (a) calculate phase coexistence points through Thermodynamic Integration, (b) extend these results, tracing the coexistence curve using the Gibbs–Duhem Integration method and (c) discuss the validation of the results by direct simulation of a two-phase system.

3.1. Calculation of coexistence points

Equilibrium between multiple phases is achieved when there is thermal, mechanical and diffusive equilibrium, between the phases. Consequently, for two single component systems, of N molecules, at a fixed temperature, T , and pressure, P , phase coexistence is obtained when they have the same chemical potential or the same Gibbs free energy. One approach to determine a phase's TP state point Gibbs free energy is by thermodynamic integration (TI) along a path from a reference state of known Gibbs free energy, such as an ideal gas or Einstein crystal. On performing this process for two phases, their coexistence curve is determined as the locus of points with equal Gibbs free energy. Unfortunately, some phases – such as mesophases – have no ‘natural’ reference state, making

this method inapplicable for them. If the phase exhibits coexistence with another phase, where one phase's symmetry is a subset of the other, an alternative route to finding their coexistence may be possible [74]. By introducing an external field that couples to the phase transition's broken symmetry, a quasi-static integrable path between phases may be found, where the first-order transition is suppressed to a continuous transition. This permits relative free energy differences between any two of the phases' state points to be determined; consequently allowing phase coexistence to be found for free energy differences between phases of zero.

Both the SmA and Nem phases have no analytically solvable Gibbs free energy reference state; however, the external field approach mentioned above is applicable. For the Nem-Iso transition, a field that energetically favours molecular alignment may be introduced to suppress the first-order transition between phases. For the SmA-Nem transition, a field favouring nematic director-orientated molecular layering may be introduced to suppress the first-order transition between phases.

The following outlines the TI method for the Nem-Iso transition. A similar procedure was used for the SmA-Nem transition, with the field chosen to achieve this described in the Supplementary Information.

The bolaamphiphilic mesogen model's complete free energy differential dA – including the nematic coupling field strength, χ , and the end bead self-attraction strength, λ , contributions – for a closed system, may be written as

$$dA = -PdV - SdT + Ld\chi + Md\lambda \quad (4)$$

where L and M are the intensive properties respectively conjugate to χ and λ , S is entropy, and V is volume. Only the integrands P and L are required as simulations are performed isothermally and at constant λ . The calculation of L during simulation depends on the external field applied, and this choice is made to make the calculation of L straightforward. To exemplify this, L , given by the partial derivative of the Helmholtz energy with respect to the field strength is first expressed in terms of an ensemble average over the derivative of the underlying system Hamiltonian, H , with respect to field strength

$$L = \left(\frac{\partial A}{\partial \chi} \right)_{V,T,\lambda} = \frac{\partial H}{\partial \chi} \quad (5)$$

The Hamiltonian of the system can be conveniently split into a non-field-dependent part, H_0 , and a field-dependent part, H_1 ,

$$H = H_0(\mathbf{r}_N, \boldsymbol{\omega}_N, \lambda) + H_1(\mathbf{r}_N, \boldsymbol{\omega}_N, \chi) \quad (6)$$

Where the dependence on molecular centre of mass positions and principle orientation axes, are denoted by $\mathbf{r}_N$

and $\boldsymbol{\omega}_N$, respectively. Inclusion of Equations (6) into (5) gives

$$L = \frac{\partial H_1(\mathbf{r}_N, \boldsymbol{\omega}_N, \chi)}{\partial \chi} \quad (7)$$

Since the functional dependence of H_1 on χ – used to imposed nematic alignment – is arbitrary, a simple analytic function of χ is chosen to provide for a compact expression for assessing L . For the Nem-Iso phase transition, one choice of H_1 that favours molecular orientational alignment is.

$$H_1(\mathbf{r}_N, \boldsymbol{\omega}_N, \chi) = \chi \sum_{i=1}^N \sin^2 \theta_i \quad (8)$$

where θ_i are the angles between the configuration nematic director, $\mathbf{n}$, and each molecular orientation vector, $\boldsymbol{\omega}_i$. For the Nem phase most θ_i are close to 0, and consequently H_1 is close to zero. Conversely, for the Iso phase, the θ_i angles are distributed proportionally to $\sin \theta$, and H_1 takes a value near $2\chi/3$. Increasingly positive values of χ , raise H_1 for non-aligned systems and hence energetically favouring alignment.

A schematic of the TI path used for the Nem-Iso transition is depicted in Figure 3. The first path section involves an isothermal compression of the Nem phase, between volumes, V_I and V_{II} , with V_I being the Nem phase's volume at the coexistence pressure, $P_{iso-nem}$ – a quantity unknown *a priori*. This path's Helmholtz free energy change, ΔA_1 , is given by.

$$\Delta A_1 = - \int_{V_I(P_{iso-nem})}^{V_{II}} PdV|_{T,\lambda,\chi=0,nem} \quad (9)$$

where the field strength is zero, and the end beads self-attraction is fixed. The next path section involves isochorically turning on the nematic coupling field, χ , between field strengths of 0 and χ_I . The resulting Helmholtz free energy change, ΔA_2 , is given by

$$\Delta A_2 = \int_0^{\chi_I} Ld\chi|_{T,\lambda,V_{II}} = \int_0^{\chi_I} \sum_{i=1}^N \sin^2 \theta_{i\chi} d\chi|_{T,\lambda,V_{II}} \quad (10)$$

The system is then expanded – though retained in the Nem phase by the external field – to reach lower density, with the free energy change given by.

$$\Delta A_3 = - \int_{V_{II}}^{V_{III}} PdV|_{T,\lambda,\chi=\chi_I} \quad (11)$$

To complete the loop, the field was switched off isochorically – leading to an integrable Nem-Iso continuous

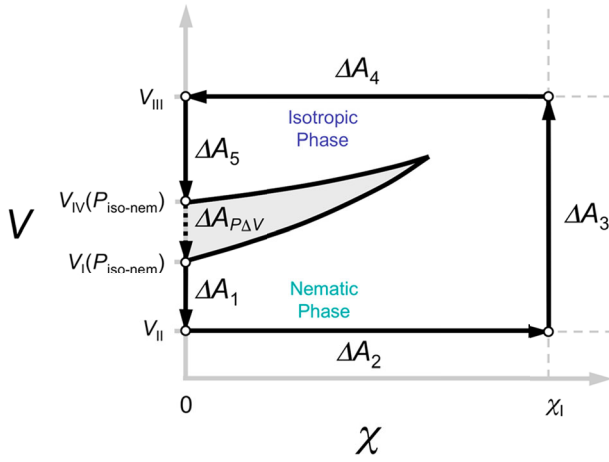


Figure 3. Schematic of the Nem-Iso TI cycle. Helmholtz free energy changes ΔA are calculated using Equations (9)–(13), and $\Delta A_{P\Delta V}$ is the Helmholtz free energy difference between coexisting phases, $P_{iso-nem}(V_{IV}-V_I)$. The greyed-out region corresponds to thermodynamically unstable volumes. Temperature is kept constant throughout.

phase transition – with free energy change

$$\Delta A_4 = - \int_{\chi_I}^0 \sum_{i=1}^N \sin^2 \theta_i d\chi \Big|_{T, \lambda, V=V_{III}} \quad (12)$$

and finally an Iso phase compression free energy change

$$\Delta A_5 = - \int_{V_{III}}^{V_{IV}(P_{Iso-Nem})} PdV \Big|_{T, \lambda, \chi=\chi_I, iso} \quad (13)$$

with V_{IV} the Iso phase's volume at the isotherm's coexistence pressure, $P_{Iso-Nem}$. In terms of Helmholtz free energy, the condition of equilibria, i.e. equivalence of Gibbs free energy, is given for the described TI loop by

$$A_{Iso}(V_{IV}) + P_{Iso-Nem} V_{IV} = A_{Nem}(V_I) + P_{Iso-Nem} V_I \quad (14)$$

or expressed in terms of the TI loop free energy changes, i.e. Equations (9)–(13), by.

$$\left(A_{Nem}(V_I) + \sum_{i=1}^5 \Delta A_i \right) + P_{Iso-Nem} V_{IV} = A_{Nem}(V_I) + P_{Iso-Nem} V_I \quad (15)$$

As A_{nem} appears on both sides of this equation, the dependence on absolute free energy is lost, as required. Rearranging the equation, gives

$$0 = \sum_{i=2}^4 \Delta A_i + \Delta A_1(P_{Iso-Nem}) + \Delta A_5(P_{Iso-Nem}) + P_{Iso-Nem}(V_{IV} - V_I) \quad (16)$$

which is the objective function to be solved for determining the coexistence pressure for the chosen isotherm. To

achieve this, simulations in the appropriate ensemble, are performed at state points on the TI path, and the output data used to construct the equations of states, $P(V)$ and $L(\chi)$. These equations are used as the integrands in Equations (9)–(13), allowing these free energy change integrals to be solved numerically. By selecting trial pressures for the coexistence pressure, the right hand side of Equation (16) may be solved by calculating each of the resultant free energy changes. The trial pressure that leads to the equality of Equation (16) being fulfilled within a prescribed tolerance is the calculated coexistence pressure, $P_{iso-nem}$.

A requisite for performing TI loops is access to the $P(V)$ and $L(\chi)$ EoSs, which allow the path section integrals to be numerically solved. To determine $P(V)$, individual simulations may be performed in the NPT ensemble at different pressures to determine a set of corresponding volumes. Similarly, to determine $L(\chi)$, simulations may be performed in a $NVT\chi$ ensemble at different field strengths χ to determine a set of corresponding L values. One approach to obtain the required functions would be to fit these simulation averages with an interpolating function – e.g. a polynomial. Alternatively, if simulations are performed sufficiently close in state space, the multiple histogram reweighting (MHR) method may be used to construct EoSs [75,76]. As opposed to using data from single simulations to obtain unique mean values, the MHR method recognises that full simulation distributions data may be recorded and combined with those from adjacent state points, to extract more simulation information content, and hence improve the efficiency of the process of constructing an EoS. This is particularly relevant in the vicinity of first-order phase transitions, where EoS gradients may vary more rapidly – necessitating additional simulations in their vicinity. Details of the simulations and methods for constructing the $P(V)$ and $L(\chi)$ EoS using the MHR method are provided in the Supplementary Information. It is possible to avoid the use of MHR methods and employ simple interpolation in the cases that the coexistence curves are rather linear; however, we used the MHR technique for the results presented herein.

Simulations used to determine the Nem-Iso (and SmA-Nem) coexistence points were performed in both the NPT and NVT ensemble using an extended-Lagrangian method [77,78], as appropriate for the TI path section under consideration. The TI loops were performed for the end bead self-attraction $\lambda = 0.4$ system only. Guided by preliminary simulations, the TI simulations were performed isothermally at $T = 3.60$ and $T = 4.53$, for the SmA-Nem and Nem-Iso coexistence points, respectively. Equilibration runs of 150,000 steps were performed for each state point simulation, followed

by data collection runs of 500,000 steps, with data collection performed at 100-step intervals. For the *NPT* ensemble simulations a pressure increment of $\Delta P = 3.1 \times 10^{-2}$ was used between consecutive state points simulated. On finding approximate coexistence points, additional simulations were performed in its vicinity to obtain improved statistics. Data collection runs between 500,000 and 1,000,000 steps were used for these additional runs. For the Nem-Iso TI loop, the field χ was increased to a maximum $\chi = 16.7$, with increments between simulations in the range $\Delta\chi = 3.33 \times 10^{-1} - 8.33 \times 10^{-1}$. For the SmA-Nem loop, the field strength was increased to a maximum of $\chi = 1.67$ with increments between simulations of $\Delta\chi = 8.33 \times 10^{-2}$. Further details of the implementation of these fields are provided in the supplementary materials.

As transitions between phases occurred at state points simulated in the vicinity of the coexistence curve, order parameters were used to classify the phase of sampled configurations. To distinguish between SmA and Nem phases the smectic order parameter, ψ , defined as

$$\Psi = \left| \frac{1}{N} \sum_{i=1}^N \exp \left(2\pi i \frac{\mathbf{r}_i \cdot \mathbf{n}}{d} \right) \right| \quad (17)$$

was used, with $\mathbf{n}$ being the unit vector normal to the smectic layering, d the smectic layer spacing, and $\mathbf{r}_i$ the centre of mass position of the i^{th} mesogen. To differentiate between Nem and Iso phases the nematic order parameter, P_2 , defined as

$$P_2 = \frac{3}{2N} \sum_{i=1}^N \cos^2 \theta_i - \frac{1}{2} \quad (18)$$

was used, with equivalent variable definitions to Equation (8). By looking at the bimodal distribution of order parameters found for simulations close to the coexistence curve, order parameter cut-offs were defined for each phase. For the Nem-Iso coexistence region, configurations with a block averaged P_2 above 0.5 were classified as Nem phase, those with values below 0.25 were taken as Iso phase. For the SmA-Nem coexistence region configurations with a block averaged ψ above 0.65 were classified as smectic, and those with values below 0.30 as Nem phase. The block average was performed over a time interval of $\Delta t = 62$. It should be noted that non-blocked averaged data was used in the MHR method used to construct equations of state.

From calculations of the Nem-Iso and SmA-Iso coexistence curves it was inferred that a SmA-Nem-Iso triple point exists for some strengths of end bead self-attraction. As SmA-Nem and Nem-Iso coexistence points were determined, the possibility of passing

through these points during a TI loop across *PT* variable space, to obtain a SmA-Iso transition state point was realised. To that end, simulations were performed in the *NPT* ensemble over a path incorporating the established coexistence points and that crossed the SmA-Iso coexistence curve. Further details of the chosen TI path and simulation details are given in the supplementary materials.

3.2. Gibbs–Duhem integration

Coexistence curves trace the intersection of the coexisting phases' Gibbs free energy surfaces. Consequently, to remain on this coexistence intersection following a change in thermodynamic variables, the associated change in both phases' Gibbs free energy must be the same. For the model under investigation, the differential of the Gibbs free energy, G , may be written as.

$$dG = VdP - SdT + Ld\chi + Md\lambda \quad (19)$$

consequently, the coexistence requirement for changes of Gibbs free energy for two phases, labelled I and II, may be written as

$$\begin{aligned} V_I dP - S_I dT + L_I d\chi + M_I d\lambda \\ = V_{II} dP - S_{II} dT + L_{II} d\chi + M_{II} d\lambda \end{aligned} \quad (20)$$

Under conditions of constant end bead self-attraction strength, λ , and field strength, χ , this equation can be written as.

$$(V_I - V_{II})dP = (S_I - S_{II})dT \quad (21)$$

Resultantly,

$$\left(\frac{\partial P}{\partial T} \right)_{\zeta, \chi, \lambda} = \frac{\Delta S}{\Delta V} \quad (22)$$

where the ΔS and ΔV are the differences in volume and entropy of the two phases, and the subscript ζ indicates the derivative applies on the coexistence path. The partial derivatives here refer to the slope of the coexistence curve at constant, χ and λ . At a coexistence point, temperature and pressure, by definition, are constant, and the difference in entropy between coexisting phases is equivalent to the ratio of the phase enthalpy difference to the temperature, $\Delta H_{enth}/T$, consequently

$$\left(\frac{\partial P}{\partial T} \right)_{\zeta, \chi, \lambda} = \frac{\Delta H_{enth}}{T \Delta V} \quad (23)$$

This Clapeyron equation relates the rate of change of pressure with temperature at a given point on the coexistence curve, to differences between the phase properties

at the coexistence point. Further Clapeyron-type equations may be derived that relate partial derivatives of the coexistence curve surface at a given point on the surface to difference between the properties of the phases at that point. For example the rate of change of pressure, P , with respect to end bead self-attraction parameter, λ , on the coexistence surface is given by

$$\left(\frac{\partial P}{\partial \lambda}\right)_{\varsigma, \chi, T} = -\frac{\Delta M}{\Delta V} \quad (24)$$

where ΔM is the difference in M between the two phases. Similarly, the rate of change of temperature, T , with respect to end bead self-attraction parameter, λ , on the coexistence surface is given by.

$$\left(\frac{\partial T}{\partial \lambda}\right)_{\varsigma, \chi, P} = \frac{T \Delta M}{\Delta H_{enth}} \quad (25)$$

where the variables are defined as before.

The Gibbs–Duhem Integration (GDI) is the generic name given to numerical techniques used to solve Clapeyron-type ordinary differential equations. The original algorithm presented by Kofke [72,73] using a predictor–corrector algorithm is employed herein. For completeness, an outline of this algorithm is given in the supplementary materials for Equation (23).

In summary, three types of GDI procedures were undertaken during this study, each based on a different Clapeyron equation. The first was a study into the isothermal variation of coexistence P with varying λ for the SmA–Nem and Nem–Iso transitions. The second was a study at constant λ of the variation of coexistence P with T for the SmA–Nem, SmA–Iso and Nem–Iso transitions. The final one was a study of the isobaric variation of coexistence T with λ for the SmA–Iso transitions. Details of their implementation are given in the supplementary materials.

3.3. *NVT ensemble coexistence simulations*

In addition to the GDI simulations, a series of *NVT* ensemble simulations were performed to investigate coexisting phases at lower temperatures. By choosing a global value of the density bracketed between the expected coexistence densities, phase separation occurred during the simulation. Analysis of each phases' densities allowed the coexistence densities to be determined. A representative snapshot of a phase separated system, along with its density distribution, is given in Figure 4. Further simulation details are provided in the supplementary material.

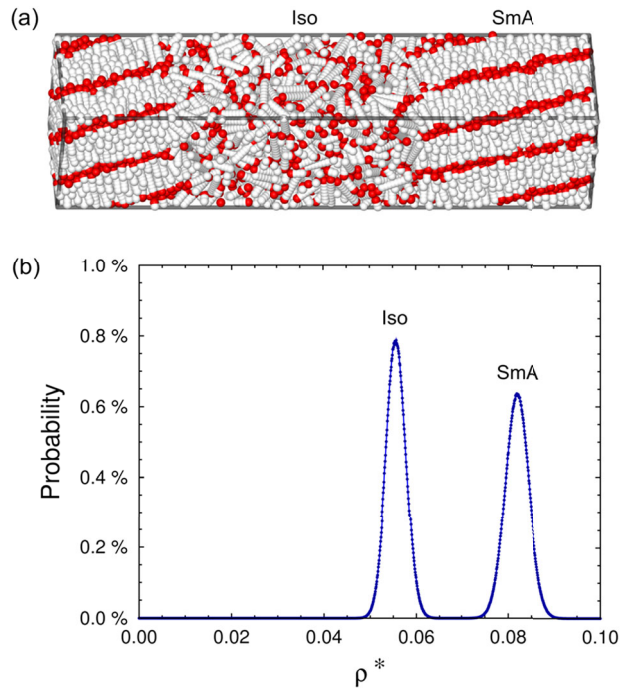


Figure 4. Illustration of the *NVT* coexistence simulations used to study crystalline–Iso and Sm A–Iso coexistence densities at lower temperatures (a) Snapshot of *NVT* ensemble simulation containing 2400 molecules with an end bead self-attraction of $\lambda = 0.4$ at $T = 0.97$, slightly below the triple point (b) Density distribution taken from the single configuration shown in the snapshot. The contribution of the interfacial region to the density profile has been systematically removed, as described in ref [79], allowing bulk phase densities to be obtained directly. Reported densities are averaged over multiple time steps.

4. Results

All simulations were performed in continuum space via molecular dynamics with a modified version of the DL_POLY_Classic simulation suite [80]. A system size of $N = 2400$ rod molecules, and a reduced timestep of $\Delta t = 0.006$ was used throughout. Orthogonal periodic boundary conditions were used for all simulations.

For the fully soft-repulsive rod system, $\lambda = 0.0$, the *PT* phase diagram is shown in Figure 5. GDI was performed down to $T = 4.3 \times 10^{-2}$ for the Nem–Iso coexistence curve and to $T = 4.0 \times 10^{-2}$ for the SmA–Nem coexistence curves. With these lower temperature bounds a SmA–Nem–Iso coexistence curve was not found, however curve extrapolation suggests it to occur at $T = 8 \times 10^{-3}$ and $P = 5 \times 10^{-3}$, assuming a crystalline–

SmA–Nem triple point is not present. During the GDI simulations average densities, ρ , of both phases were calculated, the resultant $T\rho$ phase diagram is summarised in Figure 6.

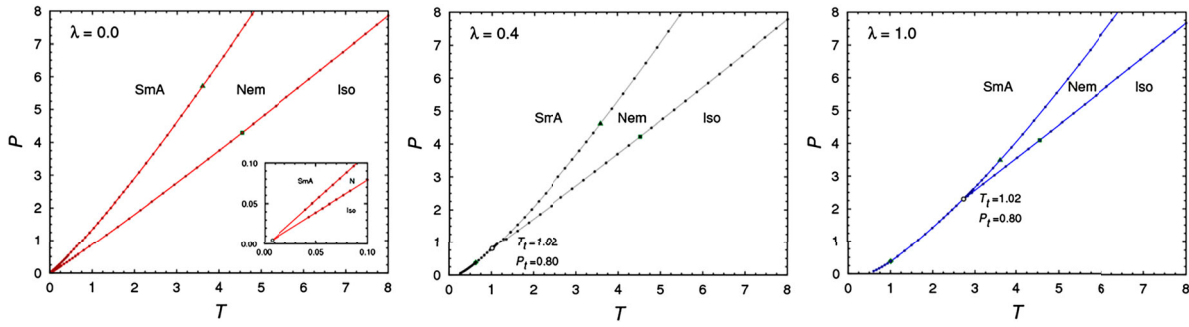


Figure 5. PT phase diagram of bolaamphiphiles with increasing level of repulsion of the end beads ($\lambda = 0.0, 0.4$ and 1.0). Data taken from GDI (red circles and line). Initial points used in Nem–Iso and SmA–Nem curves are highlighted, along with estimated triple point.

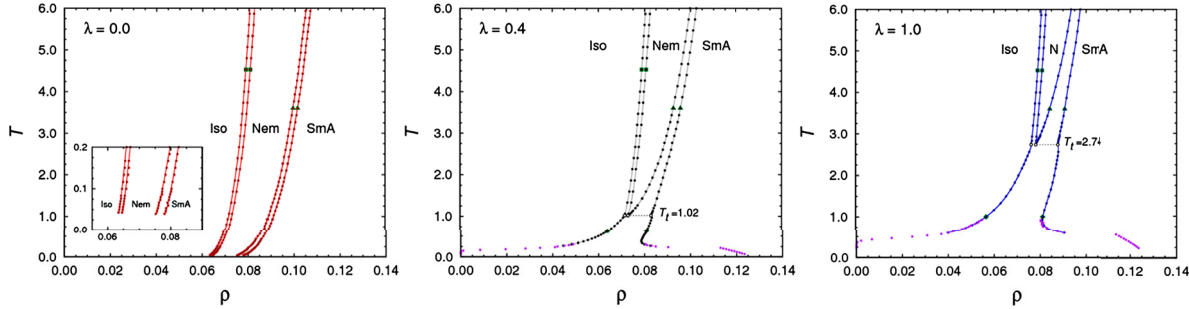


Figure 6. $T\rho$ phase diagram bolaamphiphiles with increasing level of repulsion of the end beads ($\lambda = 0.0, 0.4$ and 1.0) Data taken from GDI (red circles and line). Initial points used in Nem–Iso and SmA–Nem curves are highlighted, along with estimated triple point.

Similarly, the PT and $T\rho$ phase diagrams for the intermediate end bead self-attraction system, $\lambda = 0.4$, are reported in Figures 5 and 6 (middle). The GDI for both the SmA–Nem and Nem–Iso coexistence curve were iterated to a lower limit of $T = 1.07$, and in the range $T = 0.27$ – 0.97 for the SmA–Iso coexistence curve. With this a SmA–Nem–Iso triple point was observed. By fitting curves for the nematic coexistence density data of the Nem–Iso and SmA–Nem coexistence regions, their intersection was used to estimate the SmA–Nem–Iso triple point at $T = 1.02$. Using an average of the three fitted PT coexistence curves extrapolated to the coexistence temperature, a coexistence pressure of $P = 0.80$ was estimated. On comparison of the PT phase diagram with the $\lambda = 0.0$ system the SmA–Nem coexistence curve is seen to be shifted to higher temperatures, whilst the Nem–Iso transition is approximately invariant. In the $T\rho$ diagram above the SmA–Nem–Iso triple point the Nem–Iso coexistence curves also follow the same curves as found for the $\lambda = 0.0$ system.

In the $\lambda = 0.4$ system $T\rho$ phase diagram of Figure 6 (middle), whilst the Nem–Iso transition's $\Delta\rho$ remains relatively constant approaching the triple point, the SmA–Nem transition's $\Delta\rho$ becomes larger. On the same approach, the SmA phase's ψ order parameter increases, whilst the Nem phase's P_2 decreases, as seen in Figure 7. This increasing disparity in order and ρ leads to a

corresponding increasing ΔS near the triple point, as seen in Figure 8. Further information into the SmA–Nem transition is obtained by examining the $P\Delta V$ and internal energy, ΔU , contributions to ΔH_{enth} , reported in Figure 9 for the $\lambda = 0.0$ and $\lambda = 0.4$ systems. Here, ΔH_{enth} initially decreases with increasing T , before changing to a linear increase for the $\lambda = 0.4$ system, by definition commensurate with the ΔS behaviour. The initial decrease can be attributed to the SmA–Nem transition's larger $\Delta\rho$ close to the triple point contributing more to the $P\Delta V$ term, and a slightly higher ΔU contribution. This larger ΔU is due to higher smectic ordering allowing closer average separation of attractive end beads in the smectic phase increasing its attractive interaction U part, and lower nematic ordering in the coexisting Nem phase increasing its repulsive interaction U part. With increasing T above the triple point both of these additional contributions decrease.

From this discussion two main conclusions may be drawn. The first is that the SmA–Nem transition becomes increasingly first order on approaching the SmA–Nem–Iso triple point. The fact that a reduced number of phase transitions were observed during GDI predictor–corrector simulations close to the triple point, also suggests that transition free energy activation barrier increases in the same region. The second conclusion is that the Nem–Iso transition is first-order and appears to

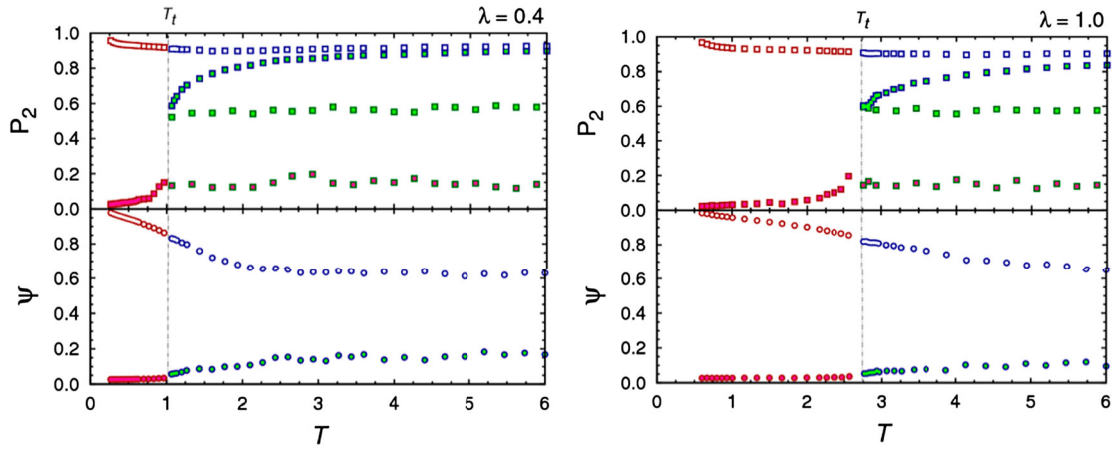


Figure 7. Plot of smectic, ψ , and nematic, P_2 , order parameter variation with temperature, for intermediate ($\lambda = 0.4$) (left) and full ($\lambda = 1$) (right) end bead self-attraction system. Nematic (squares) and smectic (circles) order parameters reported, for SmA–Nem (blue outer colour) and Nem–Iso (green outer colour) coexistence. Each phase delineated by inner colour (SmA with white, Nem with green and Iso with fuchsia).

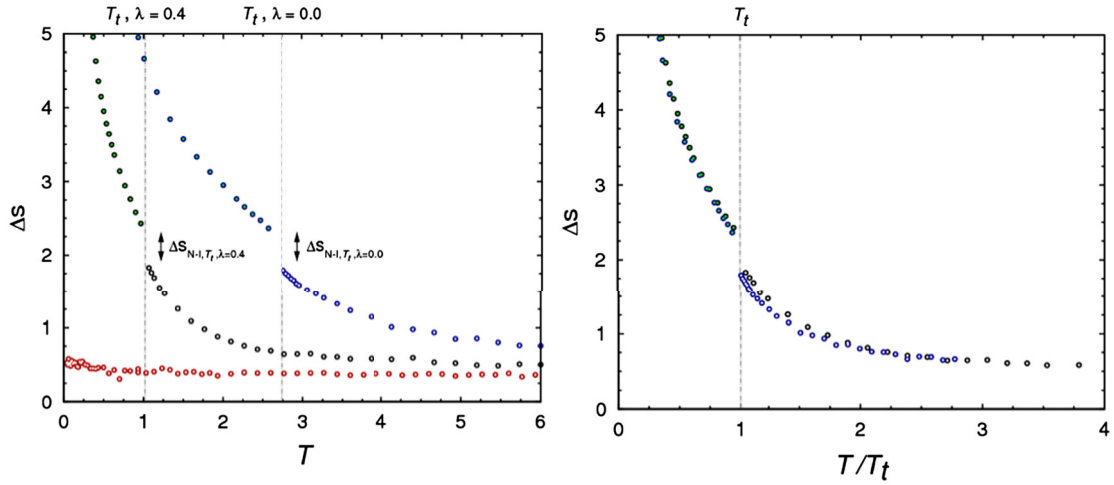


Figure 8. Plot of entropy change per molecule across SmA–Nem (white inner circle) and SmA–Iso (green inner circle) transitions, for $\lambda = 0.0$ (dark-red squares), $\lambda = 0.4$ (black circles) and $\lambda = 1.0$ (black circles) systems. Right: transitions with triple point rescaled temperature.

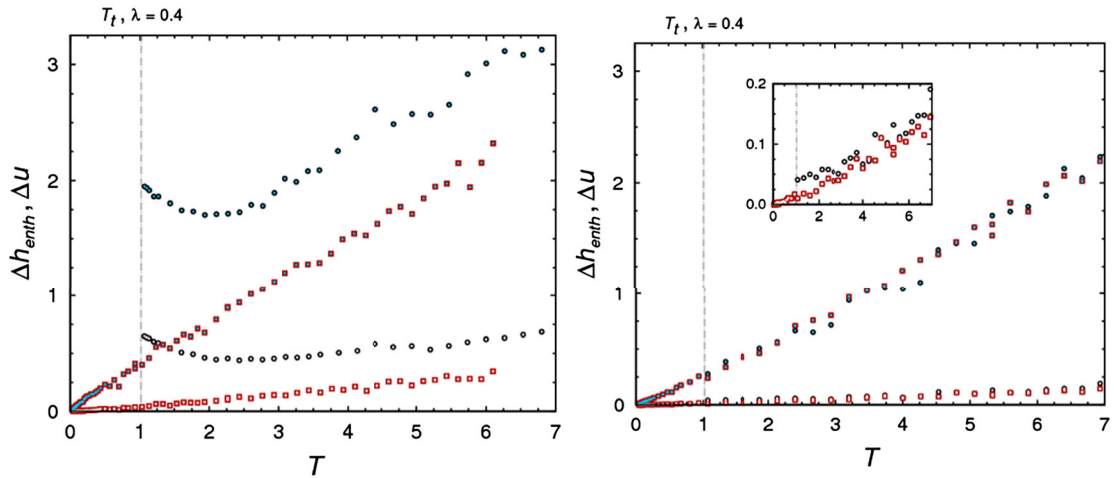


Figure 9. Plot of enthalpy (light-blue inner colour), Δh_{enth} , and internal energy (white inner colour), Δu , changes per molecule across SmA–Nem (left) and the Nem–Iso transition (right) with temperature, for $\lambda = 0.0$ (dark-red squares) and $\lambda = 0.4$ (black circles) systems.

remain at constant strength along the coexistence curve in terms of the transition entropy change.

Information may also be gained on the relative importance of self-attractive end bead interactions for each phase. From the isobaric shift of the SmA–Nem and SmA–Iso transition to higher T with increasing λ , it may be deduced that these attractions stabilise the SmA phase at higher T . Presumably they make a significant contribution to the SmA internal energy, and a less significant contribution to the nematic internal energy. As shown in Figure 8(right), the Nem–Iso transition ΔH_{enth} , and ΔU component, of both the $\lambda = 0.0$ and $\lambda = 0.4$ systems are found to follow the same trend. Furthermore as stated, above the $\lambda = 0.4$ systems SmA–Nem–Iso triple point temperature their coexisting densities are equivalent. This indicates that only repulsive interactions are important for the $\lambda = 0.4$ systems Nem and Iso coexisting phases. The slow increase of Nem–Iso transition internal energy contributions for both the $\lambda = 0.0$ and $\lambda = 0.4$ systems may be attributed to a slow increase of the Nem–Iso coexistence curves to higher densities, increasing the difference between the repulsive interaction U part of each phase. From this discussion it may be concluded that the SmA–Nem transition effectively involves breaking bonds between end beads, as their contribution to the internal energy in the Nem phase is significantly less. Consequently the $\lambda = 0.4$ systems Nem and Iso phase behaviour above the triple point is dominated by soft repulsive interactions, and is very similar to that of the $\lambda = 0.0$ system.

The PT and $T\rho$ phase diagram for the full end bead self-attraction system, $\lambda = 1.0$, are reported in Figures 5 and 6 (right). The triple point was found at approximately $T = 2.74$ and $P = 0.80$. Similar levels of LC order are observed along the coexistence curve as for the $\lambda = 0.4$ system, though shifted to higher T , as shown in Figure 7 (right). The enthalpy change associated with the SmA–Nem transition are similar in form but shifted to higher values with respect to the triple point relative position along the coexistence curve. This similarity is demonstrated well when the SmA–Nem and SmA–Iso transition entropy changes are plotted against triple point rescaled T for the $\lambda = 0.4$ and $\lambda = 1.0$ systems, given in Figure 8 (right). Here the curves follow an almost universal behaviour, indicating the increased attractions have not altered the fundamental form of phase behaviour. The additional attractions studied appear therefore to represent a linear perturbation on the underlying soft-repulsive system. The enthalpy change across the Nem–Iso transition follows the same trend as for the $\lambda = 0.0$ and $\lambda = 0.4$ systems, and consequently extends the earlier conclusions to these higher attraction strengths. Again no vapour–liquid

coexistence was found from NVT ensemble coexistence simulations.

Results from the NVT ensemble coexistence simulations are also reported in Figure 6 (right) for the range $T = 6.7 \times 10^{-2} - 3.0 \times 10^{-1}$. At lower T there is crystalline–Iso phase coexistence, whilst at higher T the SmA–Iso coexistence captured from GDI was confirmed. Here the densities found for coexisting phases by both methods were in good agreement as is evident from the plot. Figure 6 (right) shows the coexisting Iso phase's density forms a continuous curve between the crystalline–Iso and SmA–Iso coexistence regions. This is indicative of no Iso phase vapour–liquid coexistence. A prerequisite for vapour–liquid coexistence is attractive interactions between molecules, consequently its absence here suggests that attractions are relatively unimportant. This may be attributed to the models excluded volume geometry, limiting the number of rod beads that can get close enough to bond. Moreover, for end beads to bond, ordering of the rods must occur such that they may get close in space. These respective energetic and entropic penalty disfavors vapour–liquid equilibria here. Conversely, the same reasoning suggests end bead self-attractions are most important for phases where the molecules are organised allowing close positioning of end beads. This was demonstrated to be the case when considering the SmA phase.

5. Conclusions

In this paper we present the liquid crystalline phase behaviour of a bolaamphiphilic mesogen. To this end, we chose to investigate a model based on a rigid linear chain of softly repulsive beads, where attractive interactions between end beads could be parametrically varied. By performing molecular dynamics simulations and using these in free energy calculations, the global phase behaviour of our model was investigated for three levels of end bead self-attraction; soft repulsive, intermediate attraction and full attraction. We have developed a set of GDI protocols which allowed the production of phase diagrams which include the LC phases and transitions observed. In contrast to the direct coexistence calculations, the accumulation of errors as the phase transition curves are being drawn is a concern and one of the inherent drawbacks of the GDI method. However, the use of Histogram Reweighting techniques improves and minimises these errors. We refer to the reader to ref [81] for an excellent review of the capabilities and limitations of the GDI techniques. We believe our results are accurate to the extent of the size of the symbols shown in the figures.

Whilst all three levels of end bead self-attraction resulted in the formation of liquid crystalline phases, the relative stabilities of these phases varied dramatically. Under isobaric conditions the Nem–Iso coexistence temperature was found to be relatively unaffected by self-attraction strength, however Nem phase stability was found to be significantly reduced by increases in the SmA–Nem and SmA–Iso coexistence temperatures. This result may be attributed to the jump in average end bead separation that occurs with loss of SmA layering on the transition to Nem or Iso phases. This jump amounts to breaking the attractive bonds, consequently increased thermal energy is required to achieve this with increasing self-attraction strength. On passing from the smectic into the Nem or Iso phase, the attractive contribution to internal energy is observed to become insignificant, with the underlying soft-repulsive interactions dictating phase behaviour irrespective of end bead self-attraction strength. This statement is supported by the lack of vapour–liquid Iso phase coexistence, and the similarity of the Nem–Iso coexistence curves for all levels of self-attraction studied. The net result of this behaviour is to increase the SmA–Nem–Iso triple points to higher temperatures and pressures with increasing end bead self-attraction. Finally, the nature of the Nem–Iso and SmA–Nem phase transitions were studied. Whilst both transitions were found to be first order, the SmA–Nem transition was found more pronounced at temperatures just above the SmA–Nem–Iso triple points.

It is interesting to note, that in contrast to our work, for a similar model based on a rigid chain of 11 fully soft-repulsive particles interacting with a softer r^{-12} dependence, a SmA–Nem–crystalline triple point was proposed [47]. This difference presumably arises from the use of a softer potential creating an effectively shorter aspect ratio mesogen than studied here.

Our results on a model bolaamphiphile suggest that the introduction of strongly associating groups at terminal positions in mesogenic molecules provides a mean of tuning the temperature stability range of the liquid crystalline phases.

Acknowledgement and dedication

EAM wishes to dedicate this manuscript to his late dear friend, and a pioneer of the modelling of liquid crystals, Prof. Luis F. Rull. Luis was a brilliant scholar and a kind friend who profoundly impacted EAM's life and career. We are all deeply saddened by Luis' passing, but are grateful for the time that we shared with him.

Some figures were drawn using VMD [82].

Disclosure statement

No potential conflict of interest was reported by the author(s).

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