Perturbation theory versus thermodynamic integration. Beyond a mean-field treatment of pair correlations in a nematic model liquid crystal

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Abstract

The phase behaviour and structure of a simple square-well bulk fluid with anisotropic interactions is described in detail. The orientation dependence of the intermolecular interactions allows for the formation of a nematic liquid-crystalline phase in addition to the more conventional isotropic gas and liquid phases. A version of classical density functional theory (DFT) is employed to determine the properties of the model and comparisons are made with the corresponding data from Monte Carlo (MC) computer simulations in both the grand canonical and canonical ensembles, providing a benchmark to assess the adequacy of the DFT results. A novel element of the DFT approach is the assumption that the structure of the fluid is dominated by intermolecular interactions in the *isotropic* fluid. A so-called augmented modified mean-field

(AMMF) approximation is employed accounting for the influence of anisotropic interactions. The AMMF approximation becomes exact in the limit of vanishing density. We discuss advantages and disadvantages of the AMMF approximation with respect to an accurate description of different branches of the phase diagram, the degree of orientational order, and orientation-dependent pair correlations. The performance of the AMMF approximations is found to be good in comparison with the MC data; the AMMF approximation has clear advantages with respect to an accurate and more detailed description of the fluid structure. Possible strategies to improve the DFT are discussed.

Introduction

Liquid-crystalline phases have been recognized unequivocally as separate states of matter since the early twentieth century[?] , after the accidental discovery by Reinitzer[?] of two "melting points" for cholesteryl benzoate in 1888 which was confirmed by Lehmann[?] the following year using polarized light microscopy. Friedel[?] coined the terms nematic, smectic, and cholesteric (now often referred to as chiral nematic) to denote the three most important classes of liquid crystals (or mesomorphic states as he preferred to refer to them).

As their name implies, liquid crystals have properties which are intermediate between those of liquids and crystals (solids): in isotropic (I) liquid phases the molecules (mesogens) are orientationally and positionally disordered; nematic (N) phases are characterized by one degree of orientational order with the mesogenic molecules aligned along a preferred direction (the director); smectic phases are also orientationally ordered but possess an additional degree of positional order with the molecules preferentially organized in layers; cholesteric phases are similar to nematic phases but where the nematic director exhibits a periodic twist along a perpendicular helical axis, and solid phases possess full long-range positional (and orientational) order.

The development of molecular theories for liquid crystals has been an active area of

research since their discovery, with much progress being made following the advent of exact numerical molecular-simulation techniques. Comprehensive reviews and textbooks have been devoted to this vast body of literature with varying emphasis placed on the different perspectives relating to the molecular nature of liquid-crystalline order.[? ? ? ? ? ? ? ? ? ? ? ? ?]

Here we briefly introduce the key molecular approaches and highlight the features that are relevant to our current study, leaving out a discussion of the phenomenological approach of Landau and de Gennes[? ?] which (though widely used as a semi-empirical theory to represent the macroscopic orientational and positional order in liquid crystals) does not provide an explicit link between the macroscopic behaviour and the molecular interactions.

Broadly speaking there are two seemingly contrasting perspectives to the molecular description of liquid-crystalline order. The first originates from the hypothesis introduced by Born[? ?] that anisotropic attractive (dipolar) interactions between the mesogenic molecules are responsible for the formation of orientationally ordered phases by allowing for a lower configurational energy than that of the corresponding isotropic liquid phase. Born applied a mean-field approximation to describe the isotropic-nematic (IN) transition in a simple model of dipolar molecules; in this case the anisotropic phase is also ferroelectric (polar nematic) with the molecular dipoles aligned along a preferential direction.

In developing their mean-field approach, Maier and Saupe[? ? ?] advocated Born's suggestion, again assuming that the anisotropic nature of the attractive interactions between molecules allows for the stabilization of the liquid-crystalline states. As a consequence of its tractable mathematical formulation to represent the temperature dependence of the orientational order parameters, the use of the Maier-Saupe and related mean-field approaches[? ? ? ?] is now widespread in the analysis and correlation of experimental data for practical applications.[? ?] Apart from deficiencies arising from the use of a mean-field treatment for the attractive interactions (which we assess specifically in our paper), a key criticism often directed at the Maier-Saupe theory is the neglect of the anisotropy in the shape of the molecules which is a consequence of repulsive interactions.[?]

The second perspective, introduced by Onsager[?] , is that liquid-crystalline phases can be attributed to the repulsive interactions between anisotropic molecular cores in the fluid. In Onsager's view, the driving force for orientational order is the reduction of the excluded volume resulting from the repulsive interactions between pairs of particles (examined at the level of the second virial coefficient): at low densities it is the dominant contribution of the (ideal) orientational entropy to the free energy that leads to the stabilization of the isotropic phase; at higher densities the particles will be closer to each other and the rigid repulsive cores can align to form an anisotropic (N) phase which decreases the free volume and leads to a gain in *translational* entropy that more than compensates for the loss in *orientational* entropy. In order to undertake his analysis, Onsager constructed a (Helmholtz) free energy functional (in terms of a single-particle orientational distribution function at the level of the second virial coefficient) which can be considered as one of the first examples of classical density functional theory (DFT) (the square-gradient free-energy functional of the single-particle density introduced by van der Waals[?] to represent the vapour-liquid interface in 1893* is arguably the earliest DFT of all.) Entropy driven phase transitions are now well accepted.

The importance of entropy in the stabilization of a solid phase for systems of purely hard spheres without attractive interactions was first demonstrated by Alder and Wainwright[?] , at the time of the birth of molecular-dynamics simulations. Onsager's hypothesis of the role of entropy in the formation of nematic (and in some cases smectic) phases was subsequently confirmed by computer simulations of repulsive anisotropic particles including hard discs[? ?] , ellipsoids of revolution[? ?] , and hard spherocylinders.[? ? ? ?]

It is evident from the rich variety of mesogens exhibiting nematic phases[?] that the location of the IN phase transition is very sensitive to the specific nature of the intermolecular interactions, including the repulsions between molecular cores (characterized by the rigidity and aspect ratio of the particles), anisotropic attractions (due to multipolar and hydrogen-

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bonding interactions), and/or π-π stacking of aromatic cores) and the flexibility of side chains. Both the attractive and repulsive interactions between mesogens are clearly important in stabilizing the liquid-crystalline state, and a comprehensive theoretical treatment should incorporate both of these features at least in a generic form.

A natural route is to take a leaf from the seminal theory of van der Waals[?] [†] for isotropic liquids, combining the Maier-Saupe and Onsager treatments of liquid crystals to incorporate both the attractive and repulsive contributions in the free energy of the system.[?] The premise of perturbative approaches for fluids of molecules with attractive interactions is that the structure is dominated by repulsive forces between the molecules, and a description of the thermophysical properties of the reference fluid is therefore paramount.[? ? ?]

This type of generalized van der Waals treatment of liquid crystals dates back to the work by Kimura[?], Gelbart[? ?], Cotter[?], and Vertogen[?] together with their co-workers in the 1970s and 1980s. The full armoury of modern statistical mechanics has now been deployed on the description of liquid-crystalline systems including mean-field, modified mean-field, molecular-field, integral equation and density functional theories (for a comprehensive list of references until 2009 see Ref. [?] and in addition Refs. [? ? ? ? ? ? ? ? ? ?]) as representative examples of the various approaches employed in the intervening years.

We do not consider approaches based upon lattice models originating from the seminal paper by Flory[?] in our current discussion, because the fluid structure and correlations are artificially omitted in a lattice treatment. In the majority of cases (see, for example, Refs. [? ? ? ? ? ? ? ? ? ? ?]) the mean-field (van der Waals) or modified mean-field (low density) approximation is employed to represent the free-energy functional; in a few cases the pair correlation function of the reference fluid is incorporated employing integral equation theories[? ?] or accounted for by including high-body perturbation contributions.[?]

Of particular relevance to our present treatment from a conceptual point of view is the treatment of pair correlations in the work of Singh.[?] He solved numerically the orientation-

[†]See Ref. [?] for a translation into English.

dependent Ornstein-Zernike equation amended by the Percus-Yevick closure to investigate the temperature dependence of the IN phase transition for the Gay-Berne model. One of the key findings is that the IN phase transition is weakly first-order, similar to what we observe for our model system and what is also known from experiments.[?]

To incorporate the orientation dependence of intermolecular correlations, Singh[?] expanded the (direct and total) correlation functions in the basis of rotational invariants. In this approach orientation-dependent correlation functions are fully described by distance-dependent expansion coefficients multiplied by certain combinations of spherical harmonics.[?] We follow the same route but only for the orientation-dependent pair correlation function. Unfortunately, Singh[?] did not show results for the expansion coefficients of this latter function. Therefore, a direct comparison of our results with the ones obtained in Ref. **?** is precluded. Before describing the main attributes of our approach in treating the density dependence of the interparticle correlations within a perturbative DFT of the isotropic and nematic states, it is important to highlight some of the general aspects about the types of perturbation theories that are appropriate to describe classical fluids.

The first perturbation theory of liquids and vapour-liquid equilibria was proposed by van der Waals in his doctoral thesis[?] whereby the repulsive and attractive contributions to the thermodynamic properties are considered separately: he developed an expression from the pressure of a system of purely hard repulsive spheres in the low-density, second-virial-coefficient limit, and the contribution due to the attractive interactions was then treated in a perturbative manner at the mean-field level by assuming that the (density) correlations between particles in the fluid can be neglected.

Two seemingly equivalent but subtly different generic methodologies have then been employed in the development of perturbation theories of the fluid state, both involving the calculation of the contribution to the free energy on addition of a perturbation to a reference interaction potential with known (or tractable) thermodynamic properties.

One is based on a (continuous) thermodynamic integration (TI) of the free energy in

terms of a coupling parameter gradually linking the full and reference potentials; the other involves a determination of the free energy perturbation (FEP) associated with a small but finite contribution to the interaction potential, usually analyzed in the form of an expansion in the inverse temperature. The lack of appreciation of the distinction between the two approaches is perhaps not surprising because the corresponding expressions for the free-energy perturbation are formally identical but only at leading order.

Approaches based on the TI stem back to the seminal paper by Kirkwood[?] in which he introduced the potential of mean force. The TI method is now a well-established tool in statistical thermodynamics and is commonly employed for the numerical determination of free-energy contributions in molecular simulation.[?] The main ingredient in the application of a TI coupling approach is a representation of the effect of the coupling parameter (which links reference and perturbation potential) on the pair correlations in the fluid. This methodology has been the basis for the treatment of polar interactions in anisotropic liquid-crystalline systems using DFT at the mean-field and modified mean-field level in previously mentioned studies (see discussion and references in Ref. **?**); as we will demonstrate later in our paper, such an approach relies critically on the nature of the approximation employed to describe the pair correlation function of the system with the intermediate coupling interaction.

A more commonly employed approach in the application of perturbation theory to fluids is to expand the free energy of the system characterized by the full interaction in a Taylor series about that of a reference (purely repulsive) system. Peierls[?] was arguably the first to propose such an expansion of the free energy (partition function) as a series in the inverse of the temperature (commonly referred to as "high-temperature expansion") within a general statistical-mechanical framework of a system where the overall potential energy is decomposed into a reference and a "small" perturbation contribution; in this instance Peierls applied his theory to determine the diamagnetic susceptibility of electrons in a magnetic field.

A high-temperature perturbation expansion for the angle average of the pair potential between molecules with permanent dipoles had been proposed 20 years earlier by Keesom[?]

to determine the second virial coefficient of dipolar particles, but no direct link with the free energy of the condensed fluid was made. One should acknowledge that a second-order perturbation expansion for the partition function of dipolar particles of the Peierls form was employed early on by Van Vleck[?] to determine the thermodynamic properties of the system. Perturbation expansions of this type were popularized by Landau and Lifshitz[?] in the 1950s (particularly in the theoretical physics community), and also followed the independent developments in seminal papers by Longuet-Higgins[?], Barker[? ?], Pople[? ?], and Zwanzig.[?]

In his study Longuet-Higgins[?] extended the regular solution theory of mixtures using a perturbation expansion, while the aim of the work of Barker[? ?] was the formulation of perturbation theories for dipolar fluids based on expansions about thermodynamic properties of nonpolar reference systems. Gubbins and Twu[? ?] later popularized this type of high-temperature perturbation approach to describe polar and quadrupolar fluids within engineering applications.

Zwanzig[?] is often credited as the originator of the high-temperature expansions employed in FEP theories because of the more generic nature of the formalism presented in his paper. The popular and ubiquitous Barker and Henderson (BH)[? ?] and Weeks, Chandler and Anderson (WCA)[?] perturbation theories are implementations of the Zwanzig[?] formalism with different decompositions of the reference and perturbative intermolecular potentials and with the expansions taken to different order. In both the BH and WCA treatment, the inter-particle correlations required to determine the average perturbative contributions to the free energy correspond to those of the purely repulsive reference system.

As we show later, this is not necessarily the case when one develops a perturbation approach based upon thermodynamic integration over a coupling parameter linking the reference and perturbed systems. It is important to appreciate that although Zwanzig[?] employed a multinomial expansion in his development, perturbation expansions can be carried out as Taylor expansions about the coupling parameter[?]; this could be part of the reason for the common misconception of the equivalence between TI methods involving coupling

parameters (à la Kirkwood) and high-temperature perturbation theory (à la Peierls).

In our current work we develop a TI perturbation DFT for molecules with anisotropic interactions based on a coupling approach. The correspondence with standard high-temperature FEP expansions is discussed in detail, pointing out the subtle similarity and difference between the two approaches. Based on different approximations for the pair correlation function of the system with intermediate values of the coupling parameter, we demonstrate the equivalence of the various perturbation methodologies at the first-order level and highlight the importance of retaining the effect of the perturbation interaction on the structure of the fluid. Our formulation is developed for both isotropic fluid and anisotropic nematic phases, allowing for an assessment of the perturbation theory in describing both the vapour-liquid and isotropic fluid-nematic phase transitions and the degree of orientational order in the anisotropic phase. Important mathematical details of our treatment have been deferred to various Appendices.

Model system

We consider a liquid crystal composed of N mesogens interacting through a pairwise-additive potential of the form

$$\varphi\left(\boldsymbol{r}_{12},\omega_1,\omega_2\right)=\varphi_{\mathrm{iso}}\left(r_{12}\right)+\varphi_{\mathrm{aniso}}\left(\boldsymbol{r}_{12},\omega_1,\omega_2\right), \tag{1}$$

where $\boldsymbol{r}_{12}=\boldsymbol{r}_1-\boldsymbol{r}_2$ is the distance vector between the centers of mass of mesogens 1 and 2 located at $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, respectively, with a corresponding magnitude $r_{12}=|\boldsymbol{r}_{12}|$. The orientations of the mesogens are specified by the sets of Euler angles $\omega_i=(\theta_i,\phi_i)$ $(i=1,2)$ where θ_i and ϕ_i are the respective polar and azimuthal angles of particle i. The mesogens are therefore assumed to have uniaxial symmetry.

The interaction potential φ in eq. (**??**) is split into isotropic and anisotropic contributions.

The isotropic contribution is given by

$$\varphi_{\mathrm{iso}}\left(r_{12}\right)=\varphi_{\mathrm{hs}}\left(r_{12}\right)+\varphi_{\mathrm{sw}}\left(r_{12}\right), \tag{2}$$

where

$$\begin{aligned}\varphi_{\mathrm{sw}}\left(r_{12}\right) &= \begin{cases} 0, & r_{12}<\sigma \wedge r_{12}>\lambda\sigma \\ -\varepsilon, & \sigma \leq r_{12} \leq \lambda\sigma \end{cases} \\ &= -\varepsilon\Theta\left(r_{12}-\sigma\right)\Theta\left(\lambda\sigma-r_{12}\right)\end{aligned} \tag{3}$$

represents an attractive (square) well of depth ε and width $\lambda\sigma$, and Θ denotes the Heaviside function. Throughout our work the range of the interaction is taken as $\lambda=\frac{3}{2}$. In eq. (**??**),

$$\varphi_{\mathrm{hs}}\left(r_{12}\right)=\begin{cases}\infty, & r_{12}\leq 0 \\ 0, & r_{12}>\sigma\end{cases} \tag{4}$$

describes the interaction between two hard-sphere cores of diameter σ.

For the ansiotropic interaction potential in eq. (**??**) we adopt

$$\varphi_{\mathrm{aniso}}\left(\boldsymbol{r}_{12},\omega_1,\omega_2\right)=\varepsilon'\varphi_{\mathrm{sw}}\left(r_{12}\right)P_2\left[\widehat{\boldsymbol{u}}\left(\omega_1\right)\cdot\widehat{\boldsymbol{u}}\left(\omega_2\right)\right], \tag{5}$$

where ε' is a dimensionless coupling parameter, $P_2\left(x\right)=\frac{1}{2}\left(3x^2-1\right)$ is the second Legendre polynomial, and $\widehat{\boldsymbol{u}}$ is a unit vector specifying the orientation of a mesogen. The anisotropic part of the interaction potential therefore incorporates the orientation dependence of intermolecular interactions in the well-known Maier-Saupe mesogenic model.[?] A consequence of the form of eq. (**??**) is that for fixed orientations ω_1 and ω_2, φ_{aniso} is isotropic regardless of the orientation of the intermolecular vector $\boldsymbol{r}_{12}$.

Because $\varphi_{\mathrm{aniso}}\propto P_2$, a parallel or antiparallel arrangement of the pricipal axes of mesogens 1 and 2 is energetically favoured. In addition, φ_{aniso} is invariant if $\omega'=\left(\theta',\phi'\right)\rightarrow-\omega'=$

$(\pi - \theta', \pi + \phi')$ where the prime is used to indicate that the inversion operation is performed on *either* ω_1 *or* ω_2. These features of φ_{aniso} are indispensable for the formation of nematic phases under favorable thermodynamic conditions.

An alternative formulation of eq. (**??**) can be obtained by using rotational invariants defined as [see, for example, eq. (A.195a) of Ref. **?**]

$$\Phi_{l_1 l_2 l}\left(\omega_1, \omega_2, \omega\right) = \sum_{m_1 m_2 m} C\left(l_1 l_2 l; m_1 m_2 m\right) \mathcal{Y}_{l_1 m_1}\left(\omega_1\right) \mathcal{Y}_{l_2 m_2}\left(\omega_2\right) \mathcal{Y}^*_{lm}\left(\omega\right), \tag{6}$$

where C is a Clebsch-Gordan coefficient, l' (i.e., l_1, l_2, or l) is a positive, semidefinite integer, $m' \in [-l', l']$, $\mathcal{Y}_{l'm'}$ is a spherical harmonic, the asterisk denotes the complex conjugate, and ω is a set of Euler angles specifying the orientation of $\widehat{\boldsymbol{r}}_{12} = \boldsymbol{r}_{12}/r_{12}$ in a reference space-fixed frame. In modern theoretical physics, Clebsch-Gordan coefficients arise naturally in the theory of angular momentum coupling in quantum mechanics.[? ?]

A special case of eq. (**??**) is

$$\Phi_{220}\left(\omega_1, \omega_2, \omega\right) = \frac{1}{\sqrt{4\pi}} \frac{1}{\sqrt{5}} \sum_{m=-2}^{2} (-1)^m \mathcal{Y}_{2m}\left(\omega_1\right) \mathcal{Y}_{2\underline{m}}\left(\omega_2\right), \tag{7}$$

where we used $\mathcal{Y}_{00} = 1/\sqrt{4\pi}$ and $m_1 = -m_2 \equiv \underline{m}$ as a consequence of the selection rule $m_1 + m_2 = m$ for nonvanishing Clebsch-Gordan coefficients for the special case $l = m = 0$. Using the addition theorem [see eq. (A.33) of Ref. **?**] together with the Condon-Shortley phase convention for spherical harmonics [see eq. (A.3) of Ref. **?**] it is straightforward to show that

$$\Phi_{220}\left(\omega_1, \omega_2, \omega\right) = \frac{\sqrt{5}}{(4\pi)^{3/2}} P_2\left(\cos\gamma\right), \tag{8}$$

where γ is the angle between ω_1 and ω_2 and therefore

$$\varphi_{\text{aniso}}\left(\boldsymbol{r}_{12}, \omega_1, \omega_2\right) = \frac{(4\pi)^{3/2}}{\sqrt{5}} \varepsilon' \varphi_{\text{sw}}\left(r_{12}\right) \Phi_{220}\left(\omega_1, \omega_2, \omega\right) \tag{9}$$

is the alternative expression for the anisotropic part of the potential in eq. (**??**).

Theoretical considerations

The impact of pair correlations on the phase behaviour of a thermotropic liquid crystal is investigated in our current work. Our point of departure in this venture is the grand potential functional[?]

$$\Omega\left[\rho\left(\boldsymbol{r},\omega\right)\right]=\mathcal{F}\left[\rho\left(\boldsymbol{r},\omega\right)\right]-\mu\int\mathrm{d}\boldsymbol{r}\int\mathrm{d}\omega\,\rho\left(\boldsymbol{r},\omega\right) \tag{10}$$

which is expressed as a generalized Legendre transform of the Helmholtz free-energy functional $\mathcal{F}$, where μ is the chemical potential and ρ is the generic single-particle distribution function.[?] In general, $\mathcal{F}$ can be decomposed into an ideal-gas, an excess part, and a contribution from an external field when present.

The free energy from thermodynmic integration

A configuration of N mesogens is represented by a point $\boldsymbol{\Gamma}_N=\left(\boldsymbol{r}^N,\omega^N\right)$ in the $5N$-dimensional configurational space, where $\boldsymbol{r}^N=\{\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N\}$ and $\omega^N=\{\omega_1,\omega_2,\ldots,\omega_N\}$ are shorthand notations for center-of-mass positions and orientations of the N particles, respectively. Moreover, we assume that the total configurational potential energy Φ can be decomposed into a sum of a reference contribution and a "coupled" contribution which together account for the full interaction according to

$$\Phi(\boldsymbol{\Gamma}_N;\xi)=\Phi_0(\boldsymbol{r}^N)+\xi\Phi_1(\boldsymbol{\Gamma}_N), \tag{11}$$

where $0\leq\xi\leq1$ is a dimensionless coupling parameter that allows us to specify a linear path taking us from the reference system (subscript 0) to the system of interest (subscript 1).

At the molecular level of description we can thus write[?]

$$\beta\mathcal{F}\left(\xi\right)=-\ln Z\left(\xi\right), \tag{12}$$

where

$$Z\left(\xi\right)=\int \mathrm{d}\mathbf{\Gamma}_N\,\exp\left[-\beta\Phi(\mathbf{\Gamma}_N;\xi)\right] \tag{13}$$

is the configuration integral and $\beta\equiv 1/k_{\mathrm{B}}T$ (k_{B} is Boltzmann's constant). From eqs. (**??**) and (**??**) one can represent the partial derivative of the free-energy with respect to the coupling parameter as

$$\left(\frac{\partial\mathcal{F}}{\partial\xi}\right)_{N,V,T}=\frac{1}{Z\left(\xi\right)}\int \mathrm{d}\mathbf{\Gamma}_N\,\Phi_1(\mathbf{\Gamma}_N)\exp\left[-\beta\Phi(\mathbf{\Gamma}_N;\xi)\right]=\left\langle\Phi_1(\mathbf{\Gamma}_N)\right\rangle_{N,V,T;\xi}, \tag{14}$$

where $\left\langle\ldots\right\rangle_{N,V,T;\xi}=Z^{-1}\int \mathrm{d}\mathbf{\Gamma}_N\,\ldots\exp\left(-\beta\Phi\right)$ is an average in the canonical ensemble.

Considering the pairwise-additive interaction potential φ_1, that is

$$\Phi_1(\mathbf{\Gamma}_N)=\frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\ j\neq i}}^{N}\varphi_1\left(\boldsymbol{r}_i,\boldsymbol{r}_j,\omega_i,\omega_j\right), \tag{15}$$

we can rewrite eq. (**??**) as

$$\begin{aligned}\left(\frac{\partial\mathcal{F}}{\partial\xi}\right)_{N,V,T} &= \frac{N\left(N-1\right)}{2Z\left(\xi\right)}\int \mathrm{d}\mathbf{\Gamma}_N\,\varphi_1(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega_1,\omega_2)\exp\left[-\beta\Phi(\mathbf{\Gamma}_N;\xi)\right]\\ &= \frac{1}{2}\int \mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2\int \mathrm{d}\omega_1\,\mathrm{d}\omega_2\,\varphi_1(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega_1,\omega_2)\rho(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega_1,\omega_2;\xi),\end{aligned} \tag{16}$$

where

$$\rho(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega_1,\omega_2;\xi)=\frac{N!}{(N-2)!}\frac{1}{Z\left(\xi\right)}\int \mathrm{d}\mathbf{\Gamma}_{N-2}\,\exp\left[-\beta\Phi(\mathbf{\Gamma}_N;\xi)\right] \tag{17}$$

is the generic two-particle distribution function.[?] At this stage one introduces the pair correlation function g from the relation with the single-particle distribution functions:

$$\rho(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega_1,\omega_2;\xi)=\rho(\boldsymbol{r}_1,\omega_1)\rho(\boldsymbol{r}_2,\omega_2)g(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega_1,\omega_2;\xi). \tag{18}$$

Replacing the two-particle generic distribution in eq. (**??**) with eq. (**??**), one can formally

integrate eq. (??) to give[?]

$$\begin{aligned}\Delta\mathcal{F} &\equiv \mathcal{F}-\mathcal{F}_0=\int_0^1 \mathrm{d}\xi\,\left(\frac{\partial\mathcal{F}}{\partial\xi}\right)_{N,V,T}\\ &= \frac{1}{2}\int_0^1 \mathrm{d}\xi\int \mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2\int \mathrm{d}\omega_1\,\mathrm{d}\omega_2\,\varphi_1(\boldsymbol{r}_{12},\omega_1,\omega_2)\\ &\quad\times\rho(\boldsymbol{r}_1,\omega_1)\rho(\boldsymbol{r}_2,\omega_2)g(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega_1,\omega_2;\xi),\end{aligned}\tag{19}$$

where $\mathcal{F}$ is the excess free energy functional of the fully interacting anisotropic system ($\xi=1$) and $\mathcal{F}_0$ is the free energy functional of the (isotropic, $\xi=0$) reference system, respectively. The expression given in eq. (??) is well-known[? ?] and forms the central building block on which the present treatment is based. Notice that in deriving eq. (??) an external potential is required that changes with ξ such that the generic single-particle distribution function remains unaltered during the coupling procedure.

It is important to point out that eq. (??) is exact provided φ_1 is pairwise additive in the sense of eq. (??).[?] The coupling constant ξ in eq. (??) plays the role of a mathematical "switch" allowing one to link the reference system continuously to the system of interest. There is a fundamental difference between this type of coupling approach and the traditional perturbative treatments proposed by, for example, Zwanzig[?], Smith and Alder[?], or Barker and Henderson[?] (see also Section 4.1 of Ref. ?).

In perturbative approaches of this type it is explicitly assumed that $\Phi_1 \ll \Phi_0$. The structure of the perturbed system is thereby very similar to that of the reference system, enabling one to express $\mathcal{F}$ in terms of powers of Φ_1 using the radial pair correlation function of the reference system to represent g. If the latter is a hard-sphere fluid, g is known, representing the main charm of these approaches. However, if the underlying assumption $\Phi_1 \ll \Phi_0$ is not satisfied quite a few higher-order terms in the free-energy expansion need to be incorporated, which can be computationally cumbersome. An example is the approach proposed by Stell *et al.* for the Stockmayer fluid,[?] where a fluid of nonpolar particles is

taken as a reference system. By means of Gibbs ensemble MC simulations van Leeuwen *et al.*[?] have demonstrated that the approach is adequate only for low-density states and weak dipole moments.

Similar difficulties with the choice of a reference system have been observed for the sequence of phase transitions (isotropic-nematic and nematic-smectic A) in a fluid composed of hard spherocylinders: the addition of a weak dipole destabilized the nematic relative to the isotropic phase[? ?] but (for a central dipole) stabilised the smectic A[?] – perhaps reflecting that for some high-density states, the structure of the reference hard-core system is a nematic while that of the dipolar system is a smectic A.

By contrast, the theory proposed in our current work is free of these deficiencies because it is not based on the assumption relating the magnitude of Φ_0 to that of Φ_1, providing additional flexibility in defining Φ_0 and Φ_1. Unfortunately, however, coupling approaches also suffer a disadvantage since, unlike the Zwanzig and Barker-Henderson perturbation theories, the pair correlation function g depends on the coupling parameter ξ. As a result, rather than having to represent a single g for the reference system, a different structure has to be considered for each value of ξ. These different pair correlation functions are, of course, unknown so that an *ansatz* has to be made in order to parametrize g in terms of ξ. Whether or not the *ansatz* chosen is physically sensible can then only be decided *a posteriori*. In any event, the fundamental difference between thermodynamic integration and perturbation theories as proposed by Zwanzig[?] or Barker and Henderson[?] should not be disregarded.

As we mention early on in the paper there are subtle differences in the implementation of the perturbation approach within the Kirkwood coupling[?] and the Peierls expansion approaches.[?] The coupling approach provides a formally exact calculation of the free energy associated with a perturbation potential in terms of an integral over a coupling parameter. The Peierls/Zwanzig expansion[? ?] can be obtained as a Taylor expansion of the exact coupling relation about the uncoupled reference system (as beautifully described in the book by Hansen and McDonald[?]); at this level, the two approaches are formally equivalent. The key

issue in this case is that one is computing averages of the moments of the configurational energy assuming that the structure of the system is that of the reference (usually repulsive) system. In order to incorporate the effect of the structure of the fluid due to the perturbation potential (cf., the coupling parameter) one has to make appropriate approximations for the full orientation-dependent pair correlation function g; this is the principal aim of our current work. The equivalence of the various perturbation approaches therefore depends on what approximation is made for g (see also Sec. **??** below).

Reference system and perturbation

Two prerequisites have to be satisfied in order to make use of eq. (**??**). The first is to decide how to decompose the *total* configurational potential energy into contributions Φ_0 and Φ_1 in the spirit of eq. (**??**). The choice of reference system and perturbation is by no means unique.

To accommodate the decomposition into the reference and perturbation contributions, we *define* Φ_0 and Φ_1 in such a way that

$$\left\langle \varphi_1 \left(\boldsymbol{r}_{12}, \omega_1, \omega_2 \right) \right\rangle_{\omega_1,\omega_2} = \frac{1}{\left(4\pi\right)^2} \int \mathrm{d}\omega_1 \, \mathrm{d}\omega_2 \, \varphi_1 \left(\boldsymbol{r}_{12}, \omega_1, \omega_2 \right) = 0. \tag{20}$$

Therefore, for the present model, $\varphi_1 = \varphi_{\mathrm{aniso}}$ on account of its "multipole-like" character.[?] This "multipole-like" nature can be realized from eq. (**??**) and the fact that

$$\begin{aligned} \int \mathrm{d}\omega_1 \mathrm{d}\omega_2 \, \Phi_{220} \left(\omega_1, \omega_2, \omega \right) &= \left(4\pi\right)^{3/2} \int \mathrm{d}\omega_1 \mathrm{d}\omega_2 \, \Phi_{000} \left(\omega_1, \omega_2, \omega \right) \Phi_{220} \left(\omega_1, \omega_2, \omega \right) \\ &= \sqrt{4\pi} \delta_{l_1 0} \delta_{l_2 0} \delta_{l 0} \end{aligned} \tag{21}$$

where $\Phi_{000} = \left(4\pi\right)^{-3/2}$, $\delta_{l'0}$ ($l' = l_1, l_2,$ or l) is a Kronecker symbol, and eq. (**??**) has also been used. Because of eq. (**??**) we thus conclude that [cf., eq. (**??**)]

$$\varphi_0 \left(r_{12} \right) = \varphi \left(\boldsymbol{r}_{12}, \omega_1, \omega_2 \right) - \varphi_1 \left(\boldsymbol{r}_{12}, \omega_1, \omega_2 \right) = \varphi_{\mathrm{iso}} \left(r_{12} \right) \tag{22}$$

following from the definition of $\varphi_1 = \varphi_{\text{aniso}}$ together with eq. (**??**). We note that this definition of reference system and perturbation follows in spirit the decomposition used in the overwhelming body of literature on perturbation theories of the free energy in fluid systems composed of anisometric molecules.

Because of the definition of φ_0 in eq. (**??**) it is clear that the reference free energy can be represented as $\mathcal{F}_0 = \mathcal{F}^{\text{hs}} + \mathcal{F}^{\text{sw}}$ using a perturbative treatment *à la* Zwanzig[?] or Barker and Henderson.[?] Because we will eventually be dealing with homogeneous bulk phases, the hard-sphere contribution can be represented by the well-known Carnahan-Starling equation of state[?] which provides an excellent description of the hard-sphere fluid and allows us to introduce[?]

$$\frac{\beta\mathcal{F}^{\text{hs}}}{V} \equiv \beta f^{\text{hs}}(\rho) = \rho\frac{4\eta - 3\eta^2}{(1-\eta)^2}, \tag{23}$$

where $\eta \equiv \frac{\pi}{6}\rho\sigma^3$ is the hard-sphere packing fraction in a bulk fluid of (number) density $\rho = N/V$.

To compute the free-energy contribution $\mathcal{F}^{\text{sw}}$ we invoke a traditional high-temperature perturbation treatment[? ? ? ?] :

$$\frac{\beta\mathcal{F}^{\text{sw}}}{V} = 2\pi\beta\rho^2 \int_0^\infty \mathrm{d}r_{12}\, r_{12}^2\, \varphi_{\text{sw}}(r_{12})\, g_{\text{hs}}(r_{12}), \tag{24}$$

to leading (i.e., first) order[‡]. In eq. (**??**), g_{hs} is the radial pair correlation function of the hard-sphere reference system at the density of interest.

Noticing now that the integrand in eq. (**??**) is negative semidefinite we may employ the first mean-value theorem for definite integrals which allows us to rewrite eq. (**??**) as[?]

$$\begin{aligned}\frac{\beta\mathcal{F}^{\text{sw}}(\rho)}{V} \equiv \beta f^{\text{sw}} &= 2\pi\beta\rho^2 g_{\text{hs}}^{\text{c}}(\eta_{\text{eff}}) \int_0^\infty \mathrm{d}r_{12}\, r_{12}^2 \varphi_{\text{sw}}(r_{12}) \\ &\simeq -\frac{2\pi}{3}\beta\varepsilon\rho^2\sigma^3 g_{\text{hs}}^{\text{c}}(\eta_{\text{eff}})\left(\lambda^3 - 1\right),\end{aligned} \tag{25}$$

[‡]Notice a typographical error in eq. (13) of Ref. **?** , cf. eq. (37) of Ref. **?** .

where $g_{\rm hs}^{\rm c} = \lim_{r_{12}\to\sigma^+} g_{\rm hs}$ is the hard-sphere radial pair correlation function at contact and for an *effective* packing fraction $\eta_{\rm eff}$. Notice that both $\mathcal{F}^{\rm hs}$ and $\mathcal{F}^{\rm sw}$ in the respective eqs. (**??**) and (**??**) are no longer free-energy *functionals* but have become *functions* of the number density ρ instead.

To parametrize $g_{\rm hs}^{\rm c}$ in terms of $\eta_{\rm eff}$, $\mathcal{F}^{\rm sw}$ obtained from eq. (**??**) can be matched to that computed from eq. (**??**) using an accurate solution of the Ornstein-Zernike equation for the hard-sphere pair correlation function within the reference hypernetted chain (RHNC) closure.[**?**] For the square-well potential one eventually obtains the parametrization[**?**]

$$\eta_{\rm eff} = c_1(\lambda)\,\eta + c_2(\lambda)\,\eta^2 + c_3(\lambda)\,\eta^3, \tag{26}$$

where c_1, c_2, and c_3 can be represented by quadratic polynomials

$$\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 2.25855 & -1.50349 & 0.249434 \\ -0.66927 & 1.40049 & -0.827739 \\ 10.15760 & -15.04270 & 5.308270 \end{pmatrix} \begin{pmatrix} 1 \\ \lambda \\ \lambda^2 \end{pmatrix} \tag{27}$$

in terms of λ [see eq. (**??**)]. Using the contact-value theorem for the pressure in the hard-sphere fluid [see eq. (2.5.26) of Ref. **?**]

$$\frac{\beta P}{\rho} = 1 + 4\eta_{\rm eff} g_{\rm hs}^{\rm c}(\eta_{\rm eff}) \tag{28}$$

in combination with the Carnahan-Starling equation of state at $\eta_{\rm eff}$ one can write

$$g_{\rm hs}^{\rm c}(\eta_{\rm eff}) = \frac{1-\eta_{\rm eff}/2}{(1-\eta_{\rm eff})^3}. \tag{29}$$

Hence, with eq.s (**??**) – (**??**) we are in a position to compute $\mathcal{F}^{\rm sw}$ from eq. (**??**) keeping in mind that this is based upon first-order Barker-Henderson perturbation theory.

Key elements of classical density functional theory

After defining the perturbation potential φ_1 in the preceding section we now turn to the treatment of pair correlations in our model system. Because the interaction potential φ has two discontinuities at $r_{12} = \sigma$ and at $r_{12} = \lambda\sigma$ it is convenient to introduce the so-called cavity correlation function[?] :

$$\begin{aligned} y\left(\boldsymbol{r}_{12}, \omega_1, \omega_2; \xi\right) &= g\left(\boldsymbol{r}_{12}, \omega_1, \omega_2; \xi\right) \exp\left[\beta\varphi\left(\boldsymbol{r}_{12}, \omega_1, \omega_2; \xi\right)\right] \\ &= g\left(\boldsymbol{r}_{12}, \omega_1, \omega_2; \xi\right) \exp\left\{\beta\left[\varphi_0\left(r_{12}\right) + \xi\varphi_1\left(\boldsymbol{r}_{12}, \omega_1, \omega_2\right)\right]\right\}. \end{aligned} \tag{30}$$

The cavity correlation function remains continuous everywhere despite the discontinuities in φ (and the corresponding ones in g).[?] We expand y around $\xi = 0$. Retaining only the leading term the expansion gives $y = y_0 + \mathcal{O}(\xi)$ which, on rearrangement yields

$$g\left(\boldsymbol{r}_{12}, \omega_1, \omega_2; \xi\right) = g_0\left(r_{12}\right) \exp\left[-\beta\xi\varphi_1\left(\boldsymbol{r}_{12}, \omega_1, \omega_2\right)\right]. \tag{31}$$

It is important to realize that in this expression g_0 is the radial pair correlation function of the reference system ($\xi = 0$) in which φ_{iso} governs the intermolecular interactions [see eq. (**??**)]. Because of the appearance of g_0 and in line with accepted terminology in the literature[? ? ? ? ? ? ? ? ? ?] we shall refer to eq. (**??**) as the "augmented modified mean-field" (AMMF) approximation.

Inserting eq. (**??**) into eq. (**??**) then gives

$$\beta\Delta\mathcal{F}\left[\rho\left(\boldsymbol{r}, \omega\right)\right] = -\frac{1}{2}\int \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2\, g_0\left(r_{12}\right) \int \mathrm{d}\omega_1\, \mathrm{d}\omega_2\, \rho\left(\boldsymbol{r}_1, \omega_1\right) \rho\left(\boldsymbol{r}_2, \omega_2\right) f\left(\boldsymbol{r}_{12}, \omega_1, \omega_2\right) \tag{32}$$

after performing the integration over $\mathrm{d}\xi$ where

$$f\left(\boldsymbol{r}_{12}, \omega_1, \omega_2\right) = \exp\left[-\beta\varphi_1\left(\boldsymbol{r}_{12}, \omega_1, \omega_2\right)\right] - 1 \tag{33}$$

is the orientation-dependent Mayer f-function associated with the perturbation potential φ_1. If one assumes that the particles in the system are uncorrelated (corresponding to $g_0 = 1$), the AMMF free-energy contribution defined by eq. (**??**) reduces to a second-virial theory analogous to that introduced early on by Onsager[?] for hard-core particles.[? ?]

We expand f in the basis of rotational invariants:

$$f(\boldsymbol{r}_{12}, \omega_1, \omega_2) = \sum_{l_1 l_2 l} f_{l_1 l_2 l}(r_{12}) \, \Phi_{l_1 l_2 l}(\omega_1, \omega_2, \omega) . \tag{34}$$

By way of eq. (**??**) this expression may be inverted to give

$$f_{l_1 l_2 l}(r_{12}) = \frac{4\pi}{2l+1} \int \mathrm{d}\omega_1 \, \mathrm{d}\omega_2 \, f(\boldsymbol{r}_{12}, \omega_1, \omega_2) \, \Phi^*_{l_1 l_2 l}(\omega_1, \omega_2, \omega) . \tag{35}$$

Notice that the approximation introduced in eq. (**??**) becomes exact in the limit of vanishing density. Eq. (**??**) relies on the assumption that the structure of the fluid is determined by the spherically symmetric interactions between the mesogens; thus, one implicitly assumes that the anisotropic attractive interactions do not contribute to the structure of the liquid crystal.

We now apply the above considerations to the phase equilibria between the isotropic gas and liquid and the nematic bulk phases of a thermotropic liquid crystal. In the absence of an external field the single-particle generic distribution function of the homogeneous phase can be represented as

$$\rho(\boldsymbol{r}, \omega) = \rho \alpha(\omega) , \tag{36}$$

where ρ is the number density and the orientation distribution function α is normalized according to

$$\int \mathrm{d}\omega \, \alpha(\omega) = 1. \tag{37}$$

As a result of the decomposition made in eq. (**??**) we transform variables in eq. (**??**) according to $\boldsymbol{r}_1 \to \boldsymbol{r}'_1 = \boldsymbol{r}_1$, $\boldsymbol{r}_2 \to \boldsymbol{r}'_2 = \boldsymbol{r}_{12}$, express $\mathrm{d}\boldsymbol{r}_{12}$ in spherical coordinates, and

perform the one trivial integration over $\mathrm{d}\boldsymbol{r}_1'$ analytically to obtain

$$\begin{aligned}\frac{\beta\Delta\mathcal{F}\left[\rho,\alpha\left(\omega\right)\right]}{V} &= -\frac{\rho^2}{2}\sum_{l_1l_2l}\int_0^\infty \mathrm{d}r_{12}\, r_{12}^2 g_0\left(r_{12}\right) f_{l_1l_2l}\left(r_{12}\right) \\ &\quad\times\int \mathrm{d}\omega_1\,\mathrm{d}\omega_2\mathrm{d}\omega\,\alpha\left(\omega_1\right)\alpha\left(\omega_2\right)\Phi_{l_1l_2l}\left(\omega_1,\omega_2,\omega\right). \end{aligned} \tag{38}$$

In eq. (**??**) the integration over orientations can be carried out analytically as we explain in Appendix **??**. The final result can then be cast compactly as

$$\frac{\beta\Delta\mathcal{F}}{V} = \rho^2\sum_{l=0}^{\infty}\alpha_l^2 u_l, \tag{39}$$

where members of the set $\{\alpha_l\}$ are coefficients in the expansion of the orientation distribution function in terms of Legendre polynomials $\{P_l\}$ as we explain in Appendix **??**. The expansion coefficients allow us to introduce order parameters

$$\mathcal{O}_l = \frac{2}{2l+1}\alpha_l \tag{40}$$

defined such that $\mathcal{O}_l \in [0,1]$ regardless of l.

Last but not least, we derive in Appendix **??** explicit expressions for the coefficients $\{f_{ll0}\}$ on which the energy parameters $\{u_l\}$ depend through the expression

$$u_l = \frac{(-1)^{l+1}}{\sqrt{\pi}\left(2l+1\right)^{3/2}}\int_0^\infty \mathrm{d}r_{12}\, r_{12}^2\, g_0\left(r_{12}\right) f_{ll0}\left(r_{12}\right). \tag{41}$$

An inspection of eq. (**??**) shows that in principle the set $\{u_l\}$ is countably infinite. However, in practice only its first few members matter. This is because as one can see from eqs. (**??**) and (**??**), with increasing l coefficients u_l become smaller very quickly. The diminishing of the energy parameters is not only caused because the prefactors become progressively smaller but also because the power of the leading terms in $\beta\varepsilon\varepsilon' \lesssim 1$ increases with l. In practice, $\beta\varepsilon\varepsilon'$ is of the order of 10^{-1} for intermediate coupling strengths ε' and over the temperature

range relevant to this work. Thus, in view of these conditions we include only terms up to $l = 4$ in eq. (**??**).

Orientation-dependent pair correlation function

To investigate the adequacy of our description of fluid structure and in particular the validity of the approximation introduced in eq. (**??**), we examine the phase diagram of our model liquid crystal. An in-depth evaluation of the capacity of eq. (**??**) is also possible by directly investigating the orientation-dependent pair correlation function. We therefore introduce two approaches to g, one suitable in MC simulations and the other one in DFT. Because MC is a first-principles numerical method, the MC results serve as a benchmark for the AMMF DFT. This comparison sheds light on the performance of eq. (**??**) from a structural perspective.

Because g (like f) depends on $\boldsymbol{r}_{12}$, ω_1, and ω_2 we can expand it in terms of $\{\Phi_{l_1 l_2 l}\}$, cf. eq. (**??**). Using the definition of $\Phi_{l_1 l_2 l}$ given in eq. (**??**) we can write

$$\begin{aligned} g\left(\boldsymbol{r}_{12}, \omega_1, \omega_2\right) &= \sum_{l_1 l_2 l} g_{l_1 l_2 l}\left(r_{12}\right) \Phi_{l_1 l_2 l}\left(\omega_1, \omega_2, \omega\right) \\ &= \sum_{l_1 l_2 l} g_{l_1 l_2 l}\left(r_{12}\right) \sum_{m_1 m_2 m} C\left(l_1 l_2 l; m_1 m_2 m\right) \\ &\quad \times \mathcal{Y}_{l_1 m_1}\left(\omega_1\right) \mathcal{Y}_{l_2 m_2}\left(\omega_2\right) \mathcal{Y}^*_{l m}\left(\omega\right), \end{aligned} \tag{42}$$

where $\{g_{l_1 l_2 l}\}$ is a set of expansion coefficients. It is important to note that the expansion in eq. (**??**) is undertaken in a *space-fixed* frame of reference.

Alternatively, one may choose an *intermolecular* frame of reference in which the z-axis is parallel to $\widehat{\boldsymbol{r}}_{12}$. The intermolecular frame is completely equivalent to the space-fixed one. Therefore, it offers another option to describe the molecular orientations in space. Employing the intermolecular frame implies that $\omega \to \omega' = (0, \phi')$. We henceforth indicate the intermolecular frame by using primed variables. It is then immediately clear that in

eq. (**??**) [cf. eq. (A.55) of Ref. **?**]

$$\mathcal{Y}_{lm}\left(0,\phi'\right)=\sqrt{\frac{2l+1}{4\pi}}\delta_{m0}. \tag{43}$$

One further uses the selection rule for nonzero Clebsch-Gordan coefficients which gives $m_1 = -m_2 = \underline{m}$ such that $\sum\limits_{m_1 m_2 m} \rightarrow \sum\limits_{m}$ and hence we can reexpress eq. (**??**) as

$$g\left(r_{12},\omega_1',\omega_2'\right)=\sum_{l_1 l_2 l}\sqrt{\frac{2l+1}{4\pi}}g_{l_1 l_2 l}\left(r_{12}\right)\sum_{m}C\left(l_1 l_2 l;m\underline{m}0\right)\mathcal{Y}_{l_1 m}\left(\omega_1'\right)\mathcal{Y}_{l_2\underline{m}}\left(\omega_2'\right). \tag{44}$$

It is important to note that in the intermolecular frame of reference, g depends only on r_{12} rather than $\boldsymbol{r}_{12}$. Eq. (**??**) also permits one to introduce expansion coefficients in the intermolecular frame. These are related to the set $\{g_{l_1 l_2 l}\}$ in the space-fixed frame through the expression

$$g\left(r_{12};l_1 l_2 m\right)=\sum_{l}\sqrt{\frac{2l+1}{4\pi}}\,C\left(l_1 l_2 l;m\underline{m}0\right)g_{l_1 l_2 l}\left(r_{12}\right). \tag{45}$$

With this expression we can rewrite eq. (**??**) compactly as

$$\widetilde{g}\left(r_{12},\omega_1',\omega_2'\right)=4\pi g\left(r_{12},\omega_1',\omega_2'\right)=4\pi\sum_{l_1 l_2 m}g\left(r_{12};l_1 l_2 m\right)\mathcal{Y}_{l_1 m}\left(\omega_1'\right)\mathcal{Y}_{l_2\underline{m}}\left(\omega_2'\right), \tag{46}$$

where $m\in\left[-\min\left(l_1,l_2\right),\min\left(l_1,l_2\right)\right]$ and we have included an extra factor of 4π following earlier work by Streett and Tildesley[**?**] for reasons that will become clear from the subsequent discussion.

To obtain the expansion coefficients we use the fact that the spherical harmonics form a complete orthonormal set of functions and use eq. (A.39) of Ref. **?** to obtain

$$g\left(r_{12};l_1 l_2 m\right)=\frac{1}{4\pi}\int \mathrm{d}\omega_1'\mathrm{d}\omega_2'\,\widetilde{g}\left(r_{12},\omega_1',\omega_2'\right)\mathcal{Y}^{*}_{l_1 m}\left(\omega_1'\right)\mathcal{Y}^{*}_{l_2\underline{m}}\left(\omega_2'\right). \tag{47}$$

A special case of this expression corresponds to $l_1 = l_2 = m = 0$. This leads to

$$\begin{aligned} g\left(r_{12};000\right) &= \frac{1}{\left(4\pi\right)^2}\int \mathrm{d}\omega_1'\mathrm{d}\omega_2'\,\widetilde{g}\left(r_{12},\omega_1',\omega_2'\right) = \left\langle \widetilde{g}\left(r_{12},\omega_1',\omega_2'\right)\right\rangle_{\omega_1',\omega_2'} \\ &= 4\pi\left\langle g\left(r_{12},\omega_1',\omega_2'\right)\right\rangle_{\omega_1',\omega_2'} = 4\pi g\left(r_{12}\right), \end{aligned} \tag{48}$$

where $\left\langle \ldots \right\rangle_{\omega_1',\omega_2'}$ denotes an unweighted average over molecular orientations in the intermolecular frame and $\mathcal{Y}_{00} = 1/\sqrt{4\pi}$ has also been employed. It is important to realize that the radial pair correlation function g appearing on the far right-hand side of eq. (**??**) describes the structure of a system in which the intermolecular interactions are governed by the *full* potential φ introduced in eq. (**??**). However, for the AMMF approximation in eq. (**??**), only the radial pair correlation function g_0 is considered. It describes the structure of the reference system in which the intermolecular interactions are solely governed by $\varphi_0 = \varphi_{\mathrm{iso}}$ [see eq. (**??**)].

To proceed we again follow Streett and Tildesley[**?**] and define the ensemble average

$$\left\langle X\right\rangle_{\mathrm{shell}} \equiv \frac{\int \mathrm{d}\omega_1'\mathrm{d}\omega_2'\,x\left(r_{12},\omega_1',\omega_2'\right)\alpha\left(\omega_1'\right)\alpha\left(\omega_2'\right)g\left(r_{12},\omega_1',\omega_2'\right)}{\int \mathrm{d}\omega_1'\mathrm{d}\omega_2'\,\alpha\left(\omega_1'\right)\alpha\left(\omega_2'\right)g\left(r_{12},\omega_1',\omega_2'\right)} \tag{49}$$

of some pairwise-additive quantity x where the center-of-mass position of one mesogen is taken as the origin of the coordinate system and the second one is located in a small spherical shell of thickness $\mathrm{d}r_{12}$ at a distance r_{12} from this origin.

The previous expression can be simplified because in the *intermolecular* frame of reference $\alpha = 1/4\pi$ due to the normalization condition [see eq. (**??**)]. This holds even in the nematic phase where α in the *space-fixed* frame of reference would not at all be a constant (cf., Figure **??**). However, in the intermolecular frame of reference the coordinate system rotates with respect to a fixed nematic director $\widehat{\boldsymbol{n}}_+$ [see eq. (**??**) below] and thus any preferred orientation of the molecules cannot be detected as long as molecules do not exhibit long-range positional correlations (as is the case for the smectic A phase but not for the nematic phase).

Following these arguments we can rearrange eq. (**??**) and obtain

$$(4\pi)^3 \, g\left(r_{12}\right) \langle X \rangle_{\text{shell}} = \int \mathrm{d}\omega_1' \mathrm{d}\omega_2' \, x\left(r_{12}, \omega_1', \omega_2'\right) g\left(r_{12}, \omega_1', \omega_2'\right) . \tag{50}$$

Let us now take

$$x\left(r_{12}, \omega_1', \omega_2'\right) \equiv x_{12}\left(\omega_1', \omega_2'\right) = \mathcal{Y}_{l_1 m}^{*}\left(\omega_1'\right) \mathcal{Y}_{l_2 \underline{m}}^{*}\left(\omega_2'\right) \tag{51}$$

for a pair of molecules separated by a distance r_{12}. Then a comparison between eqs. (**??**) and (**??**) reveals that

$$g\left(r_{12}; l_1 l_2 m\right) = (4\pi)^2 \, g\left(r_{12}\right) \left\langle \mathcal{Y}_{l_1 m}^{*}\left(\omega_1'\right) \mathcal{Y}_{l_2 \underline{m}}^{*}\left(\omega_2'\right) \right\rangle_{\text{shell}} \tag{52}$$

which is suitable for an evaluation in a molecular simulation if one computes the radial pair correlation function and the ensemble average over the shell from histograms.

Unfortunately, eq. (**??**) is not suitable for a corresponding DFT-based investigation of orientation dependent pair correlations. In this case, the space-fixed frame of reference is much more appropriate and hence the expansion coefficients $g_{l_1 l_2 l}$ are relevant. Fortunately, the two types of expansion coefficients are related. Starting from eq. (**??**), multiplying both sides of the equation by $C\left(l_1 l_2 l'; m \underline{m} 0\right)$, and summing the resulting expression over m we obtain

$$g_{l_1 l_2 l}\left(r_{12}\right) = \sqrt{\frac{4\pi}{2l+1}} \sum_{m} C\left(l_1 l_2 l; m \underline{m} 0\right) g\left(r_{12}; l_1 l_2 m\right) \tag{53}$$

which follows from the orthogonality of the Clebsch-Gordan coefficients [see eq. (A.141) of Ref. **?**]. Together, eqs. (**??**) and (**??**) enable a computation of $\{g_{l_1 l_2 l}\}$ from molecular simulations. Thus, a direct comparison between MC data and DFT calculations is possible.

Phase behaviour of the model liquid crystal

Equilibrium states

From the discussion in the preceding section it follows that the excess Helmholtz free energy of our system is

$$\mathcal{F}\left[\rho, \alpha\left(\omega\right)\right] = \mathcal{F}_0\left(\rho\right) + \Delta\mathcal{F}\left[\rho, \alpha\left(\omega\right)\right] = \mathcal{F}^{\mathrm{hs}}\left(\rho\right) + \mathcal{F}^{\mathrm{sw}}\left(\rho\right) + \Delta\mathcal{F}\left[\rho, \alpha\left(\omega\right)\right], \tag{54}$$

where $\mathcal{F}^{\mathrm{hs}}$, $\mathcal{F}^{\mathrm{sw}}$, and $\Delta\mathcal{F}$ are given in eqs. (**??**), (**??**), and (**??**), respectively. Because we are dealing with a homogeneous bulk phase [see eq. (**??**)] the excess free energy is a *function* of ρ and a *functional* of α.

In addition, there is also an ideal-gas contribution which for uniaxially symmetrical particles can be cast as[?]

$$\beta\mathcal{F}^{\mathrm{id}}\left[\rho\left(\boldsymbol{r}, \omega\right)\right] = \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\omega\, \rho\left(\boldsymbol{r}, \omega\right) \left\{\ln\left[4\pi\rho\left(\boldsymbol{r}, \omega\right)\Lambda^5\mathcal{M}/\mathcal{I}\right] - 1\right\}, \tag{55}$$

where $\mathcal{M}$ is the mass of the particle and $\mathcal{I}$ is the moment of inertia. The extra factor of 4π has been included to guarantee that in the isotropic phase and for mesogens of uniaxial symmetry all contributions from the orientation dependence of the generic singlet distribution function to $\mathcal{F}^{\mathrm{id}}$ vanish. Making use of eqs. (**??**) and (**??**)

$$\frac{\beta\mathcal{F}^{\mathrm{id}}\left[\rho, \alpha\left(x\right)\right]}{V} \equiv \beta f^{\mathrm{id}}\left[\rho, \alpha\left(x\right)\right] = \rho\left[\ln\left(\rho\Lambda^5\mathcal{M}/\mathcal{I}\right) - 1\right] + \rho\int_{-1}^{1} \mathrm{d}x\, \alpha\left(x\right) \ln\left[2\alpha\left(x\right)\right], \tag{56}$$

where $x \equiv \cos\theta$ has also been used. The first term on the far right-hand side is the kinetic contribution to the free-energy density f^{id}. This is reflected by the exponent 5 of the thermal de Broglie wavelength Λ which arises because particles of uniaxial symmetry have three translational and two rotational degrees of freedom. As we are exclusively concerned with systems at thermodynamic equilibrium, specific values of Λ, $\mathcal{M}$, and $\mathcal{I}$ are not relevant.

The second term on the far right-hand side of eq. (**??**) accounts for the loss in orientational entropy upon the formation of an ordered (i.e., nematic) phase.

From eqs. (**??**), (**??**), (**??**), (**??**), (**??**), and (**??**) we obtain the grand potential as

$$\frac{\beta\Omega\left[\rho,\alpha\left(x\right)\right]}{V}=\beta f^{\mathrm{id}}\left(\rho\right)+\beta f^{\mathrm{hs}}\left(\rho\right)+\beta f^{\mathrm{sw}}\left(\rho\right)+\rho^{2}\sum_{l=0}^{\infty}\alpha_{l}^{2}u_{l}-\beta\rho\mu, \tag{57}$$

where eqs. (**??**) and (**??**) have also been used. Because eq. (**??**) is based on the assumption that the generic singlet density correlation function can be decoupled as in eq. (**??**), it is clear that the grand potential is a *function* of ρ and a *functional* of α.

Thermodynamic stability

From eq. (**??**) it follows that thermodynamically stable states must satisfy the equations

$$\frac{\beta}{V}\left(\frac{\partial\Omega}{\partial\rho}\right)_{T,\mu} = 0 \tag{58a}$$

$$\frac{\beta}{V}\frac{\delta\Omega}{\delta\alpha\left(x\right)} = \chi\left(T,\rho\right), \tag{58b}$$

where the operator δ indicates a functional derivative and the Lagrangian multiplier χ is introduced to ensure that solutions of eq. (**??**) automatically satisfy the normalization eq. (**??**).

Eq. (**??**) immediately gives a relationship between the contributions to the chemical potential:

$$\beta\mu^{\mathrm{id}}+\beta\mu^{\mathrm{hs}}+\beta\mu^{\mathrm{sw}}+2\rho\sum_{l=0}^{\infty}\alpha_{l}^{2}u_{l}-\beta\mu=0, \tag{59}$$

where $\mu^{\mathrm{hs}}\equiv\left(\partial f^{\mathrm{hs}}/\partial\rho\right)_{T}$, $\mu^{\mathrm{sw}}\equiv\left(\partial f^{\mathrm{sw}}/\partial\rho\right)_{T}$, $\mu^{\mathrm{id}}\equiv\left(\partial f^{\mathrm{id}}/\partial\rho\right)_{T}$ can easily be obtained from the expressions given in eqs. (**??**), (**??**), and (**??**), respectively.

Solving eq. (**??**) for $\beta\mu$ and replacing the corresponding term in eq. (**??**) allows us to rewrite the latter expression compactly as

$$\frac{\beta\Omega}{V}=-\beta P^{\mathrm{CS}}-\beta P^{\mathrm{sw}}-\rho^{2}\sum_{l=0}^{\infty}\alpha_{l}^{2}u_{l}=-\beta P, \tag{60}$$

where P is the pressure and

$$\frac{\beta P^{\mathrm{CS}}}{\rho} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}, \tag{61a}$$

$$\frac{\beta P^{\mathrm{sw}}}{\rho} = \frac{2\pi}{3}\beta\varepsilon\rho\sigma^3\left(\lambda^3-1\right)\left\{g_{\mathrm{hs}}^{\mathrm{c}}\left(\eta_{\mathrm{eff}}\right)+\frac{\mathrm{d}g_{\mathrm{hs}}^{\mathrm{c}}\left(\eta_{\mathrm{eff}}\right)}{\mathrm{d}\eta_{\mathrm{eff}}} \times\left[c_1\left(\lambda\right)\eta+2c_2\left(\lambda\right)\eta^2+3c_3\left(\lambda\right)\eta^3\right]\right\}. \tag{61b}$$

The expression given in eq. (**??**) is, of course, the celebrated Carnahan-Starling equation of state[?] ; eqs. (**??**) and (**??**) have been utilized to arrive at eq. (**??**) after a couple of straightforward and simple algebraic manipulations.

To solve eq. (**??**) we insert eq. (**??**) into eq. (**??**) and perform the functional derivative in eq. (**??**). This yields [see eq. (**??**)]

$$\begin{aligned}\alpha\left(x\right) &= \frac{1}{2}\exp\left[\left(\chi-\rho\right)/\rho\right]\exp\left[-\rho\sum_{l=0}^{\infty}\left(2l+1\right)u_l\alpha_l P_l\left(x\right)\right] \\ &\equiv \frac{1}{2}\exp\left[\left(\chi-\rho\right)/\rho\right]\Psi\left(x\right).\end{aligned} \tag{62}$$

Because of the normalization eq. (**??**) we can solve eq. (**??**) for the Lagrangian multiplier to obtain

$$\frac{\chi\left(T,\rho\right)-\rho}{\rho} = -\ln\frac{1}{2}\int_{-1}^{1}\mathrm{d}x\,\Psi\left(x\right). \tag{63}$$

With this expression and eq. (**??**) it is easy to verify that

$$\int_{-1}^{1}\mathrm{d}x\,\alpha\left(x\right)\ln\left[2\alpha\left(x\right)\right] = \frac{\chi\left(T,\rho\right)-\rho}{\rho}-2\rho\sum_{l=0}^{\infty}\alpha_l^2 u_l. \tag{64}$$

Using now the definition of μ^{id} (see above) we realize from eq. (**??**) that

$$\beta\mu^{\mathrm{id}} = \ln\left(\rho\Lambda^5 m/\mathcal{I}\right)-\ln\frac{1}{2}\int_{-1}^{1}\mathrm{d}x\,\Psi\left(x\right)-2\rho\sum_{l=0}^{\infty}u_l\alpha_l^2, \tag{65}$$

where eqs. (**??**) and (**??**) have also been employed. Hence, from eq. (**??**) we arrive at

$$\beta\mu = \ln\left(\rho\Lambda^5 m/\mathcal{I}\right) - \ln\frac{1}{2}\int_{-1}^{1}\mathrm{d}x\,\Psi\left(x\right) + \beta\mu^{\mathrm{hs}} + \beta\mu^{\mathrm{sw}}. \tag{66}$$

Phase coexistence

Consider now two thermodynamic equilibrium phases labeled $'$ and $''$. At coexistence the equations

$$P' = P'' \tag{67a}$$

$$\mu' = \mu'' \tag{67b}$$

$$T' = T'' \tag{67c}$$

need to be satisfied. Henceforth, we shall adopt the convention that $\rho' \leq \rho''$ where the equality holds at the (gas-liquid) critical point. In addition, members of the subset $\{\alpha_l'\}_{l>0}$ vanish for the isotropic phase. The reason is that in the isotropic phase $\alpha = 1/4\pi$ because of eq. (**??**) and because $\int_{-1}^{1}\mathrm{d}x\,P_l\left(x\right) = \delta_{l0}$. From eq. (**??**) one finds that the first coexistence condition corresponds to roots of the equation

$$\begin{aligned} r_1 \stackrel{!}{=} 0 \;\; = \;\; & -\beta P^{\mathrm{CS}}(\rho') + \beta P^{\mathrm{CS}}(\rho'') - \beta P^{\mathrm{sw}}(\rho') + \beta P^{\mathrm{sw}}(\rho'') \\ & -\frac{u_0}{4}(\rho'^2 - \rho''^2) + \rho''^2\sum_{l=2}^{\infty}\alpha_l^2 u_l, \end{aligned} \tag{68}$$

where here and below the exclamation mark above the equal sign signifies that we have to solve for the zeros of the expression on the far right-hand side. Notice, that within the AMMF framework the fifth term on the right-hand side of eq. (**??**) will also be present if the two coexisting phases are gas and isotropic liquid. Hence, within the AMMF approximation one expects the gas-liquid critical point to be elevated compared with an isotropic square-well bulk fluid because $u_0 < 0$ [see eq. (**??**)]; this lowers the excess free energy of the anisotropic

compared with that of the isotropic square-well bulk fluid. One immediate consequence is that the critical temperature is shifted upward slightly compared with the isotropic square-well bulk fluid.

Because of eq. (**??**), eq. (**??**) gives rise to a second relation

$$\begin{aligned} r_2 \stackrel{!}{=} 0 \quad &= \quad \ln\left(\frac{\rho'}{\rho''}\right) + \frac{u_0}{2}(\rho' - \rho'') + \ln\frac{1}{2}\int_{-1}^{1} \mathrm{d}x\, \Gamma\left(x\right) \\ &\quad + \beta\mu^{\mathrm{hs}}(\rho') - \beta\mu^{\mathrm{hs}}(\rho'') + \beta\mu^{\mathrm{sw}}(\rho') - \beta\mu^{\mathrm{sw}}(\rho''), \end{aligned} \tag{69}$$

where

$$\Gamma\left(x\right) \equiv \exp\left(\rho u_0/2\right) \Psi\left(x\right). \tag{70}$$

The term proportional to u_0 has been treated separately in eqs. (**??**) and (**??**) because it will always be present at the AMMF level of approximation regardless of the physical nature of phases $'$ and $''$ (see also discussion at the end of Section **??**).

In addition to eqs. (**??**) and and (**??**), we need to solve $k/2+2$ eqs. of the form

$$r_{k/2+2} \stackrel{!}{=} 0 = \alpha_k - \frac{2k+1}{2}\frac{\int_{-1}^{1} \mathrm{d}x\, \Gamma\left(x\right) P_k\left(x\right)}{\int_{-1}^{1} \mathrm{d}x\, \Gamma\left(x\right)}, \tag{71}$$

where we limit ourselves to $k = 2, 4$.

Results

Preliminary remarks

Throughout our work all physical quantities are expressed in terms of dimensionless (i.e., "reduced") units. For example, length is given in units of σ, energy in units of ε, and temperature in units of $\varepsilon/k_{\mathrm{B}}$. Other derived quantities such as, for example, density or pressure are then cast in terms of suitable combinations of those basic units.

To solve eqs. (**??**), (**??**), and (**??**) we employ a simple Newton-Raphson scheme described

in detail in Ref. **?** . To obtain convergence a physically sensible initial guess is crucial. For example, at gas-nematic coexistence the initial choice for $\rho' = 10^{-5}$ and $\rho'' = 1.0$ together with $\mathcal{O}_2 = \mathcal{O}_4 = 1.0$ would constitute such a physically sensible initial guess. With a temperature increment of $\Delta T = 10^{-6}$ – 10^{-5} one then takes the converged solution of eqs. (**??**) – (**??**) at T as initial solutions at $T + \Delta T$. This way one will find solutions even very close to the gas-liquid critcal point.

The complementary Monte Carlo (MC) simulations are carried out in the grand canonical ensemble as far as state points along gas-nematic and gas-isotropic liquid branches of the phase diagram are concerned. Grand-canonical simulations are appropriate because the nematic and isotropic liquid phases at coexistence are of moderate density such that the inevitable insertion and deletion of mesogens can be realized with sufficiently large acceptance ratios. The moderate density of isotropic-liquid and nematic phases along their respective phase boundaries is a generic feature of the present model. To analyze the transition between isotropic liquid and nematic phases MC simulations in the canonical ensemble are undertaken.

Phase behaviour from Monte Carlo simulations

The generation of a Markov chain of configurations in the grand canonical ensemble proceeds in a sequence of individual steps. First, one of the existing N mesogens in the system is displaced or rotated with equal probability. If a mesogen is to be displaced its new position will be in a small cube of side length δs centered on the original center-of-mass position. The magnitude of δs is adjusted during each simulation such that about $40 - 60\%$ of all displacement attempts are accepted on average. We employ the conventional Metropolis criterion[? ?] to decide whether an individual attempt is accepted. If a mesogen is to be rotated instead, one of the three Cartesian axes is selected and the mesogen is then rotated about that axis by a small angle increment. As for δs, this angle increment is again adjusted during an individual run such that $40 - 60\%$ of all attempts are accepted on average. Again

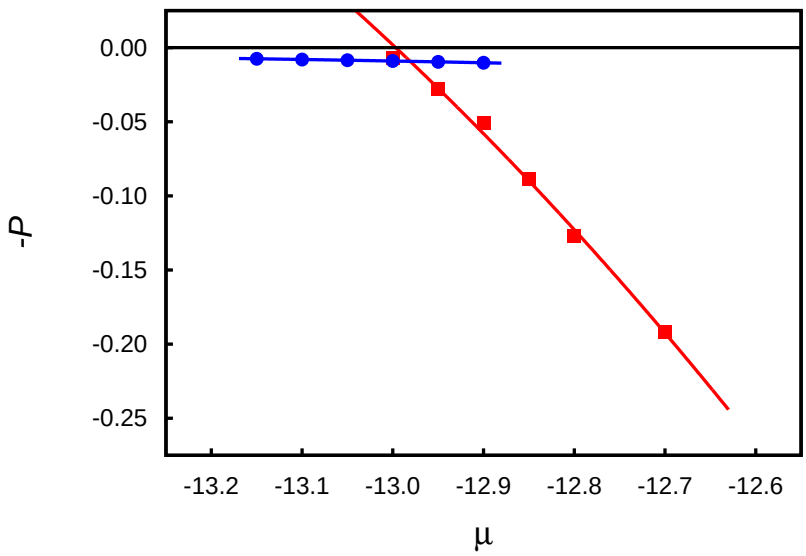


Figure 1: The negative pressure $-P$ (corresponding to the grand-potential density) as a function of chemical potential μ for $T = 0.90$ and $\varepsilon' = 0.40$; (■) nematic and (●) gas phase. The continuous curves are quadratic polynomials fitted to the discrete data points and are intended to guide the eye. The intersection of both demarcates the chemical potential at coexistence μ_x. The black horizontal solid line reveals that all the thermodynamically states considered are mechanically stable, that is $P > 0$.

a standard Metropolis criterion is employed for the rotation acceptance.

After N attempts to displace or rotate the mesogens, N attempts are made to either create a new mesogen or to eliminate one of the existing particles. Creation and deletion of the mesogens is attempted with equal average probability. Again a Metropolis criterion is employed to accept the deletion and creation attempts.[??] Clearly, at the end of this grand canonical branch the actual number N' may differ in general from the initial number. Together the $2N$ processes constitute an MC cycle. Our simulations are based on runs comprising 2.0×10^5 such cycles where the first 5.0×10^3 cycles are reserved for equilibration which is achieved very quickly for the present model unlike for other model systems where the shape anisotropy of the mesogens is much larger. In addition, we adjust the system volume such that on average each run involves about 2.0×10^3 mesogens. The canonical ensemble MC simulations for the finite-size scaling analysis (see below) represent an exception; here

it is inherent that different system sizes are utilised in the methodology.

The key quantity to be computed in the grand canonical MC simulations is $\Omega \propto -P$ [see eq. (**??**)]. We begin deriving a suitable expression for P in a fluid composed of molecules with orientational degrees of freedom by starting from the Clausius virial expressed here as [see eq. (E.14) of Ref. **?**]

$$\frac{\beta P}{\rho} = 1 + \frac{\beta\rho}{6} \int \mathrm{d}\boldsymbol{r}_{12}\, r_{12} \left\langle \frac{\partial\varphi\left(\boldsymbol{r}_{12},\omega_1,\omega_2\right)}{\partial r_{12}} g\left(\boldsymbol{r}_{12},\omega_1,\omega_2\right) \right\rangle_{\omega_1,\omega_2}, \tag{72}$$

where again $\langle \ldots \rangle_{\omega_1,\omega_2}$ denotes an unweighted average over orientations in a space-fixed frame of reference. Employing the expansion given in eq. (**??**) as well as the orthogonality of rotational invariants [see eq. (**??**)] it is relatively straightforward to arrive at

$$\begin{aligned} \frac{\beta P}{\rho} &= 1 + \frac{2\pi}{3}\rho\sigma^3 \left\{ \frac{g_{000}\left(\sigma^+\right)}{\left(4\pi\right)^{3/2}} - \lambda^3 \left[\frac{g_{000}\left(\lambda\sigma^-\right)}{\left(4\pi\right)^{3/2}} - \frac{g_{000}\left(\lambda\sigma^+\right)}{\left(4\pi\right)^{3/2}} \right] \right\} \\ &\quad + \frac{2\pi}{3}\frac{\varepsilon'}{\sqrt{5}}\rho\sigma^3 \left\{ \frac{g_{220}\left(\sigma^+\right)}{\left(4\pi\right)^{3/2}} - \lambda^3 \left[\frac{g_{220}\left(\lambda\sigma^-\right)}{\left(4\pi\right)^{3/2}} - \frac{g_{220}\left(\lambda\sigma^+\right)}{\left(4\pi\right)^{3/2}} \right] \right\}, \end{aligned} \tag{73}$$

where the expansion coefficients g_{000} and g_{220} have to be taken at contact**?** (cf., Fig. **??** below). The superscripts of the arguments indicate whether this contact value is to be computed as a left $(-)$ or right-sided $(+)$ limiting value in a mathermatical sense. Noticing from eqs. (**??**) and (**??**) that

$$\frac{g_{000}\left(r_{12}\right)}{\left(4\pi\right)^{3/2}} = g_0\left(r_{12}\right) \tag{74}$$

one arrives at the well-known expression**? ?**

$$\frac{\beta P}{\rho} = 1 + \frac{2\pi}{3}\rho\sigma^3 \left\{ g\left(\sigma^+\right) - \lambda^3 \left[g\left(\lambda\sigma^-\right) - g\left(\lambda\sigma^+\right) \right] \right\} \tag{75}$$

in the limiting case of a system with purely isotropic square-well interactions [i.e., for $\varepsilon' = 0$ in eq. (**??**)]. Because of the thermodynamic relation $\left[\partial\left(V^{-1}\Omega\right)/\partial\mu\right]_{T,V} = -\rho$ one expects curves of different slopes for phases of (sufficiently) different densities (i.e., gas and nematic

liquid). Hence, plots of $-P$ versus μ for a given T will eventually intersect at the chemical potential $\mu_{\rm x}$ at which eqs. (**??**) and (**??**) are satisfied simultaneously.

This analysis is precluded for thermodynamic states for which an isotropic liquid coexists with a nematic phase. This is because for most of these states the densities are too high for any grand canonical ensemble MC simulation to be sufficiently efficient. It becomes prohibitively difficult to create new or delete already existing mesogens. Moreover, the density *difference* between isotropic and nematic phases is too small so that the slopes of plots of $-P$ versus μ are too alike to be discernible. Consequently, the intersection $\mu_{\rm x}$ is very difficult if not impossible to locate (note, that this is also an issue at the gas-liquid critical point). To circumvent this problem we turn to a finite-size scaling analysis and employ MC simulations in the canonical rather than the grand canonical ensemble.

The key quantity here is the so-called (instantaneous) alignment tensor[?]

$$\mathbf{Q} = \frac{1}{2N} \sum_{i=1}^{N} \left[3\widehat{\boldsymbol{u}}\left(\omega_i\right) \otimes \widehat{\boldsymbol{u}}\left(\omega_i\right) - \mathbf{1} \right], \tag{76}$$

where the operator $\otimes$ denotes the tensor product. As a consequence of this definition, $\mathbf{Q}$ is a real, symmetric and traceless second-rank tensor that can be represented by a 3×3 matrix. The alignment tensor satisfies the eigenvalue equation

$$\mathbf{Q}\, \widehat{\boldsymbol{n}}_{\pm,0} = s_{\pm,0} \widehat{\boldsymbol{n}}_{\pm,0}, \tag{77}$$

where $s_- < s_0 < s_+$ are the three eigenvalues and $\widehat{\boldsymbol{n}}_{\pm,0}$ are the associated eigenvectors. We follow standard practice[?] and define the nematic order parameter as $\langle s_+ \rangle$, where now $\langle \ldots \rangle$ indicates an average taken in the canonical ensemble. We obtain $s_{\pm,0}$ and $\widehat{\boldsymbol{n}}_{\pm,0}$ by solving the secular equation corresponding to eq. (**??**). This is achieved analytically using Cardano's[§] formula.[?]

Plots of $\langle s_+ \rangle$ in Figure **??**(a) indicate that at sufficiently high T in the isotropic phase, the

[§]Gerolamo Cardano (1501–1576), Italian mathematician, physician, inventor, astrologer, and gambler.

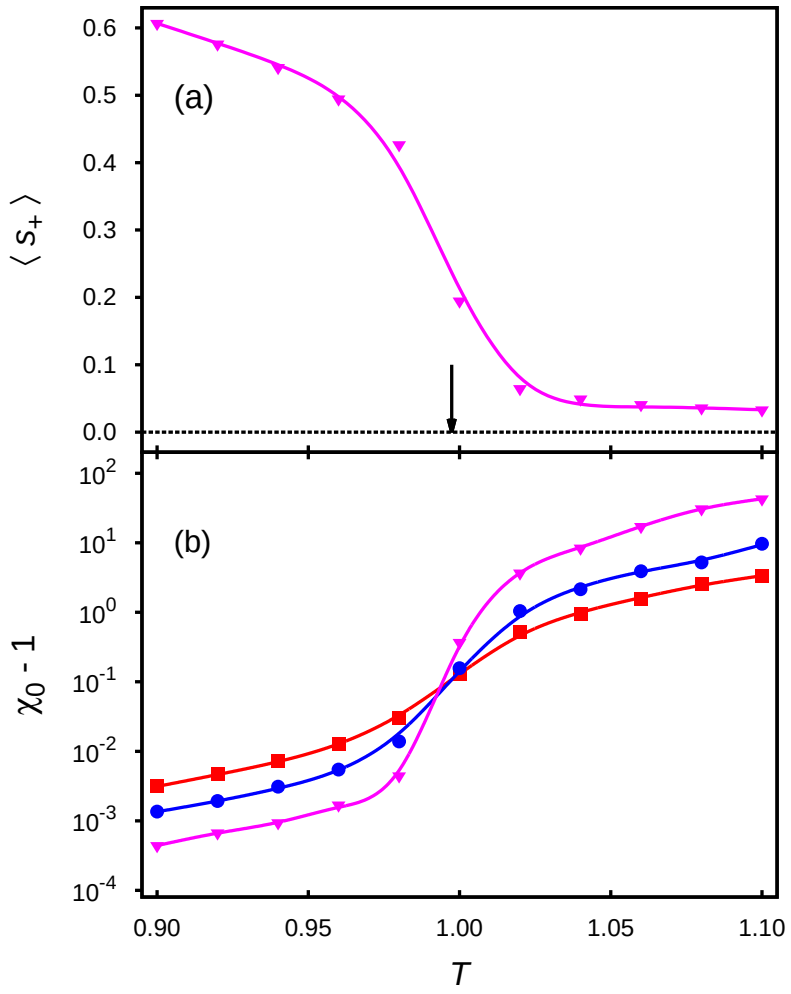


Figure 2: (a) Nematic order parameter $\langle s_+ \rangle$ as a function of temperature T for a system comprising $N = 5324$ mesogens at a fixed density of $\rho = 0.80$. The arrow demarcates the temperature $T_{\rm IN}$ at the isotropic-nematic phase transition located through plots of a second-order Binder cumulant presented in part (b) of the figure. (b) Plots of the second-order Binder cumulant $\chi_0 - 1$ of the middle eigenvalue s_0 of the alignment tensor $\mathbf{Q}$ for the same thermodynamic states considered in part (a) of the figure; (■) $N = 500$, (●) $N = 1372$, and (▼) $N = 5324$. The continuous curves are fits of a spline function to the discrete data points. In both parts of the figure data are presented for a coupling constant of $\varepsilon' = 0.40$ [see eq. (**??**)].

nematic order parameter nearly vanishes. However, on account of the inevitable finiteness of the system employed in the MC simulations, $\langle s_+ \rangle$ is not exactly zero in the isotropic phase.[?] As one lowers T, $\langle s_+ \rangle$ eventually rises as one crosses the IN phase transition. However, given

the resolution of our data, the variation of $\langle s_+ \rangle$ across that transition is found to be rather smooth; one would anticipate this for an order parameter at a second-order phase transition in a finite system, whereas $\langle s_+ \rangle$ should change discontinuously at a (sufficiently strong) first-order transition.

The severe rounding of $\langle s_+ \rangle$ visible in Figure **??**(a) is again a finite-size effect and indicates that for the present model system the IN phase transition is only weakly first-order. This conclusion was drawn in Ref. **?** on the basis of a much more elaborate finite-size scaling analysis of the IN phase transition in a closely related model system.

Following the methodology of Ref. **?** we locate the temperature $T_{\rm IN}$ of the isotropic-nematic phase transition through the second-order Binder cumulant

$$\chi_0 - 1 \equiv \frac{\langle s_0^2 \rangle}{\langle s_0 \rangle^2} - 1 = \frac{\langle s_0^2 \rangle - \langle s_0 \rangle^2}{\langle s_0 \rangle^2} \tag{78}$$

of the middle eigenvalue of $\mathbf{Q}$. This quantity has a transparent physical meaning as the expression on the far right-hand side of eq. (**??**) indicates that $\chi_0 - 1$ characterizes fluctuations in s_0. As first pointed out by Eppenga and Frenkel[**?**] and verified later for a model closely related to the present one[**?**] , $\chi_0 - 1 \propto N$ in the isotropic phase.

In the nematic phase, however, $\chi_0 - 1 \to 0$ where the value of the cumulant should be the smaller the larger the value of N. Thus, one anticipates pairs of cumulants for different N to intersect. In fact, on account of the weak first-order nature of the IN phase transition one finds that there is a unique intersection as one would anticipate for a true second-order transition.[**?**] Comparing plots in Figures **??**(a) and **??**(b) one realizes that $T_{\rm IN}$ obtained from the cumulant analysis agrees quite nicely with the inflection point in the plot shown in Figure **??**(a).

Plots in Figure **??**(b) confirm the existence of an apparently unique intersection of all three curves plotted. It is apparent that curves for different system sizes are "spread out" in the isotropic phase, intersect at $T_{\rm IN}$, and decline strongly for $T < T_{\rm IN}$. The variation of

$\chi_0 - 1$ is more pronounced around $T \approx T_{\mathrm{IN}}$ for larger N indicating that the system-size-related roundedness of the IN phase transition decreases for larger systems. In other words, with increasing N the first-order character of the phase transition becomes more pronounced. Unfortunately, such an approach does not permit us to determine the true densities of the coexisting isotropic liquid and nematic phases.

Phase behaviour and orientational order from density functional theory

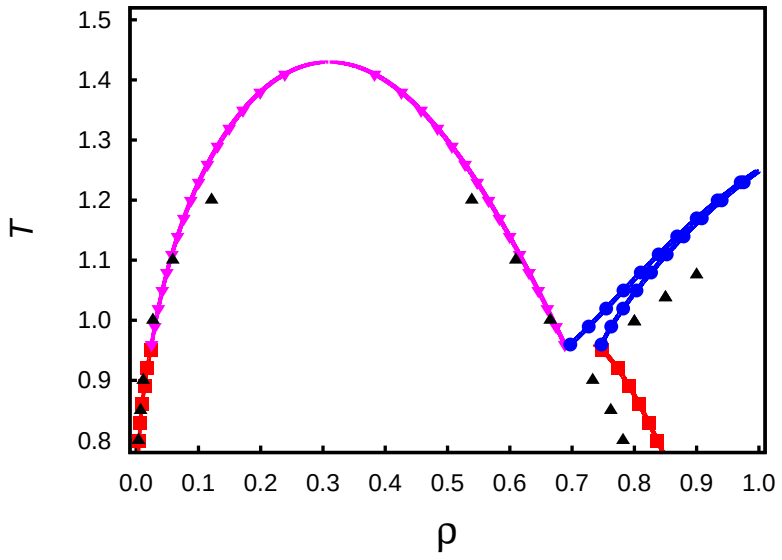


Figure 3: Temperature T versus density ρ representation of the phase diagram for model mesogens with an intermediate coupling constant $\varepsilon' = 0.40$ [see eq. (**??**)]; (■) gas-nematic, (▼) gas-isotropic liquid, (●) isotropic liquid-nematic phase coexistence; (▲) are corresponding data from MC simulations.

Next we turn to a consideration of the phase behaviour of a liquid crystal with a moderately strong coupling of φ_{aniso}. DFT results plotted in Figure **??** reveal that at sufficiently low T we have coexistence between a gas and a nematic phase. This phase coexistence ends at a triple point $T_{\mathrm{tr}} \simeq 0.96$ at which the nematic and the gas phase coexist with an isotropic liquid phase. At higher temperatures $T > T_{\mathrm{tr}}$ the nematic phase is in coexistence with the

isotropic liquid whereas the latter coexists independently with a gas phase. Coexistence between gas and isotropic liquid is bounded at a critical point located at $T_c \simeq 1.45$ and $\rho_c \simeq 0.31$.

The agreement between the DFT calculations and the corresponding MC data in Figure **??** is quite reasonable even for states for which one of the coexisting phases is the nematic. For example, the deviation between MC and DFT data for coexisting nematic phase is only about 7%. Moreover, the deviation seen for the densities of coexisting isotropic liquid and nematic phases is roughly of the same order of magnitude. However, here the slope of the data is slightly smaller for the MC compared with the DFT data. However, one has to keep in mind that the densities are quite high so that in reality the nematic may already be close to a solid phase transition that is not accounted for by our DFT. Nevertheless, we have verified that the simulated structural information for states considered in Figure **??** is consistent with fluid (isotropic and nematic) phases (see discussion in Section **??**).

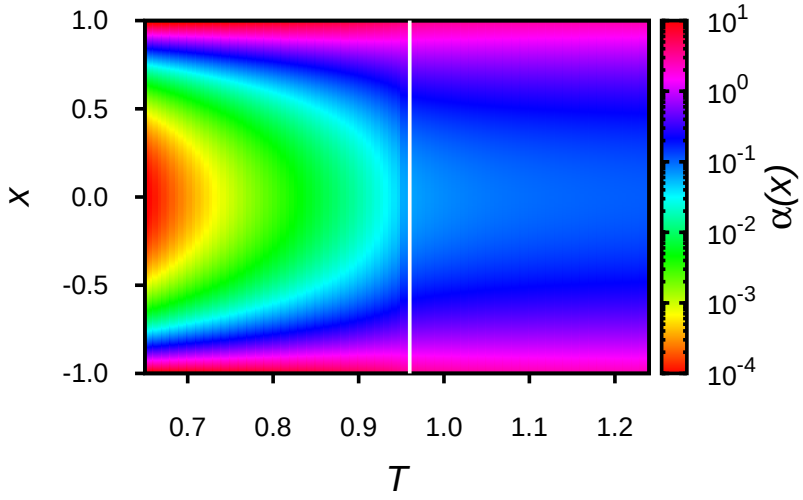


Figure 4: DFT results for the orientation distribution function $\alpha(x)$ of the model mesogen as a function of temperature T. Data are shown for the coexisting nematic phase at $\varepsilon' = 0.40$ (see Figure **??**). The value of $\alpha(x)$ is indicted by the colour bar on the right of the figure. The white vertical line demarcates the triple-point temperature $T_{tr} \simeq 0.96$.

Another characteristic indicated by the plots in Figure **??** is that for a coupling constant

of $\varepsilon' = 0.40$ the density difference between the coexisting isotropic liquid and nematic states is rather small as expected. Thus, coexisting densities would be impossible to calculate from plots such as the ones shown in Figure **??**. In addition, the DFT data reveal that up to the highest densities considered there is a noticeable albeit minute density difference between isotropic and nematic phases. This suggests that this part of the phase diagram does not end in a second critical point but that instead this phase transition remains very weakly first-order. On the one hand, this is consistent with Landau-de Gennes theory. However, one has to bear in mind that this is a phenomenological theory in which one *assumes* from the outset that the IN phase transition is first-order. In our approach, on the other hand, no such assumption is invoked. Hence, unlike Landau-de Gennes theory our approach has predictive power as far as the physical nature of the IN phase transition is concerned.

The agreement is less satifactory for gas-isotropic liquid coexistence when $T \gtrsim 1.20$. This is a well-understood feature that can be ascribed to the relative inadequacy of the present treatment of the free-energy contribution of the reference system at the level of first-order Barker-Henderson perturbation theory (see Section **??**). However, strategies to improve the prediction for the gas-isotropic liquid coexistence in the near-critical region are available.[? ?] The emphasis of our current work is on an assessment of the adequacy of the present version of DFT in describing the phase coexistence phases in the nematic. Consequently, no attempts have been made to improve the agreement between DFT and MC results in the near-critical region.

It is also instructive to analyze the orientation distribution function α for nematic states coexisting with either gas or isotropic-liquid states. It is clear from the plot in Figure **??** that α is symmetric about $x = 0$ reflecting the head-tail symmetry of the nematic director (i.e., the fact that $\widehat{\boldsymbol{n}}_+$ and $-\widehat{\boldsymbol{n}}_+$ are equivalent). Moreover, α increases to relatively high values as $|x| \to 1$ and is quite peaked at $|x| = 1$. This indicates that the majority of the mesogens are aligned with the nematic director. As T increases towards $T_{\rm tr}$, the orientation distribution function becomes somewhat less peaked at $|x| = 1$ because the thermal energy

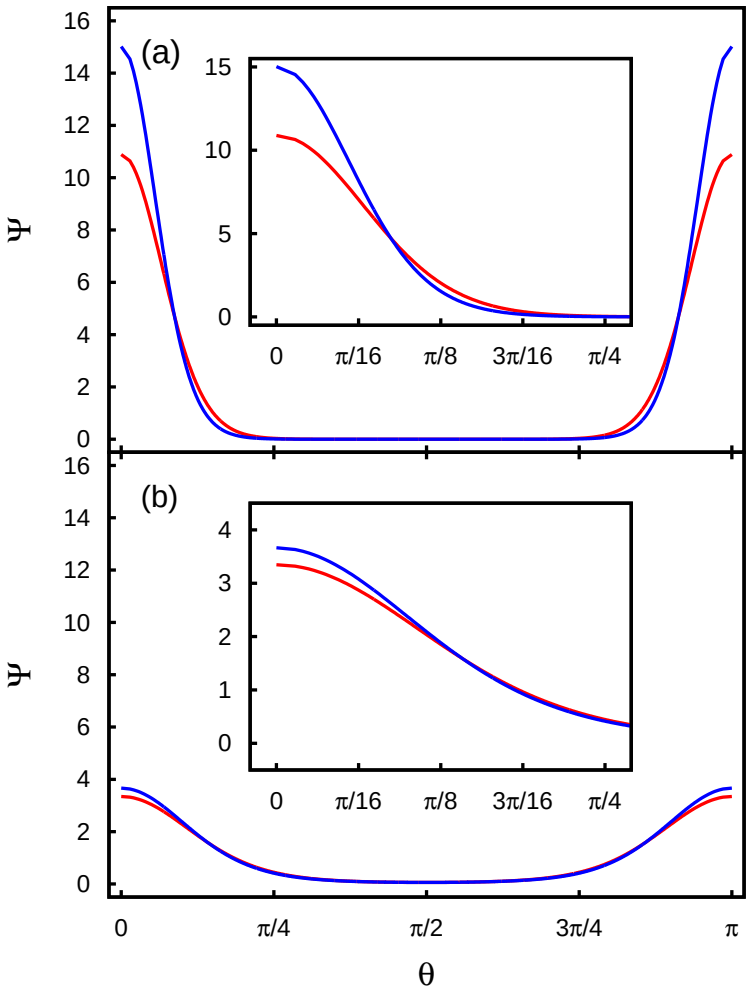


Figure 5: The *normalized* orientation distribution function Ψ [see eq. (**??**)] as a function of the angle θ for the model mesogen obtained from DFT calculations; (a) $T = 0.65$, (b) $T = 0.96$ (see Figure **??**). (—) only α_2 is included in the definition of Ψ whereas (—) also the contribution proportional to α_4 is taken into account.

of the molecules is increasing. Above $T_{\rm tr}$ (i.e., for a nematic coexisting with an isotropic liquid phase, cf. Figure **??**), α does not vary much with increasing T.

To enable a comparison with a recent experimental study of polymeric systems[?] we show plots of the orientation distribution function Ψ [cf., eq. (**??**)] as a function of the angle θ between the average orientation of mesogens with respect to the nematic director $\widehat{\boldsymbol{n}}_+$ in Figure **??**. By means of electron paramagnetic resonance spectra Yankova *et al.*[?] analyze

in Figure 8 of their paper how second, fourth, and sixth moments of the order parameter distribution contribute to the overall distribution. It turns out that with only the second moment, the order parameter distribution is represented rather crudely whereas the sixth-order moment gives only a marginal improvement over a distribution based on just the second- and fourth-order moments; the orientation distribution function based on only the moment of second order is much smaller but wider compared with the one based on both the second- and fourth-order moments.

These general trends are reflected by our data as shown in Figure **??**(a). For $T = 0.65$ and at $\theta = 0$ and $\theta = \pi$ the difference between Ψ involving only α_2 and the one employing both α_2 and α_4 can be as large as 23%. In addition, the description of Ψ including only α_2 is marginally wider than the one computed from both α_2 and α_4. This width is more pronounced experimentally.[?] All these effects diminish relatively quickly as revealed in Figure **??**(b) for $T = 0.95$. We note that this temperature is already rather close to the triple point (see Figure **??**).

At this stage additional insight is gained by considering an even simpler *ansatz* for g than the one introduced in eq. (**??**). Assuming that the interaction potential φ_0 of the isotropic reference system is solely responsible for the structure of the fluid we introduce the approximation

$$g\left(\boldsymbol{r}_{12}, \omega_1, \omega_2\right) = g_0\left(r_{12}\right). \tag{79}$$

Thus, the integrand in eq. (**??**) is proportional to the perturbation potential φ_1. As before [cf., eq. (**??**)] and to facilitate an analytic integration over orientations, we expand φ_1 in the basis of rotational invariants according to

$$\varphi_1\left(\boldsymbol{r}_{12}, \omega_1, \omega_2\right) = \sum_{l_1 l_2 l} \varphi_{l_1 l_2 l}\left(r_{12}\right) \Phi_{l_1 l_2 l}\left(\omega_1, \omega_2, \omega\right). \tag{80}$$

Elements of the set $\{\varphi_{l_1 l_2 l}\}$ are expansion coefficients. Similar to eq. (**??**) we can solve eq. (**??**) for these expansion coefficients. However, because $\varphi_1 \propto \Phi_{220}$ and because of eq. (**??**) it is

immediately clear that the triple sum in eq. (**??**) vanishes so that φ_{220} is the only nonzero expansion coefficient.

Inserting now eq. (**??**) into eq. (**??**), employing the decomposition of the generic single-particle distribution function [cf., eq. (**??**)], and performing the integration over orientations as detailed in Appendix **??**, we eventually obtain

$$\frac{\beta\Delta\mathcal{F}}{V} = \rho^2\alpha_2^2 u_2, \tag{81}$$

where

$$\begin{aligned} u_2 &= \frac{8\pi}{25}\beta\varepsilon' \int\limits_0^\infty \mathrm{d}r_{12}\, r_{12}^2 g_0\left(r_{12}\right)\varphi_{\mathrm{sw}}\left(r_{12}\right) \\ &\simeq -\frac{8\pi}{75} g_{\mathrm{hs}}^{\mathrm{c}}\left(\eta_{\mathrm{eff}}\right)\beta\varepsilon\varepsilon'\sigma^3\left(\lambda^3-1\right). \end{aligned} \tag{82}$$

This expression matches the term proportional to $\beta\varepsilon\varepsilon'$ in eq. (**??**). To arrive at eq. (**??**) we again employed the first mean-value theorem for definite integrals [cf., eq. (**??**)] together with eq. (**??**). Eq. (**??**) is the counterpart of eq. (**??**) obtained above within the AMMF approximation.

However, unlike eq. (**??**), eq. (**??**) contains an infinite number of terms *in principle*. This is a direct consequence of the high-temperature expansion of the orientation-dependent Mayer f-function [cf. eq. (**??**)] on which the expression for $\Delta\mathcal{F}$ rests at the AMMF level of approximation. Then the truncation of the sum in eq. (**??**) is related to the truncation of the expansion in eq. (**??**) [and is therefore related to the number of terms in the linear combination of different rotational invariants; cf., for example, eqs. (**??**) and (**??**)].

Similarly, because of eq. (**??**) the orientation distribution function [cf., eq. (**??**)] is solely (and therefore rather crudely) determined by α_2. On the contrary, within the AMMF approximation and depending on the truncation of the expansion in eq. (**??**), a whole set of expansion coefficients $\{\alpha_l\}_{l\geq 2}$ can be employed to characterize the orientation distribution

function in greater (and with *in principle* arbitrary) detail (cf., Figure **??**).

Most notably, however, the *ansatz* in eq. (**??**) also causes u_0 to vanish. Hence, terms proportional to u_0 in eqs. (**??**) and (**??**) disappear. As a consequence and irrespective of the coupling constant ε', the coexistence curve of the *anisotropic* bulk square-well fluid for $T_{\rm tr} \lesssim T \leq T_{\rm c}$ remains unaltered compared with that of its *isotropic* counterpart.

Orientation-dependent correlations in the nematic phase

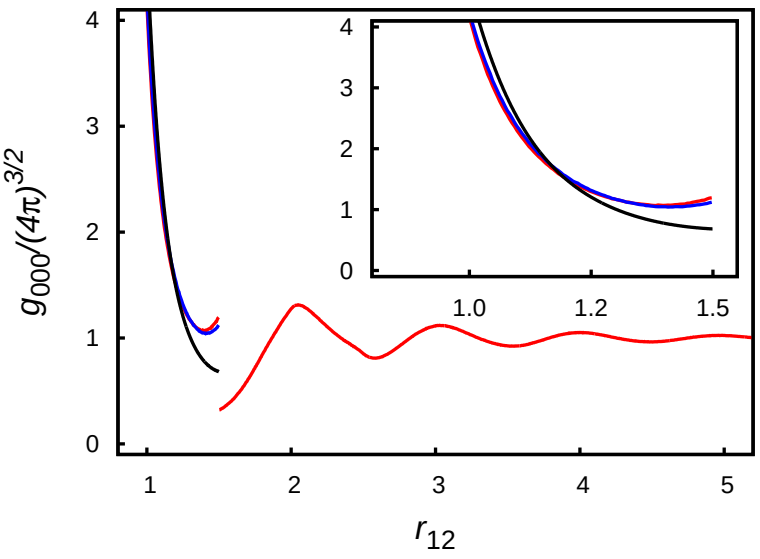


Figure 6: Plots of the expansion coefficient $g_{000}/\left(4\pi\right)^{3/2}$ of the orientation-dependent pair correlation function of the model mesogen [$\varepsilon' = 0.40$, cf. eq. (**??**)] as a function of intermolecular separation r_{12} for a temperature $T = 0.90$ and a density of $\rho = 0.85$; (—) MC data [see eq. (**??**)], (—) from eq. (**??**) using g_0 for the isotropic reference system also from MC. In addition, (—) is also obtained from eq. (**??**) where g_0 has been replaced by $g_{\rm hs}$ at the same density. The latter is obtained as a numerical solution of the Ornstein-Zernike integral equation using the RHNC closure.[?] The inset shows the expansion coefficient on an expanded scale $1.00 \leq r_{12} \leq 1.50$ where φ_1 is nonzero.

To gain deeper insight into the reliability of the AMMF approximation introduced in eq. (**??**) we now turn to a discussion of expansion coefficients $\{g_{l_1 l_2 l}\}$ which are accessible by

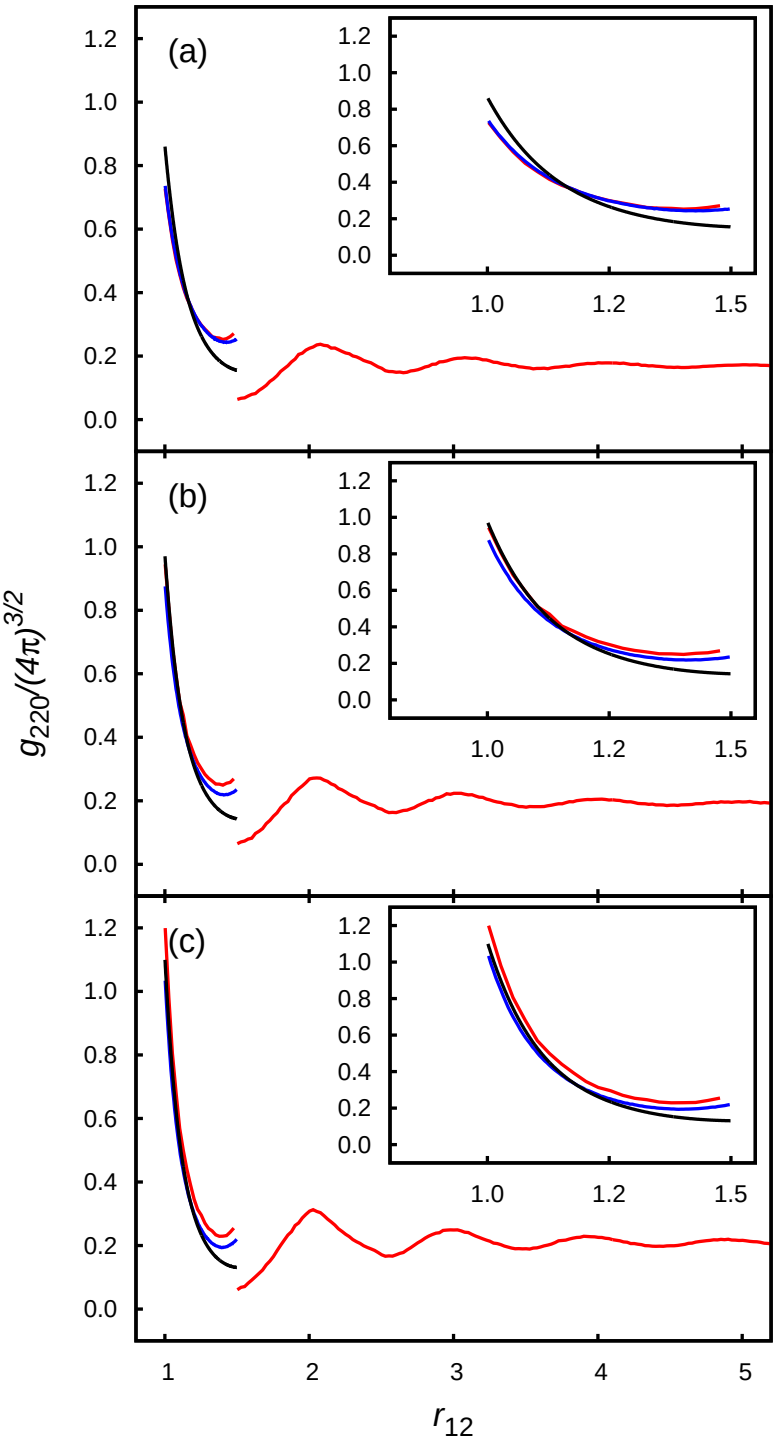


Figure 7: As Figure **??**, but for the expansion coefficient $g_{220}/\left(4\pi\right)^{3/2}$ and densities $\rho = 0.80$ (a), $\rho = 0.85$ (b), and $\rho = 0.90$ (c) (see also Figure **??**).

MC simulations through the expression

$$g_{ll0}\left(r_{12}\right) = \sqrt{4\pi} \sum_{m=-l}^{l} \left(-1\right)^{l+m} \left(2l+1\right)^{-1/2} g\left(r_{12}; llm\right). \tag{83}$$

This expression follows directly from eq. (**??**) and eq. (A.157) of the book by Gray and Gubbins.[**?**] Explicit expressions for the expansion coefficients in the intermolecular frame of reference are given in eq. (**??**). On account of symmetry and because of the summation over m expansion coefficients in the intermolecular frame of reference, the coefficients depend only on $|m|$. Moreover, as demonstrated in Appendix **??** for expansion coefficients of the orientation-dependent Mayer f-function, only $\{g_{ll0}\}$ are relevant for our model which is a consequence of the orientation dependence of φ_1 in eq. (**??**).

In the following discussion we focus on coefficients for $l = 0$ and $l = 2$. The plots presented in Figure **??** reveal that the agreement between g_{000} obtained from eqs. (**??**) and (**??**) and that from eq. (**??**) is remarkably good over the range $1.00 \leq r_{12} \leq 1.50$. This observation lends credibility to our approximation that the hard-core contribution $\varphi_{\rm hs}$ predominantly determines the structure of the nematic phase. Unfortunately, the long-range parts of g_{000} are completely inacessible on account of the temperature expansion on which eq. (**??**) is based. This is because eq. (**??**) involves the Heaviside function, cutting off φ_1 at $r_{12} = \lambda\sigma$.

It is evident from the plots of the next-to-leading coefficient g_{220} presented in Figures **??**(a) – **??**(c) that at contact this coefficient is about five times smaller than its counterpart g_{000}. This feature becomes clear in Figure **??** and by realizing from eq. (**??**) that at leading order g_{220} is proportional to $g_0\beta\varepsilon\varepsilon'/\sqrt{5}$ whereas $g_{000} \propto g_0$. For the present choice of parameters $\beta\varepsilon\varepsilon'/\sqrt{5} \simeq 0.16$.

Another feature that is apparent from Figures **??**(a) – **??**(c) is that the contact value of g_{220} is rather sensitive to the density. It increases with density and changes by about a factor of 1.50 between the lowest and the highest density considered in Figures **??**(a) – **??**(c). One also notices that the agreement between the MC data obtained via eqs. (**??**) together with

(**??**) – (**??**) on the one hand and eq. (**??**) on the other hand for all data sets in Figures **??** and **??**(a) – **??**(c) is remarkably good.

In addition, we present in Figures **??** and **??**(a) – **??**(c) plots of eqs. (**??**) where we replace g_0 by the hard-sphere radial pair correlation function $g_{\rm hs}$ at the same densities. We obtain $g_{\rm hs}$ by numerically solving the Ornstein-Zernike equation employing the RHNC closure.[?] This provides some insight into the quality of the approximation introduced by replacing g_0 by $g_{\rm hs}^{\rm c}$ in the expression for u_l in eq. (**??**). We find that $g_{\rm hs}^{\rm c}$ agrees very well with g_0 at contact though a slight overshoot can be seen. The decay of $g_{\rm hs}$ over the range $\sigma \leq r \leq \lambda\sigma$ is a bit too marked compared with g_0. This causes $g_{\rm hs}$ to underestimate the intermolecular correlations in the reference system such that $g_{\rm hs}$ is systematically smaller than g_0 as r_{12} increases towards $r_{12} = \lambda\sigma$. However, one should again stress that the overall agreement between $g_{\rm hs}$ and g_0 over the range $\sigma \leq r_{12} \leq \lambda\sigma$ is quite satisfactory.

Summary, discussion, and conclusions

In this work we investigate the phase behaviour and structure of a simple model liquid crystal interacting via an anisotropic square-well potential. The anisotropic part incorporates an orientation dependence of the type introduced by Maier and Saupe.[?] In Maier and Saupe's model the orientation dependence is modeled such that a configuration is energetically favoured in which a pair of mesogens are parallel. As a result, the model is capable of representing the formation of a nematic in addition to the more conventional gas and isotropic liquid phases. The structure and phase behaviour of this model is investigated within the framework of classical DFT.

A model very closely related to the one employed here has been investigated earlier by Teixera and Telo da Gama.[?] However, these authors employed the so-called simple mean-field approximation of the van der Waals type in which pair correlations are disregarded altogether for $r_{12} > \sigma$.

Here we employ a more sophisticated treatment of the orientation-dependent pair correlations. By partitioning the total interaction potential φ into an isotropic contribution φ_0 and an anisotropic (perturbation) contribution φ_1, we assume that the structure of the fluid phases is dominated by interactions described by φ_0. Here we represent φ_0 by the (isotropic) square-well potential which defines our reference system. The anisotropic potential is of "multipolar" character in the sense that the unweighted orientational average of φ_1 vanishes.

We continuously transform the reference fluid into the fully interacting system by gradually turning on the anisotropic perturbation. The degree to which the anisotropic potential φ_1 is "switched on" is controlled by a dimensionless coupling parameter ξ. This procedure implies a similar continuous transformation of the radial pair correlation function g_0 of the reference system into the fully orientation dependent g in a system in which interactions are described by the full anisotropic potential φ. Hence, for each value of ξ a different orientation-dependent pair correlation function g needs to be considered which is unknown *a priori*.

It is then clear that a physically sensible *ansatz* is required for the dependence of g on ξ. Here, we consider the influence of φ_1 on g from an exact description in the limit $\rho \to 0$. By analogy with earlier treatments we refer to this approach as the AMMF approximation. In previous studies this type of approach is referred to as the modified mean-field (MMF) approximation[? ? ? ? ? ? ? ? ? ? ?] involving an *ansatz* for g which corresponds to a coupling of the full potential φ (rather than the anisotropic contribution φ_1 alone as in our current treatment) that is again correct only in the low-density limit.

The use of the MMF approximation has two major consequences. In comparison with the AMMF approximation, in which packing effects of the mesogens in dense fluid phases are accounted for in a much more realistic fashion, the widths of the two-phase regions are usually highly overestimated. Moreover, the critical density in the AMMF approximation is more realistic. These differences arise because the correlation length is grossly overestimated in the MMF approximation, an effect which is more pronounced at lower T.

In our DFT, the free energy associated with the reference isotropic system is then treated with a high-temperature Barker-Henderson perturbation theory.[?] At first order this perturbation theory yields an expression for the free energy that is *formally* identical to the one that is obtained within the present thermodynamic integration coupling approach if one uses as an *ansatz* for the radial pair correlation of the reference system the expression $g_0 = g_{\rm hs} \exp\left(-\beta\varphi_{\rm sw}\right)$. Expanding the exponential function in this *ansatz* in terms of powers of $\beta\varphi_{\rm sw}$ and retaining only the linear term yields an expression for the free energy of the reference system that is equivalent to the first-order perturbation theory of Barker and Henderson. However, this equivalence is in form only as the philosophy behind Barker and Henderson's perturbation theory and our thermodynamic integration is fundamentally different.

Whereas in Barker and Henderson's theory an expansion of the free energy about that of a hard-sphere reference system is utilized, knowledge of the orientation-dependent pair correlation is required for each strength of the coupling of the anisotropic part of the interaction potential to that of the reference system. Hence, in the perturbation approach of Barker and Henderson only a single and analytically available pair correlation function is required.

It then turns out that the AMMF approximation and the first-order Barker-Henderson theory overestimate the critical temperature significantly as demonstrated here by comparison with grand canonical ensemble MC simulations. This deficiency is quite well known and strategies to improve the near-critical description are available in principle. For example, rather than truncating the Barker-Henderson high-temperature expansion at lowest order, higher-order contributions could be included. A quantitatively correct description of near-critical vapour-liquid coexistence in Mie fluids is possible by taking the Barker-Henderson expansion up to third order.[?]

However, it needs to be stressed that for *any* theory describing the free energy (or any other thermodynamic potential) by an analytic function of the relevant thermodynamic fields, one anticipates that the critical behaviour is governed by classical critical exponents.

Nevertheless, the size of the classical near-critical T–ρ range can be narrowed substantially if a more elaborate description of the free energy of the isotropic reference system is employed.

However, in our current work we are concerned with the performance of the AMMF approximation in that part of the phase diagram in which one of the coexisting phases is the nematic. Consequently, no attempts have been made at this stage to improve the description of the gas-liquid critical regime by using a more sophisticated description of the reference system capable of narrowing the near-critical regime and thus counterbalancing the classical critical scaling to a greater extent.

Another advantageous feature of the AMMF approximation is that it permits access to the structure of the liquid crystal. This is because on account of the temperature expansion of f, one can in principle characterize Ψ in great detail by a countable infinite set of order parameters $\{\mathcal{O}_l\}$. However, in practice it turns out that the expansion in eq. (**??**) converges rather quickly[?] so that Ψ can be assumed to be nearly fully characterized by $\mathcal{O}_2$ and $\mathcal{O}_4$ alone. In addition, orientation dependent pair correlations are accounted for semi-quantitatively.

At the same time, the relative magnitudes of the coefficients g_{000} and g_{220} indicates that the expansion of g in eq. (**??**) may converge rather quickly as does the corresponding expansion of α in eq. (**??**). Thus, only a few of the coefficients $\{g_{ll0}\}$ may suffice to give a rather accurate description of orientation-dependent pair correlations in the nematic phase.

It should also be emphasized that within the AMMF approximation the expansion coefficients $\{g_{ll0}\}$ are nonzero only over the range $\sigma \leq r_{12} \leq \lambda\sigma$. Thus, the AMMF approximation is incapable of capturing long-range correlations in the nematic phase. In terms of the phase behaviour this is not a serious problem because $\Delta\mathcal{F}$ in eq. (**??**) is proportional to $\varphi_{\rm sw}$ [see eqs. (**??**) and (**??**) – (**??**)]. Thus, long-range correlations do not contribute to $\Delta\mathcal{F}$ but are cut off because of the square-well attraction in eq. (**??**).

If the radial pair correlation function of the reference fluid is replaced by a hard-sphere pair correlation function of a fluid at the same density the performance of the AMMF

approximation turns out to be somewhat less good. This is most likely the reason for the discrepancy between the phase diagram determined with DFT and the exact MC data because the DFT results are obtained by replacing g_0 in eq. (**??**) by the contact value $g_{\rm hs}^{\rm c}$ of the hard-sphere radial pair correlation function. However, without this replacement one would have to parametrize g_0 in terms of ρ *and* T for each and every ε and λ if the first mean-value theorem is still to be invoked to avoid time-consuming numerical integrations in computing the coefficients $\{u_l\}$.

Finally, we believe the treatment developed in this work to be quite useful with respect to experimental systems. This conclusion is bolstered by the work of Wu *et al.*[?] who investigated the nematogen poly-γ-benzoyl-L-glutamate, a rather rigid polypeptide, in dimethylformamide. Experimentally, this system exhibits a nematic-nematic phase transition which is captured quantitatively by a combination of an Onsager-type of treatment of the hard repulsive interactions with a superimposed van der Walls dispersion attraction despite the simple mean-field treatment at second-virial level (i.e., complete neglect of) intermolecular correlations. A similar if not improved performance is therefore anticipated for the present, more sophisticated approach in which intermolecular correlations are incorporated in a much more realistic fashion.

Integrals over molecular orientations

In this Appendix we seek to evaluate the integrals over orientations in eq. (**??**). On account of the uniaxial symmetry of φ_1 it is physically sensible to expect this symmetry to be reflected by the orientation distribution function as well. Thus, we expand α in terms of Legendre polynomials according to

$$2\pi\alpha\left(\omega\right)=\alpha\left(\cos\theta\right)=\sum_{l=0}^{\infty}\alpha_l P_l\left(x\right), \tag{84}$$

where $\{\alpha_l\}$ are expansion coefficients. Because of eq. (A.9b) of Ref. **?** we can invert eq. (**??**) to give

$$\alpha_l = \frac{2l+1}{2} \int_{-1}^{1} \mathrm{d}x \, \alpha(x) \, P_l(x) \,. \tag{85}$$

Notice, in particular, that $\alpha_0 = \frac{1}{2}$ irrespective of the nature of the phase in question. This is because $P_0 = 1$ and eq. (**??**) is always satisfied.

Because of the definition of rotational invariants given in eq. (**??**) it is, however, more convenient to express α in terms of spherical harmonics. The conversion of eq. (**??**) to the latter set of basis functions is enabled through the relation

$$P_L(x) = \sqrt{\frac{4\pi}{2L+1}} \mathcal{Y}_{L0}(\omega) \,. \tag{86}$$

Using this relation and eq. (**??**) we obtain

$$\begin{aligned} \int \mathrm{d}\omega_1 \, \mathrm{d}\omega_2 \, \mathrm{d}\omega \, \alpha(\omega_1) \, \alpha(\omega_2) \, \Phi_{l_1 l_2 l} \;\; &= \;\; \left(\frac{1}{2\pi}\right)^2 \sum_{L_1=0}^{\infty} \sum_{L_2=0}^{\infty} \sqrt{\frac{(4\pi)^2}{(2L_1+1)(2L_2+1)}} \alpha_{L_1} \alpha_{L_2} \\ &\quad \times \int \mathrm{d}\omega_1 \, \mathrm{d}\omega_2 \, \mathrm{d}\omega \, \mathcal{Y}_{L_1 0}(\omega_1) \, \mathcal{Y}_{L_2 0}(\omega_2) \, \Phi_{l_1 l_2 l} \end{aligned} \tag{87}$$

in eq. (**??**) where we temporarily dropped the arguments of $\Phi_{l_1 l_2 l}$ to ease the notational burden.

An inspection of eq. (**??**) reveals that eq. (**??**) involves $\mathcal{Y}^*_{lm}$ in the integrand. Consequently and according to eq. (A.38) of Ref. **?** , the integral over $\mathrm{d}\omega$ vanishes except for $l = m = 0$. Thus, we can rewrite eq. (**??**) as

$$\begin{aligned} &\int \mathrm{d}\omega_1 \, \mathrm{d}\omega_2 \, \mathrm{d}\omega \, \mathcal{Y}_{L_1 0}(\omega_1) \, \mathcal{Y}_{L_2 0}(\omega_2) \, \Phi_{l_1 l_2 l} = \sqrt{4\pi} \sum_m C(l_1 l_2 0; m \underline{m} 0) \\ &\times \int \mathrm{d}\omega_1 \, \mathrm{d}\omega_2 \, \mathcal{Y}_{L_1 0}(\omega_1) \, \mathcal{Y}_{l_1 m}(\omega_1) \, \mathcal{Y}_{L_2 0}(\omega_2) \, \mathcal{Y}_{l_2 \underline{m}}(\omega_2) \,, \end{aligned} \tag{88}$$

where we also used the selection rule $m_1 + m_2 = m$ for nonvanishing Clebsch-Gordan coefficients ($m = 0$). From eq. (A.27) of Gray and Gubbins[?] one then realizes that $l_1 = L_1$,

$l_2 = L_2$ and that $m = \underline{m} = 0$. Invoking also eq. (A.167) of the book by Gray and Gubbins[?] allows us to conclude that in addition, $l_1 = l_2$. In other words, the sum over m in the previous expression vanishes as well as the double sum over L_1 and L_2 in eq. (??). Hence, we finally arrive at

$$\int \mathrm{d}\omega_1 \, \mathrm{d}\omega_2 \, \mathrm{d}\omega \, \alpha\left(\omega_1\right) \alpha\left(\omega_2\right) \Phi_{l_1 l_2 l} = \frac{2}{\sqrt{\pi}} \left(-1\right)^{l'} \left(2l'+1\right)^{-3/2} \alpha_{l'}^2 \delta_{l_1 l_2}, \tag{89}$$

where $l_1 = l_2 = l'$ and $\delta_{l_1 l_2}$ is the Kronecker symbol. Using this result in eq. (??) we finally arrive at eq. (??).

Orthogonality of rotational invariants

In this Appendix we demonstrate that rotational invariants are orthogonal. To accomplish this consider the integral

$$\begin{aligned} & \int \mathrm{d}\omega_1 \, \mathrm{d}\omega_2 \, \Phi_{l_1 l_2 l}\left(\omega_1, \omega_2, \omega\right) \Phi^*_{l'_1 l'_2 l'}\left(\omega_1, \omega_2, \omega\right) \\ = & \sum_{\substack{m_1 m_2 m \\ m'_1 m'_2 m'}} C\left(l_1 l_2 l; m_1 m_2 m\right) C\left(l'_1 l'_2 l'; m'_1 m'_2 m'\right) \mathcal{Y}^*_{lm}\left(\omega\right) \mathcal{Y}_{l'm'}\left(\omega\right) \\ & \times \int \mathrm{d}\omega_1 \, \mathcal{Y}_{l_1 m_1}\left(\omega_1\right) \mathcal{Y}^*_{l'_1 m'_1}\left(\omega_1\right) \int \mathrm{d}\omega_2 \, \mathcal{Y}_{l_2 m_2}\left(\omega_2\right) \mathcal{Y}^*_{l'_2 m'_2}\left(\omega_2\right). \end{aligned} \tag{90}$$

Using in this expression eq. (A.39) of Ref. ? we find that

$$\begin{aligned} & \sum_{\substack{m_1 m_2 m \\ m'_1 m'_2 m'}} C\left(l_1 l_2 l; m_1 m_2 m\right) C\left(l'_1 l'_2 l'; m'_1 m'_2 m'\right) \mathcal{Y}^*_{lm}\left(\omega\right) \mathcal{Y}_{l'm'}\left(\omega\right) \delta_{l_1 l'_1} \delta_{m_1 m'_1} \delta_{l_2 l'_2} \delta_{m_2 m'_2} \\ = & \sum_m \mathcal{Y}^*_{lm}\left(\omega\right) \mathcal{Y}_{l'm'}\left(\omega\right) \delta_{l_1 l'_1} \delta_{l_2 l'_2} \delta_{l l'} = \sum_m \left|\mathcal{Y}_{lm}\right|^2 \delta_{l_1 l'_1} \delta_{l_2 l'_2} \delta_{l l'}. \end{aligned} \tag{91}$$

Using Ünsold's theorem [see eq. (A.35) of Ref. **?**] one finally obtains the orthogonality relation for rotational invariants

$$\int \mathrm{d}\omega_1\, \mathrm{d}\omega_2\, \Phi_{l_1 l_2 l}\left(\omega_1, \omega_2, \omega\right) \Phi^*_{l_1' l_2' l'}\left(\omega_1, \omega_2, \omega\right) = \frac{2l+1}{4\pi} \delta_{l_1 l_1'} \delta_{l_2 l_2'} \delta_{l l'}. \tag{92}$$

Expansion coefficients of the Mayer f-function

To compute the expansion coefficients $\{f_{ll0}\}$ of the orientation dependent Mayer f-function in eq. (**??**) at AMMF level we assume that $\beta\varphi_1 \ll 1$. This is approximately justified because the relevant part of the phase diagrams investigated in this work covers a temperature range $T = \mathcal{O}\left(1\right)$ (see Figure **??**) and coupling constants $\varepsilon' = \mathcal{O}(10^{-1})$ [see eq. (**??**)]. Hence, from eq. (**??**) we have

$$\begin{aligned} f\left(\boldsymbol{r}_{12}, \omega_1, \omega_2\right) &\simeq 1 - \beta\varphi_1 + \frac{\left(\beta\varphi_1\right)^2}{2!} - \frac{\left(\beta\varphi_1\right)^3}{3!} \pm \ldots - 1 \\ &= -\beta\varphi_1 + \frac{\left(\beta\varphi_1\right)^2}{2!} - \frac{\left(\beta\varphi_1\right)^3}{3!} + \mathcal{O}[(\beta\varphi_1)^4]. \end{aligned} \tag{93}$$

Inserting this into eq. (**??**) one realizes that this gives rise to integrals of the form

$$I^{(n)} \equiv \frac{4\pi}{2l+1} \int \mathrm{d}\omega_1\, \mathrm{d}\omega_2\, \Phi^n_{220}\left(\omega_1, \omega_2, \omega\right) \Phi^*_{l_1 l_2 l}\left(\omega_1, \omega_2, \omega\right). \tag{94}$$

Clearly, $I^{(1)} = \delta_{l_1 2} \delta_{l_2 2} \delta_{l 0}$ where eq. (**??**) has also been used. Henceforth, we shall be dropping the arguments of rotational invariants in the remainder of this Appendix to ease the notational burden.

For $n \geq 2$ the integrand in eq. (**??**) contains powers of Φ_{220}. These can be reduced to linear combinations of other rotational invariants by applying the product rule iteratively

[see eq. (B8) of Ref. **?**]. As an example, consider

$$\begin{aligned}\Phi_{220}\Phi_{220} &= (-1)^{2+2+0+2+2+0}\,(4\pi)^{-3/2}\sum_{\mu_1\mu_2\mu}\left[(2\cdot 0+1)^2\,(2\cdot 0+1)^2\,(2\cdot 2+1)\,(2\cdot 2+1)\right.\\ &\quad\left.\times\,(2\cdot 2+1)\,(2\cdot 2+1)\,(2\mu_1+1)\,(2\mu_2+1)\right]\\ &\quad\times\begin{pmatrix}2 & 2 & \mu_1\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}2 & 2 & \mu_2\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}0 & 0 & \mu\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}2 & 2 & 0\\ 2 & 2 & 0\\ \mu_1 & \mu_2 & \mu\end{Bmatrix}\Phi_{\mu_1\mu_2\mu}, \qquad (95)\end{aligned}$$

where μ_1, μ_2, and μ are positive semidefinite integers and $(\cdot\,\cdot\,\cdot)$ and $\{\cdot\,\cdot\,\cdot\}$ are Wigner $3j$ and $9j$ symbols, respectively. Inserting this expression into eq. (**??**) ($n = 2$) it is clear from eq. (**??**) that the only nonzero result is the one for which $\mu_1 = \mu_2 = l$ and $\mu = 0$. In this case the previous expression simplifies to

$$\Phi_{220}\Phi_{220} = (4\pi)^{-3/2}\,5^2\sum_l (2l+1)\begin{pmatrix}2 & 2 & l\\ 0 & 0 & 0\end{pmatrix}^2\begin{Bmatrix}2 & 2 & 0\\ 2 & 2 & 0\\ l & l & 0\end{Bmatrix}\Phi_{ll0}. \qquad (96)$$

We are now in a position to draw a couple of additional conclusions. Because the $3j$ symbol is intimately linked to the Clebsch-Gordan coefficient [see eq. (A.139) of Ref. **?**], the parity relation [see eq. (A.155) of Ref. **?**] holds from which it follows that l must be an even integer or vanish. In addition, the entries on the top line of the $3j$ symbol must satisfy the triangle inequality [see eq. (A.131) of Ref. **?**] which further restricts l to even numbers in the interval $[0, 4]$.

Moreover, the $9j$ symbol in eq. (**??**) can be reduced to a $6j$ symbol and eventually to a constant $(2l+1)^{-1/2}/5$ by eqs. (A.292) and (A.285) of Ref. **?** . Putting all this together it is straightforward to verify that finally

$$(4\pi)^{3/2}\,\Phi_{220}\Phi_{220} = \Phi_{000}\delta_{l0} + \frac{2\sqrt{5}}{7}\Phi_{220}\delta_{l2} + \frac{6}{7}\Phi_{440}\delta_{l4}. \qquad (97)$$

The evaluation of the triple product $\Phi_{220}\Phi_{220}\Phi_{220}$ proceeds exactly the same only that in this case the product rule has to be applied twice. One eventually arrives at the expression

$$\Phi_{220}\Phi_{220}\Phi_{220} = (4\pi)^{-3}\, 5\sqrt{5} \sum_l \Phi_{ll0} \sum_\mu \left[(2\mu+1)^2\,(2l+1)\right]^{1/2} \begin{pmatrix} 2 & 2 & \mu \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} 2 & \mu & l \\ 0 & 0 & 0 \end{pmatrix}^2 . \tag{98}$$

Applying again the parity selection rule [see eqs. (A.155), (A.139) of Ref. **?**] to the first $3j$ symbol in this expression one concludes that μ must be an even integer. The second $3j$ symbol then suggests that l must be even, too. In addition, from the triangle inequality [see eq. (A.131) of Ref. **?**], μ is limited to the interval $[0, 4]$ implying $l \in [0, 6]$. However, some care has to be taken because in evaluating the sum over μ not all combinations of μ and l give nonvanishing results. For example, because of the triangle inequality, the case $l = 0$ gives only a nonzero summand if $\mu = 2$. The triple product may then eventually be cast as

$$(4\pi)^3\, \Phi_{220}\Phi_{220}\Phi_{220} = \frac{2\sqrt{5}}{7}\Phi_{000}\delta_{l0} + \frac{15}{7}\Phi_{220}\delta_{l2} + \frac{36\sqrt{5}}{77}\Phi_{440}\delta_{l4}. \tag{99}$$

Finally, eqs. (**??**) and (**??**) (together with the expression for $I^{(1)}$) allow one to conclude that

$$\frac{f_{000}\,(r_{12})}{(4\pi)^{3/2}} = \frac{1}{10}\left[\beta\varepsilon'\varphi_{\rm sw}\,(r_{12})\right]^2 - \frac{1}{105}\left[\beta\varepsilon'\varphi_{\rm sw}\,(r_{12})\right]^3 \tag{100a}$$

$$\frac{f_{220}\,(r_{12})}{(4\pi)^{3/2}} = -\frac{1}{\sqrt{5}}\left\{\beta\varepsilon'\varphi_{\rm sw}\,(r_{12}) - \frac{1}{7}\left[\beta\varepsilon'\varphi_{\rm sw}\,(r_{12})\right]^2 + \frac{1}{14}\left[\beta\varepsilon'\varphi_{\rm sw}\,(r_{12})^3\right]^3\right\} \tag{100b}$$

$$\frac{f_{440}\,(r_{12})}{(4\pi)^{3/2}} = \frac{3}{35}\left\{\left[\beta\varepsilon'\varphi_{\rm sw}\,(r_{12})\right]^2 - \frac{2}{11}\left[\beta\varepsilon'\varphi_{\rm sw}\,(r_{12})\right]^3\right\}. \tag{100c}$$

With the expressions given in eqs. (**??**) – (**??**) we are eventually in a position to compute

the energy parameters

$$u_0 = -\frac{8\pi}{3} g_{\rm hs}^{\rm c}(\eta_{\rm eff})\,\sigma^3\left(\lambda^3-1\right)\left[\frac{1}{10}\left(\beta\varepsilon\varepsilon'\right)^2+\frac{1}{105}\left(\beta\varepsilon\varepsilon'\right)^3\right] \quad (101a)$$

$$u_2 = -\frac{8\pi}{75} g_{\rm hs}^{\rm c}(\eta_{\rm eff})\,\sigma^3\left(\lambda^3-1\right)\left[\beta\varepsilon\varepsilon'+\frac{1}{7}\left(\beta\varepsilon\varepsilon'\right)^2+\frac{1}{14}\left(\beta\varepsilon\varepsilon'\right)^3\right] \quad (101b)$$

$$u_4 = -\frac{8\pi}{945} g_{\rm hs}^{\rm c}(\eta_{\rm eff})\,\sigma^3\left(\lambda^3-1\right)\left[\left(\beta\varepsilon\varepsilon'\right)^2+\frac{2}{11}\left(\beta\varepsilon\varepsilon'\right)^3\right] \quad (101c)$$

from eq. (**??**).

Expansion coefficients of the orientation-dependent pair correlation function in the intermolecular frame of reference

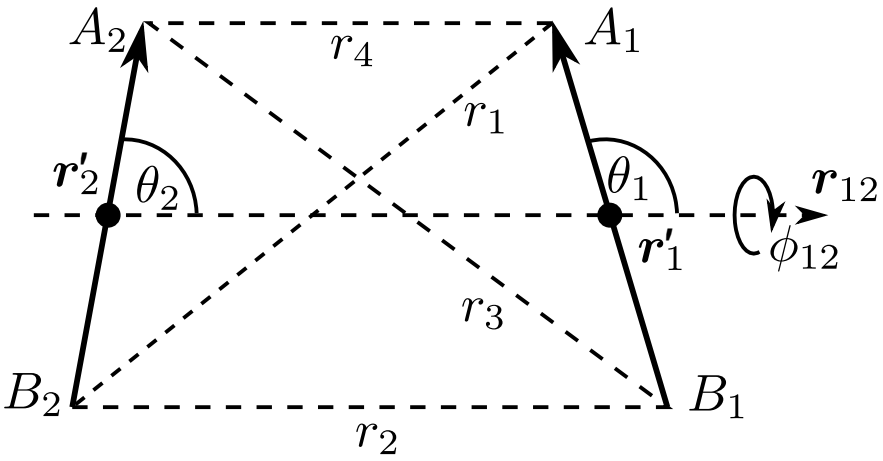


Figure 8: Sketch of a pair of molecules of uniaxial symmetry where r_{12} is the distance between their centers of mass represented by ● and $\widehat{\boldsymbol{r}}_{12}$ has been chosen so that it points from molecule 2 to molecule 1. Taking $\widehat{\boldsymbol{r}}_{12}$ as the z-axis in an intermolecular frame of reference the orientation of the molecules is given by $\widehat{\boldsymbol{u}}\,(\omega'_i)$ where $\omega'_i = (\theta'_i, \phi'_i)$ $(i = 1, 2)$; the polar angles are defined as indicated in the figure and $\phi'_{12} = \phi'_1 - \phi'_2$ is the relative azimuthal angle. Distances r_1 – r_4 are defined as shown in the sketch (adapted from Ref. **?**).

To derive explicit expressions for the expansion coefficients of the orientation dependent pair correlation function we consider an intermolecular frame of reference illustrated by the

sketch in Figure **??**. Positions of A_1 – B_2 are given by

$$\begin{aligned}
\boldsymbol{r}_{A_1} &= \boldsymbol{r}'_1 + \frac{1}{2}\widehat{\boldsymbol{u}}(\omega_1) && (102)\\
\boldsymbol{r}_{B_1} &= \boldsymbol{r}'_1 - \frac{1}{2}\widehat{\boldsymbol{u}}(\omega_1) && (103)\\
\boldsymbol{r}_{A_2} &= \boldsymbol{r}'_2 + \frac{1}{2}\widehat{\boldsymbol{u}}(\omega_2) && (104)\\
\boldsymbol{r}_{B_2} &= \boldsymbol{r}'_2 - \frac{1}{2}\widehat{\boldsymbol{u}}(\omega_2) && (105)
\end{aligned}$$

such that $|\boldsymbol{r}_{A_1} - \boldsymbol{r}_{B_1}| = |\boldsymbol{r}_{A_2} - \boldsymbol{r}_{B_2}| = 1$. With this and the definition $\boldsymbol{r}_{12} \equiv \boldsymbol{r}'_1 - \boldsymbol{r}'_2$ the four distances shown in Figure **??** can be expressed as

$$\begin{aligned}
r_1^2 &= r_{12}^2 + \boldsymbol{r}_{12}\cdot[\widehat{\boldsymbol{u}}(\omega_1) + \widehat{\boldsymbol{u}}(\omega_2)] + \frac{1}{4}[\widehat{\boldsymbol{u}}(\omega_1) + \widehat{\boldsymbol{u}}(\omega_2)]^2 && (106)\\
r_2^2 &= r_{12}^2 - \boldsymbol{r}_{12}\cdot[\widehat{\boldsymbol{u}}(\omega_1) - \widehat{\boldsymbol{u}}(\omega_2)] + \frac{1}{4}[\widehat{\boldsymbol{u}}(\omega_1) - \widehat{\boldsymbol{u}}(\omega_2)]^2 && (107)\\
r_3^2 &= r_{12}^2 - \boldsymbol{r}_{12}\cdot[\widehat{\boldsymbol{u}}(\omega_1) + \widehat{\boldsymbol{u}}(\omega_2)] + \frac{1}{4}[\widehat{\boldsymbol{u}}(\omega_1) + \widehat{\boldsymbol{u}}(\omega_2)]^2 && (108)\\
r_4^2 &= r_{12}^2 + \boldsymbol{r}_{12}\cdot[\widehat{\boldsymbol{u}}(\omega_1) - \widehat{\boldsymbol{u}}(\omega_2)] + \frac{1}{4}[\widehat{\boldsymbol{u}}(\omega_1) - \widehat{\boldsymbol{u}}(\omega_2)]^2 . && (109)
\end{aligned}$$

From these four equations one readily verifies that

$$r_{12}^2 = \frac{1}{4}\left(r_1^2 + r_2^2 + r_3^2 + r_4^2 - 2\right) \qquad (110)$$

which agrees with eq. (12) of Ref. **?** . Because $\cos\theta_1 = \widehat{\boldsymbol{u}}(\omega_1)\cdot\widehat{\boldsymbol{r}}_{12}$ it follows from eqs. (**??**) – (**??**) that

$$\cos\theta_1 = \frac{1}{4r_{12}}\left(r_1^2 - r_2^2 - r_3^2 + r_4^2\right) \qquad (111)$$

which agrees with eq. (14) of Ref. **?** if in eq. (**??**), $\theta_1 \to \theta'_2 = \theta_2 - \pi$. Similarly, because of $\cos\theta_2 = \widehat{\boldsymbol{u}}(\omega_2)\cdot\widehat{\boldsymbol{r}}_{12}$

$$\cos\theta_2 = \frac{1}{4r_{12}}\left(r_1^2 + r_2^2 - r_3^2 - r_4^2\right) \qquad (112)$$

which is in line with eq. (13) of Ref. **?** if one replaces in eq. (**??**) θ_2 by θ_1.

Because of the addition theorem for spherical harmonics [see eq. (A.33) of Ref. **?**] it follows that on the one hand

$$\cos\gamma = \widehat{\boldsymbol{u}}\left(\omega_1\right)\cdot\widehat{\boldsymbol{u}}\left(\omega_2\right) = \sin\theta_1\sin\theta_2\cos\phi_{12} + \cos\theta_1\cos\theta_2 \tag{113}$$

whereas on the other hand, with the aid of eqs. (**??**)–(**??**)

$$\widehat{\boldsymbol{u}}\left(\omega_1\right)\cdot\widehat{\boldsymbol{u}}\left(\omega_2\right) = \frac{1}{2}\left(r_1^2 - r_2^2 + r_3^2 - r_4^2\right) \tag{114}$$

and therefore

$$\cos\phi_{12} = \frac{1}{\sin\theta_1\sin\theta_2}\left(\frac{r_1^2 - r_2^2 + r_3^2 - r_4^2}{2} - \cos\theta_1\cos\theta_2\right). \tag{115}$$

Finally, this expression agrees with eq. (15) in the paper by Streett and Tildesley[**?**] provided that in eq. (**??**) variables are transformed simultaneously according to $\theta_1 \to \theta_2' = \theta_2 - \pi$ and $\theta_2 \to \theta_1$.

From the definition of the expansion coefficients in the intermolecular frame of reference [see eq. (**??**)] and keeping in mind that we wish to concentrate on the expansion coefficients g_{000} and g_{220} in the space-fixed frame of reference we need to compute

$$\begin{aligned}
g\left(r_{12};000\right) &= g_0\left(r_{12}\right) && (116)\\
g\left(r_{12};220\right) &= \frac{45}{4}g_0\left(r_{12}\right)\left\langle\left(\cos^2\theta_1 - \frac{1}{3}\right)\left(\cos^2\theta_2 - \frac{1}{3}\right)\right\rangle_{\text{shell}} && (117)\\
g\left(r_{12};221\right) &= \frac{15}{2}g_0\left(r_{12}\right)\left\langle\sin\theta_1\sin\theta_2\cos\theta_1\cos\theta_2\cos\phi_{12}\right\rangle_{\text{shell}} && (118)\\
g\left(r_{12};222\right) &= \frac{15}{4}g_0\left(r_{12}\right)\left\langle\sin^2\theta_1\sin^2\theta_2\left(\cos\phi_{12} - \frac{1}{2}\right)\right\rangle_{\text{shell}}. && (119)
\end{aligned}$$

To obtain the expansion coefficients g_{000} and g_{220} for our *ansatz* given in eq. (**??**) we proceed exactly as detailed in Appendix **??**. We expand the exponential in eq. (**??**) in a power series in terms of $\beta\varepsilon\varepsilon'$ truncated after the third-order term. This gives rise to an

expression similar to the one for f in eq. (**??**). From eq. (**??**) it is clear that

$$g_{l_1 l_2 l}\left(r_{12}\right) = \int \mathrm{d}\omega_1 \mathrm{d}\omega_2 \, \mathrm{d}\omega \, g\left(\boldsymbol{r}_{12}, \omega_1, \omega_2\right) \Phi^*_{l_1 l_2 l}\left(\omega_1, \omega_2, \omega\right). \tag{120}$$

Thus, inserting the expansion of g into this expression gives rise to integrals of the form given in eq. (**??**). These can be evaluated in exactly the same way as detailed in Appendix **??**. Thus, we only give the final result here which is

$$\begin{aligned} \frac{g_{ll0}\left(r_{12}\right)}{\left(4\pi\right)^{3/2}} &= g_0\left(r_{12}\right) \Theta\left(r_{12} - \sigma\right) \Theta\left(\lambda\sigma - r_{12}\right) \Bigg\{ \left[1 + \frac{1}{10}\left(\beta\varepsilon\varepsilon'\right)^2 + \frac{1}{105}\left(\beta\varepsilon\varepsilon'\right)^3\right] \delta_{l0} \\ &\quad + \frac{1}{\sqrt{5}} \left[\beta\varepsilon\varepsilon' + \frac{1}{7}\left(\beta\varepsilon\varepsilon'\right)^2 + \frac{1}{14}\left(\beta\varepsilon\varepsilon'\right)^3\right] \delta_{l2} \Bigg\}. \end{aligned} \tag{121}$$

It is important to note that no higher powers of $\beta\varepsilon\varepsilon'$ arise for $l = 0$ and 2 if one includes these higher-order terms in expanding the exponential in eq. (**??**). In this sense, the expression in eq. (**??**) is "exact".

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Graphical TOC Entry

