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# Advances in generalised van der Waals approaches for the isotropic-nematic fluid phase equilibria of thermotropic liquid crystals - An algebraic equation of state for attractive anisotropic particles with the Onsager trial function

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(Dated: August 14, 2009)

In this contribution we provide a review and reformulation of perturbation theories (generalised van der Waals approaches) for the description of the fluid phase behaviour and orientational ordering transitions of thermotropic nematic liquid crystals. Free energy functionals of the basic Onsager form are used as the platform for the development of a general formulation which reduces to the specific forms of the various theories that have found common use. A novel closed analytical description of the thermodynamic properties and degree of nematic order is then obtained by employing the Onsager trial function to represent the orientational distribution function in terms of a single parameter. The latter essentially constitutes an algebraic equation of state for the nematic phase appropriate for use in engineering applications. The description of ordering transitions with scaled-Onsager theories and suitable trial functions has already been illustrated by its application to systems of hard spherocylinders (HSCs), indicating that the approach provides an excellent representation of the orientational order of the hard-core (athermal) system [M. Franco Melgar, A. J. Haslam, and G. Jackson, *Mol. Phys.* **106**, 649 (2008)]. Here, the hard-body model is extended to account for attractive interactions (treated at the van der Waals level) of a general isotropic/anisotropic form (e.g., Lennard-Jonesium, square-well (SW), Maier-Saupe (MS) etc.). The adequacy of our generalised van der Waals-Onsager theory is exemplified from an analysis of the vapour-liquid, liquid-nematic, and vapour-nematic phase equilibria for hard spherocylinders with attractive square-well interactions (HSC-SW). The effect of the potential range and molecular aspect ratio on the vapour-liquid-nematic equilibria and orientational ordering transitions is examined to investigate the van der Waals limit (corresponding states) of the ordering phase behaviour. In the case of systems with an aspect ratio of  $\sim 5$  the corresponding-states limit is reached when the range is about 16 times the molecular diameter. For progressively longer molecules with an attractive range which follows their long dimension, the fluid-nematic equilibrium is enhanced, to the point that the vapour-liquid boundary becomes metastable relative to fluid-nematic equilibria. In the case of molecules of very large aspect ratio ( $\sim 50$ ) an additional region of nematic-nematic coexistence is exhibited by the system.

## I. INTRODUCTION

A general algebraic methodology for the thermodynamics of ordering transitions of mesogenic (liquid crystal forming) particles based on a free energy of the Onsager<sup>1</sup> form was introduced in our previous paper<sup>2</sup>. In Onsager approaches the molecular shape (characterised by the repulsive interactions) is traditionally considered as the key to liquid crystalline behaviour. This is a suitable description for lyotropic liquid crystals where composition (density) is the relevant thermodynamic variable; the temperature plays only a trivial role in systems of particles interacting through purely repulsive (hard core) potentials. The introduction of attractive interactions restores the significance of the temperature.

Early in the twentieth century Born<sup>3,4</sup> attributed liquid-crystalline behaviour entirely to the influence of long-range intermolecular forces arising from directionally dependent (anisotropic) electrostatic attractive interactions. Following this perspective, Maier and Saupe<sup>5,6</sup> developed a compact and tractable theory for orientational ordering transitions of polar molecules (with interactions of a quadrupolar form) from an isotropic liquid phase to a nematic (anisotropic) liquid-crystal phase. Molecular shape is not considered explicitly in their treatment. The Maier-Saupe (MS) framework provided for the first time an approach capable of describing the temperature dependence of the nematic order in liquid crystals at the molecular level. Though not without its critics early on<sup>7-11</sup>, the MS theory has been widely adopted in the liquid-crystal community as a convenient model for the orientational order of thermotropic liquid crystals, most particularly in the analysis of experimental data<sup>12-14</sup>.

The rich and varied phase behaviour exhibited by thermotropic mesogens (see the extensive compilation by Dunmur *et al.*<sup>15</sup> for nematics alone) is clearly closely related to specific features of the attractive interactions be-

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tween the molecules (e.g., London dispersion forces, polarity/multipolarity,  $\pi - \pi$  interactions between aromatic cores, electrostatic/charge transfer interactions etc.). It is instructive to highlight the particular effect of a given interaction by studying suitably chosen model systems: for example, in the case of idealised rod-shaped molecules with central point dipoles, the smectic-A (layered) phase is found to be stabilised relative to the nematic (which in some cases can also be destabilised relative to the isotropic liquid), while for particles with terminal point dipoles, smectic order is hindered<sup>16–19</sup>. Moreover, the presence of flexible tails on the end of the molecule has an opposing effect with the stabilisation of layered structures<sup>20</sup>. Attractive interactions thus play an important role in the determining the stability or otherwise of liquid-crystalline phases. It is important to reiterate, however, that the Onsager view that repulsive (excluded-volume) interactions are ultimately responsible for the stabilisation of orientationally ordered phases is now well recognised<sup>21–25</sup>. This is of course in line with the van der Waals picture<sup>26</sup> inherent in perturbation approaches where the structure of a fluid is deemed to be determined principally by the repulsive molecular cores<sup>27,28</sup>.

Clearly, a proper description of mesogenic fluids requires a consideration of both the anisotropic repulsive molecular cores and the various types of attractive interactions. The coupling of the Onsager and Maier-Saupe descriptions of liquid crystals dates back to the work of Kimura<sup>29</sup>, and of the groups of Gelbart<sup>30–34</sup>, Cotter<sup>35–41</sup>, and Vertogen<sup>42–47</sup>. A large number of studies have been carried out since then with generalised van der Waals approaches of this basic form, making use of the full armoury of mean-field, perturbation, integral equation, and density functional theories<sup>48–108</sup>; some of these examples will be referred to explicitly in the coming sections when of particular relevance to our study. As well as this vast body of work with continuum van der Waalsian models one should also acknowledge that systems of particles with both hard-core repulsive and attractive interactions have been treated extensively within a lattice-model framework (see references<sup>109–117</sup> as examples of some of the early papers); lattice models artificially omit the essential fluid nature of the structure (and the corresponding correlations between the molecules) which can lead to misleading conclusions about the effect of the various interactions, and lattice theories of liquid-crystalline systems have lost popularity in more recent times.

Regardless of the repulsive or attractive nature of the interactions between the particles, the free energy of an anisotropic fluid such as a nematic liquid crystal is a functional of the single particle orientational distribution function,  $f(\vec{\omega})$ . At equilibrium the orientational distribution function will take on a form which minimises the free energy of the system. In general a determination of the equilibrium nematic state thus involves a variational problem which can be solved by a variety of numerical techniques<sup>118</sup> including series expansions<sup>119–123</sup>, direct iteration<sup>124,125</sup>, or Monte Carlo annealing<sup>126</sup>. By

choosing an appropriate analytical description for  $f(\vec{\omega})$ , e.g., a trial function in terms of a single orientational parameter<sup>1,127–130</sup>, the solution of the equilibrium distribution can be recast as a direct parametric minimisation which is much simpler to handle and more computationally efficient, without a marked compromise in the numerical accuracy. The trial function introduced by Onsager<sup>1</sup> in his seminal paper leads to a free energy which contains a Bessel function of the orientational parameter, and a numerical solution (albeit of lower dimensionality) is still required to locate the equilibrium state of the system. Though the thermodynamic properties of the nematic state that result from a trial function treatment are more tractable than with a full functional representation, the computations in routine engineering applications remain cumbersome (as compared with, e.g., typical van der Waalsian equations of state) particularly in the case of multicomponent systems. Onsager<sup>1</sup> and Odjik<sup>129,130</sup> have also provided truncated forms of the free energy to leading order of the orientational parameter appropriate for systems of highly anisotropic particles which exhibit high degrees of nematic order. Linearised forms of the thermodynamic expressions are computationally very appealing, but unfortunately the adequacy of such a treatment rapidly deteriorates for thermotropic mesogens with more moderate (and realistic) aspect ratios<sup>2</sup>.

In previous work<sup>2</sup> we developed a general methodology for the treatment of the (scaled) Onsager free energy of hard-core molecules with the Onsager trial function which allows for an accurate a fully algebraic description of the orientational order and thermodynamic properties (equation of state). A cubic equation for the degree of orientational order of the equilibrium anisotropic state is obtained by retaining higher-order terms, and an excellent description of the equation of state and nematic order parameter for particles with moderate shape anisotropies is achieved. As we show in our current paper this methodology can be extended beyond a description of purely athermal systems to treat the nematic state of particles with attractive interactions.

As with other generalised van der Waals theories, the extended Onsager treatment described in the following sections includes both the repulsive nature of the Onsager<sup>1</sup> approach and the attractive nature of the Maier-Saupe<sup>5,6</sup> approach. A high-temperature perturbation theory is used to construct the Helmholtz free energy functional for the isotropic and anisotropic (nematic) fluid phases of non-spherical particles interacting through repulsive and attractive interactions. Specific forms of the theory are developed for Lennard-Jonesium and square-well attractive potentials with both isotropic and anisotropic contributions. By using an Onsager trial function to characterise the orientational distribution function we derive a fully algebraic equation of state for the isotropic fluid and liquid-crystal phases of the system. The specific expressions for molecules represented as hard spherocylinders (HSCs) with square-well

attractive interactions are developed as a particular example, and the resulting isotropic-anisotropic fluid phase behaviour is examined in detail.

There is a current need for a closed-form description of the thermodynamic properties of liquid crystals in a variety of technological applications. The development of an algebraic van der Waalsian equation of state for liquid crystalline fluids represents the key highlight of our current work.

## II. ANISOTROPIC INTERMOLECULAR PAIR POTENTIAL

We start by expressing the intermolecular pair potential of systems of cylindrically symmetrical particles (with rod or disk-like shapes) as a sum of the contribution due to excluded-volume interactions (steep repulsions of the overlapping molecular electronic density<sup>131</sup>) and the contribution due to the attractive interactions (induced polarisation, dispersion, multipolar etc.<sup>131-133</sup>):

$$u_{12}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) = u_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) + u_{12}^{\text{att}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2). \quad (1)$$

Here, the pair potential  $u_{12}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)$  between particles 1 and 2 is written as a function of the intermolecular vector  $\vec{r}_{12}$  (of magnitude  $r_{12}$ ) between the centres of mass of the two particles, and their orientations  $\vec{\omega}_1$  and  $\vec{\omega}_2$ . The repulsive contribution  $u_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)$  characterises the overlaps of the molecular hard cores such that

$$u_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) = \begin{cases} \infty & \text{when } r_{12} < \sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) \\ 0 & \text{when } r_{12} \geq \sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) \end{cases}. \quad (2)$$

The contact distance  $\sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)$  depends on the orientations of both particles and on the unit vector  $\hat{r}_{12} = \vec{r}_{12}/r_{12}$  between their centres. The attractive contribution  $u_{12}^{\text{att}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)$  is also a complicated function of the intermolecular vector, and the particle orientations.

In order to make the theoretical description more tractable it is usual to follow the approach of Pople<sup>134</sup> and expand the pair potential as a series in spherical harmonics<sup>12,135,136</sup>. We follow the usual van der Waals partitioning of the pair potential into repulsive and attractive parts (Equation 1). The repulsive contribution is treated explicitly while the attractive contribution is expanded in spherical harmonics:

$$u_{12}^{\text{att}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) = u_{000} + u_{202} + u_{404} + \dots \quad (3)$$

Here, the usual notation for the indices of spherical-harmonic terms is employed. The molecules are assumed to be centrosymmetric and also to have cylindrical symmetry so that the interaction is invariant to the inversion of the principal molecular axis (up-down symmetry). This means that only even terms in the series are retained, corresponding to even multipolar interactions (e.g., quadrupolar but not dipolar etc.). The first term corresponds to an isotropic attractive contribution, which

does not depend on the molecular orientations, and the higher terms to anisotropic attractions:

$$u_{12}^{\text{att}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) = u_{\text{iso}}^{\text{att}}(r_{12}) + u_{\text{aniso}}^{\text{att}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2). \quad (4)$$

The isotropic part of the attractive potential depends only on the radial distance  $r_{12} = |\vec{r}_{12}|$  between the centres of the two particles, and can be expressed as

$$u_{\text{iso}}^{\text{att}}(r_{12}) = u_{000} = -\epsilon_0 s(r_{12}), \quad (5)$$

where  $-\epsilon_0$  characterises the strength of the pair interaction, and  $s(r_{12})$  the dependence of the interaction on the interparticle separation. The attractive interactions are represented in this form for the sake of generality. In the case of the well-known Lennard-Jones attractive contribution (Sutherland potential) to the pair interaction, the dependence is given by

$$s(r_{12}) = \left(\frac{D}{r_{12}}\right)^6 \quad \text{when } r_{12} \geq \sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2), \quad (6)$$

where  $D$  is a reference diameter of the particle. For a square-well model characterised by the range parameter  $\lambda$ ,

$$s(r_{12}) = \begin{cases} 1 & \text{when } \lambda D > r_{12} \geq \sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) \\ 0 & \text{when } r_{12} \geq \lambda D. \end{cases} \quad (7)$$

The anisotropic part of the attractive interaction is assumed to be of a general form<sup>37,137-140</sup>:

$$u_{\text{aniso}}^{\text{att}}(r_{12}) = -[\epsilon_2 P_2(\cos \gamma) + \epsilon_4 P_4(\cos \gamma) + \dots] s(r_{12}), \quad (8)$$

where  $P_2(\cos \gamma) = \frac{1}{2}(3 \cos^2 \gamma - 1)$  and  $P_4(\cos \gamma) = \frac{1}{8}(35 \cos^4 \gamma - 30 \cos^2 \gamma + 3)$  are the second and fourth Legendre polynomials, and  $\cos \gamma = \vec{\omega}_1 \cdot \vec{\omega}_2$ ; the relative orientation  $\gamma$  corresponds to the angle between the principal axes of the two molecules. If one assumes a spherical repulsive core and truncates the series after the second Legendre polynomial the description essentially reduces to the Maier-Saupe potential<sup>6,52</sup>.

## III. THEORY OF THE NEMATIC PHASE

The total configurational energy  $U(\vec{r}^N, \vec{\omega}^N) = \sum_i \sum_{j>i} u_{ij}(\vec{r}_{ij}, \vec{\omega}_i, \vec{\omega}_j)$  of the system of  $N$  molecules in a volume  $V$  at a temperature  $T$  is related to the Helmholtz free energy  $A$  through the usual statistical-mechanical relation<sup>135</sup>:

$$A = -kT \ln Q_N, \quad (9)$$

where the partition function  $Q_N(V, T)$  is defined as

$$\begin{aligned} Q_N &= \frac{1}{N! \mathcal{V}^N} \iint \exp\left(-\frac{U(\vec{r}^N, \vec{\omega}^N)}{kT}\right) d\vec{r}^N d\vec{\omega}^N \\ &= \frac{Z_N(\vec{r}^N, \vec{\omega}^N)}{N! \mathcal{V}^N}. \end{aligned} \quad (10)$$



Here,  $Z_N(\vec{r}^N, \vec{\omega}^N) = \iint \exp(-U(\vec{r}^N, \vec{\omega}^N))/kT \, d\vec{r}^N d\vec{\omega}^N$  is the configurational integral, which is a function of the positions  $\vec{r}^N$  and orientations  $\vec{\omega}^N$  of all  $N$  particles, and  $\mathcal{V}$  is the de Broglie volume, which incorporates the kinetic contributions due to the translational and

rotational motion (the particles are assumed to be rigid so that there are no vibrational contributions). The relation for the average of a general function of configurational space  $W(\vec{r}^N, \vec{\omega}^N)$  in the canonical ensemble is

$$\begin{aligned} \langle W(\vec{r}^N, \vec{\omega}^N) \rangle_{NVT} &= \frac{\iint \exp\left(-\frac{U(\vec{r}^N, \vec{\omega}^N)}{kT}\right) W(\vec{r}^N, \vec{\omega}^N) \, d\vec{r}^N d\vec{\omega}^N}{\iint \exp\left(-\frac{U(\vec{r}^N, \vec{\omega}^N)}{kT}\right) \, d\vec{r}^N d\vec{\omega}^N} \\ &= \frac{1}{Z_N} \iint \exp\left(-\frac{U(\vec{r}^N, \vec{\omega}^N)}{kT}\right) W(\vec{r}^N, \vec{\omega}^N) \, d\vec{r}^N d\vec{\omega}^N. \end{aligned} \quad (11)$$

The probability of the system being in a state of configurational space  $d\vec{r}^N d\vec{\omega}^N$  is denoted by  $\wp(\vec{r}^N, \vec{\omega}^N) d\vec{r}^N d\vec{\omega}^N$ , where  $\wp(\vec{r}^N, \vec{\omega}^N)$  is clearly

$$\wp(\vec{r}^N, \vec{\omega}^N) = \frac{1}{Z_N} \exp\left(-\frac{U(\vec{r}^N, \vec{\omega}^N)}{kT}\right). \quad (12)$$

For a pairwise-additive function

$$W(\vec{r}^N, \vec{\omega}^N) = \sum_i \sum_{j>i} w_{ij}(\vec{r}_i, \vec{\omega}_i, \vec{r}_j, \vec{\omega}_j)$$

one can write the average as an equivalent expression in terms of the pair density  $\rho_{12}(\vec{r}_1, \vec{\omega}_1, \vec{r}_2, \vec{\omega}_2)$  as

$$\begin{aligned} \langle W(\vec{r}^N, \vec{\omega}^N) \rangle_{NVT} &= \frac{1}{2} \iiint \iiint d\vec{r}_1 d\vec{\omega}_1 d\vec{r}_2 d\vec{\omega}_2 \\ &\times \rho_{12}(\vec{r}_1, \vec{\omega}_1, \vec{r}_2, \vec{\omega}_2) w_{12}(\vec{r}_1, \vec{\omega}_1, \vec{r}_2, \vec{\omega}_2). \end{aligned} \quad (13)$$

The pair density corresponds to  $N(N-1)$  times the probability of finding a pair of the  $N$  molecules in the element of configurational space  $d\vec{r}_1 d\vec{\omega}_1 d\vec{r}_2 d\vec{\omega}_2$  irrespective of the positions and orientations of the remaining particles and irrespective of all translational and angular momenta, and can be expressed as<sup>135</sup>

$$\begin{aligned} \rho_{12}(\vec{r}_1, \vec{\omega}_1, \vec{r}_2, \vec{\omega}_2) &= \frac{N(N-1)}{Z_N(V, T)} \\ &\times \iint \dots \iint d\vec{r}_3 d\vec{\omega}_3 \dots d\vec{r}_N d\vec{\omega}_N \\ &\times \exp\left\{-\frac{U(\vec{r}^N, \vec{\omega}^N)}{kT}\right\}. \end{aligned} \quad (14)$$

This is related to the pair-correlation function  $g_{12}(\vec{r}_1, \vec{\omega}_1, \vec{r}_2, \vec{\omega}_2)$  through the definition

$$g_{12}(\vec{r}_1, \vec{\omega}_1, \vec{r}_2, \vec{\omega}_2) = \frac{\rho_{12}(\vec{r}_1, \vec{\omega}_1, \vec{r}_2, \vec{\omega}_2)}{\rho_1(\vec{r}_1, \vec{\omega}_1) \rho_1(\vec{r}_2, \vec{\omega}_2)}, \quad (15)$$

where  $\rho_1(\vec{r}_1, \vec{\omega}_1)$  and  $\rho_1(\vec{r}_2, \vec{\omega}_2)$  are the single-particle densities of molecules 1 and 2. In the case of a homogeneous nematic (anisotropic) phase, the single-particle densities  $\rho_1(\vec{r}, \vec{\omega}) = \rho f(\vec{\omega})$ , where  $f(\vec{\omega})$  represent the orientational distribution function, the number density  $\rho = N/V$  being constant over the entire system. The degree of orientational order of the nematic phase is commonly characterised in terms of the orientational order parameters  $S_n$ , which are defined as averages of the Legendre polynomials:

$$S_n = \int P_n(\cos \theta) f(\theta) d\vec{\omega}, \quad (16)$$

where  $P_n(\cos \theta)$  is the  $n$ th Legendre polynomial, and  $\theta$  denotes the angle between the principal molecular axis and the nematic director  $\vec{\omega}_n$  (preferred direction of the phase).

For systems of molecules interacting through separable pairwise-additive potentials of the form of Equation (1) the configurational energy can be written as a sum of the two contributions:

$$U(\vec{r}^N, \vec{\omega}^N) = U^{\text{rep}}(\vec{r}^N, \vec{\omega}^N) + U^{\text{att}}(\vec{r}^N, \vec{\omega}^N), \quad (17)$$

where  $U^{\text{rep}}(\vec{r}^N, \vec{\omega}^N) = \sum_i \sum_{j>i} u_{ij}^{\text{rep}}(\vec{r}_{ij}, \vec{\omega}_i, \vec{\omega}_j)$  is the configurational energy corresponding to the repulsive interactions (in case of hard-core molecules,  $U^{\text{rep}} = \infty$  for configurations with overlapping particles, or  $U^{\text{rep}} = 0$  for configurations without overlaps), and  $U^{\text{att}}(\vec{r}^N, \vec{\omega}^N) = \sum_i \sum_{j>i} u_{ij}^{\text{att}}(\vec{r}_{ij}, \vec{\omega}_i, \vec{\omega}_j)$  is the configurational energy due to the attractive interactions. In a standard perturbative treatment the total free energy of the system with configurational energy  $U(\vec{r}^N, \vec{\omega}^N)$  can be written as a sum of the free energy,  $A^{\text{rep}}$ , of a repulsive reference system (which in this case is also assumed to include the ideal contribution) and the perturbation term due to the attractive interactions  $A^{\text{att}}$ :

$$A = A^{\text{rep}} + A^{\text{att}}. \quad (18)$$

The key of any perturbation approach involves a thorough knowledge of the properties of the reference system, and a means of calculating the attractive perturbation. In the next section we therefore describe the treatment of the reference system that we have chosen to include in our treatment.

### A. Free energy of the repulsive reference system

An excellent representation of the nematic phase of hard core particles can be obtained from the second-virial theory of Onsager<sup>1</sup> as adapted by Parsons<sup>141</sup> and Lee<sup>142,143</sup> to include the higher-order virial contributions. The description of orientationally ordered phases with scaled Onsager free-energy functionals has already been discussed in detail<sup>2,144</sup>, so only the principal aspects are highlighted here. The free energy of a nematic phase of hard-core particles can be written as the following functional of the single-particle orientational distribution function  $f^{\text{rep}}(\vec{\omega})$  in the Onsager form as<sup>2</sup>

$$\frac{A^{\text{rep}}[f^{\text{rep}}(\vec{\omega})]}{NkT} = \frac{A_{\text{iso}}^{\text{id}}}{NkT} + \mathcal{F}_{\text{orient}}^{\text{rep}}[f^{\text{rep}}(\vec{\omega})] + G(\rho) \mathcal{F}_{\text{conf}}^{\text{rep}}[f^{\text{rep}}(\vec{\omega})]. \quad (19)$$

The isotropic contribution to the ideal free energy is given in the usual form in terms of the number density and de Broglie volume as

$$\frac{A_{\text{iso}}^{\text{id}}}{NkT} = \ln \left( \frac{\mathcal{V}\rho}{\Omega} \right) - 1 \quad (20)$$

where the solid angle  $\Omega = 4\pi$  in the case cylindrically symmetrical molecules. The Onsager orientational functionals are defined as

$$\mathcal{F}_{\text{orient}}^{\text{rep}}[f^{\text{rep}}(\vec{\omega})] \equiv \int f^{\text{rep}}(\vec{\omega}) \ln \{ \Omega f^{\text{rep}}(\vec{\omega}) \} d\vec{\omega}, \quad (21)$$

which corresponds to the orientational contribution to the ideal free energy (orientational entropy), and

$$\begin{aligned} \mathcal{F}_{\text{conf}}^{\text{rep}}[f^{\text{rep}}(\vec{\omega})] &\equiv \frac{1}{V_m} \iint V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) \\ &\times f^{\text{rep}}(\vec{\omega}_1) f^{\text{rep}}(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2 \\ &\equiv 2 \frac{B_2}{V_m} \equiv 2B_2^*, \end{aligned} \quad (22)$$

which corresponds to the excluded-volume contribution to the free energy due to the repulsive interactions (configurational entropy). Here,  $V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2)$  is the excluded volume for a pair of hard-core particles with orientations  $\vec{\omega}_1$  and  $\vec{\omega}_2$ ,  $V_m$  the volume of the molecule, and  $B_2$  the second virial coefficient.

The Parsons-Lee (PL) modification of the Onsager free energy amounts to scaling the Onsager configurational functional by a function  $G(\rho)$  of overall number density which incorporates (in an approximate manner) the contribution due to higher-body interactions. By employing

a de-coupling approximation the function can be represented as (one eighth of) the residual free energy of a system of equivalent hard spheres with the same molecular volume as the anisotropic hard core,  $V_m \equiv V_{\text{hs}}$ :

$$G(\rho) = \frac{1}{8} \left( \frac{A_{\text{hs}}^{\text{res}}}{NkT} \right) = \frac{1}{8} \int_0^\eta g_{\text{hs}}(\sigma) d\eta = \frac{4\eta - 3\eta^2}{8(1-\eta)^2}. \quad (23)$$

This expression corresponds to the well-known Carnahan and Starling<sup>28,145</sup> hard-sphere relation, conveniently expressed in terms of the packing fraction  $\eta = \rho V_m$ . When  $G(\rho) = \rho/2$  the free-energy reduces to the original second-virial theory (SVT) of Onsager<sup>1</sup>. The extension of the development to mixtures of hard-core particles is also relatively straight forward (see<sup>146</sup> for a recent review).

The functionals  $\mathcal{F}_{\text{orient}}^{\text{rep}}$  and  $\mathcal{F}_{\text{conf}}^{\text{rep}}$  represent the two main competing contributions which give rise to the orientationally ordered nematic state: the first,  $\mathcal{F}_{\text{orient}}^{\text{rep}}[f^{\text{rep}}(\vec{\omega})]$ , tends to favour a disordered isotropic state (the system loses entropy by ordering its molecular axis), while the second,  $\mathcal{F}_{\text{conf}}^{\text{rep}}[f^{\text{rep}}(\vec{\omega})]$ , favours the nematic state (orientational ordering minimises the excluded volume, and thus maximises the configurational entropy). The functional  $\mathcal{F}_{\text{conf}}^{\text{rep}}[f^{\text{rep}}(\vec{\omega})]$  is proportional to the angle average of the excluded volume, which is twice the second virial coefficient. The excluded volume can be defined in terms of the repulsive part of the intermolecular pair potential as

$$\begin{aligned} V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) &= \int \left[ 1 - \exp \left( \frac{-u_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)}{kT} \right) \right] d\vec{r}_{12} \\ &= \iint \left[ 1 - \exp \left( \frac{-u_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)}{kT} \right) \right] r_{12}^2 dr_{12} d\hat{r}_{12} \\ &= \iint_0^\sigma r_{12}^2 dr_{12} d\hat{r}_{12} = \frac{1}{3} \int \sigma^3 d\hat{r}_{12}. \end{aligned} \quad (24)$$

In the final form of the expression the excluded volume is expressed in terms of the corresponding integral of the contact distance  $\sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)$ . The usual notation for the volume integration over the vector  $\int d\vec{r}_{12} \equiv \iint r_{12}^2 dr_{12} d\hat{r}_{12}$  is used.

The equilibrium orientational distribution function  $f_{\text{eq}}^{\text{rep}}(\vec{\omega})$  for the repulsive system corresponds to that yielding the minimum in free energy. As the free energy is a functional of  $f(\vec{\omega})$  one can obtain the distribution at equilibrium from the extremum condition through the variation of the free energy with respect to  $f(\vec{\omega})$  at constant  $N$ ,  $V$ , and  $T$  subject to the additional normalisation constraint  $\int f(\vec{\omega}) d\vec{\omega} = 1$ :<sup>118</sup>

$$\begin{aligned} &\frac{\delta \{ A[f^{\text{rep}}(\vec{\omega})]/NkT + \lambda' (1 - \int f^{\text{rep}}(\vec{\omega}) d\vec{\omega}) \}}{\delta f^{\text{rep}}(\vec{\omega})} \Big|_{\text{eq}} \\ &= \frac{\delta A[f^{\text{rep}}(\vec{\omega})]/NkT}{\delta f^{\text{rep}}(\vec{\omega})} - \lambda' = 0, \end{aligned} \quad (25)$$

where the constant  $\lambda'$  is a Lagrange undetermined multiplier. The resulting integral equation obtained when

we substitute  $A^{\text{rep}}$  from Equation (19) into the Euler-Lagrange relation (Equation (25)) and perform the variation with respect to  $f^{\text{rep}}(\vec{\omega})$  is

$$\ln [\Omega f_{\text{eq}}^{\text{rep}}(\vec{\omega})] - \lambda^* + \frac{2G(\rho)}{V_m} \int V_{\text{exc}}(\vec{\omega}, \vec{\omega}_2) f_{\text{eq}}^{\text{rep}}(\vec{\omega}) d\vec{\omega}_2 = 0, \quad (26)$$

where  $\lambda^* = \lambda' - 1$  is another constant. After exponentiating both sides of this expression,

$$f_{\text{eq}}^{\text{rep}}(\vec{\omega}) = \frac{\exp(\lambda^*)}{\Omega} \exp\left(-\frac{2G(\rho)}{V_m} \int V_{\text{exc}}(\vec{\omega}, \vec{\omega}_2) f_{\text{eq}}^{\text{rep}}(\vec{\omega}) d\vec{\omega}_2\right), \quad (27)$$

and integrating over all orientations  $\vec{\omega}$  with the use of the normalisation condition  $\int f_{\text{eq}}^{\text{rep}}(\vec{\omega}) d\vec{\omega} = 1$ , the undetermined multiplier  $\exp(\lambda^*)/\Omega$  is obtained as

$$\frac{\exp(\lambda^*)}{\Omega} = \frac{1}{\int \exp\left(-\frac{2G(\rho)}{V_m} \int V_{\text{exc}}(\vec{\omega}, \vec{\omega}_2) f_{\text{eq}}^{\text{rep}}(\vec{\omega}) d\vec{\omega}_2\right) d\vec{\omega}}. \quad (28)$$

By substituting this back into Equation (27) the equilibrium orientational distribution function can be expressed as the convolution,

$$f_{\text{eq}}^{\text{rep}}(\vec{\omega}) = \frac{\exp\left(-\frac{2G(\rho)}{V_m} \int V_{\text{exc}}(\vec{\omega}, \vec{\omega}_2) f_{\text{eq}}^{\text{rep}}(\vec{\omega}) d\vec{\omega}_2\right)}{\int \exp\left(-\frac{2G(\rho)}{V_m} \int V_{\text{exc}}(\vec{\omega}, \vec{\omega}_2) f_{\text{eq}}^{\text{rep}}(\vec{\omega}) d\vec{\omega}_2\right) d\vec{\omega}}. \quad (29)$$

The form of  $f_{\text{eq}}^{\text{rep}}(\vec{\omega})$  that one obtains from Equation (29) is that which minimises the free energy of the reference (purely repulsive) system.

### B. Free-energy perturbation due to attractive interactions

The difference in free energy  $\Delta A = A^{\text{att}} = A - A^{\text{rep}}$  between the repulsive reference system and the system with the full interactions can be written in terms of the ratios of the corresponding partition functions (or configurational integrals) as

$$\Delta A = A - A^{\text{rep}} = -kT \ln \left( \frac{Q_N}{Q_N^{\text{rep}}} \right). \quad (30)$$

As the full and reference systems have the same number of particles and are at the same volume and temperature, the ratio  $Q_N/Q_N^{\text{rep}}$  is equivalent to the ratio  $Z_N/Z_N^{\text{rep}}$  of the configurational integrals:

$$\frac{Q_N}{Q_N^{\text{rep}}} = \frac{Z_N}{Z_N^{\text{rep}}} \equiv \frac{\iint \exp\left(-\frac{U}{kT}\right) d\vec{r}^N d\vec{\omega}^N}{\iint \exp\left(-\frac{U^{\text{rep}}}{kT}\right) d\vec{r}^N d\vec{\omega}^N}. \quad (31)$$

By expressing the total configurational energy in terms of the repulsive and attractive contributions (cf. Equation

(17)) one can write

$$\begin{aligned} \frac{Z_N}{Z_N^{\text{rep}}} &= \frac{\iint \exp\left(-\frac{U^{\text{rep}}}{kT}\right) \exp\left(-\frac{U^{\text{att}}}{kT}\right) d\vec{r}^N d\vec{\omega}^N}{\iint \exp\left(-\frac{U^{\text{rep}}}{kT}\right) d\vec{r}^N d\vec{\omega}^N} \\ &= \left\langle \exp\left(-\frac{U^{\text{att}}}{kT}\right) \right\rangle_{\text{rep}}. \end{aligned} \quad (32)$$

In the last line we take advantage of the general relation for the average of a general function of configurational space [cf. Equation (11)]. One should note, however, that in Equation (32) one is averaging the Boltzmann factor of the attractive perturbative energy over all configurations of the repulsive (reference) system, not the full system. The contribution to the Helmholtz free energy due to the attractive interactions can thus be written as

$$A^{\text{att}} = \Delta A = -kT \ln \left\langle \exp\left(-\frac{U^{\text{att}}}{kT}\right) \right\rangle_{\text{rep}}. \quad (33)$$

This is the basis of the well known perturbation theory derived by Zwanzig<sup>147</sup>, who generalised the earlier developments by Longuet-Higgins<sup>148</sup>, Barker<sup>149,150</sup> and Pople<sup>134,151</sup>. It is important to realise that the relation derived by Zwanzig is valid for a system with a separable configurational energy regardless of the size of the ‘‘perturbation’’ in the energy. There is, however, no guarantee that the free energy of the perturbed system will correspond to the equilibrium state with the minimum free energy when the difference in potential energy is large. Both the exponential and logarithm of Equation (33) can be expanded for small values of the potential-energy perturbation (relative to  $kT$ ); the contribution to the free energy due to the attractive interactions can thus be expressed in the form of Zwanzig’s high-temperature perturbation expansion<sup>147</sup>:

$$\begin{aligned} A^{\text{att}} &= \langle U^{\text{att}} \rangle_{\text{rep}} - \frac{1}{2!(kT)} \left\{ \langle [U^{\text{att}}]^2 \rangle_{\text{rep}} - \langle U^{\text{att}} \rangle_{\text{rep}}^2 \right\} \\ &+ \frac{1}{3!(kT)^2} \left\{ \langle [U^{\text{att}}]^3 \rangle_{\text{rep}} - 3 \langle [U^{\text{att}}]^2 \rangle_{\text{rep}} \langle U^{\text{att}} \rangle_{\text{rep}} \right. \\ &\quad \left. + 2 \langle U^{\text{att}} \rangle_{\text{rep}}^3 \right\} \dots \end{aligned} \quad (34)$$

Here, we examine a first-order perturbation theory, where an attractive free energy is approximated by the first term, i.e.,  $A^{\text{att}} \approx \langle U^{\text{att}} \rangle_{\text{rep}}$ , which according to Equation (11) can be written as

$$\begin{aligned} \langle U^{\text{att}} \rangle_{\text{rep}} &= \frac{1}{Z_N^{\text{rep}}} \iint \exp\left(-\frac{U^{\text{rep}}(\vec{r}^N, \vec{\omega}^N)}{kT}\right) \\ &\quad \times U^{\text{att}}(\vec{r}^N, \vec{\omega}^N) d\vec{r}^N d\vec{\omega}^N. \end{aligned} \quad (35)$$

Assuming that the attractive part of the configurational energy,  $U^{\text{att}}$ , can be expressed as a sum of pairwise interactions, i.e.,  $U^{\text{att}}(\vec{r}^N, \vec{\omega}^N) = \sum_i^N \sum_{j>i}^N u_{ij}^{\text{att}}(\vec{r}_{ij}, \vec{\omega}_i, \vec{\omega}_j)$



one can then write

$$\begin{aligned} \langle U^{\text{att}} \rangle_{\text{rep}} &= \frac{1}{Z_N^{\text{rep}}} \iint \exp \left( -\frac{U^{\text{rep}}(\vec{r}^N, \vec{\omega}^N)}{kT} \right) \\ &\times \sum_i^N \sum_{j>i}^N u_{ij}^{\text{att}}(\vec{r}_{ij}, \vec{\omega}_i, \vec{\omega}_j) d\vec{r}^N d\vec{\omega}^N. \quad (36) \end{aligned}$$

As there are  $\frac{1}{2}N(N-1)$  identical contributions arising from the double sum for all the interparticle pair potentials  $u_{ij}$ , the mean-attractive energy may be written in terms of an arbitrary pair (say particles 1 and 2) as

$$\begin{aligned} \langle U^{\text{att}} \rangle_{\text{rep}} &= \frac{N(N-1)}{2Z_N^{\text{rep}}} \iiint \int u_{12}^{\text{att}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) d\vec{r}_1 d\vec{\omega}_1 d\vec{r}_2 d\vec{\omega}_2 \\ &\times \iiint \dots \iiint \exp \left( -\frac{U^{\text{rep}}(\vec{r}^N, \vec{\omega}^N)}{kT} \right) d\vec{r}_3 d\vec{\omega}_3 \dots d\vec{r}_N d\vec{\omega}_N. \quad (37) \end{aligned}$$

The pair density  $\rho_{12}^{\text{rep}}(\vec{r}_1, \vec{\omega}_1, \vec{r}_2, \vec{\omega}_2)$  of the repulsive reference is defined in an analogous way to that of the full system [cf. Equation (14)] as

$$\begin{aligned} \rho_{12}^{\text{rep}}(\vec{r}_1, \vec{\omega}_1, \vec{r}_2, \vec{\omega}_2) &= \frac{N(N-1)}{Z_N^{\text{rep}}} \\ &\times \iiint \dots \iiint \exp \left( -\frac{U^{\text{rep}}(\vec{r}^N, \vec{\omega}^N)}{kT} \right) d\vec{r}_3 d\vec{\omega}_3 \dots d\vec{r}_N d\vec{\omega}_N. \quad (38) \end{aligned}$$

Substituting for the pair density of the reference the mean-attractive energy can be expressed in general form as

$$\begin{aligned} \langle U^{\text{att}} \rangle_{\text{rep}} &= \frac{1}{2} \iiint \int u_{12}^{\text{att}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) \\ &\times \rho_{12}^{\text{rep}}(\vec{r}_1, \vec{\omega}_1, \vec{r}_2, \vec{\omega}_2) d\vec{r}_1 d\vec{\omega}_1 d\vec{r}_2 d\vec{\omega}_2 \\ &= \frac{1}{2} \iiint \int u_{12}^{\text{att}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) \\ &\times \rho_1^{\text{rep}}(\vec{r}_1, \vec{\omega}_1) \rho_1^{\text{rep}}(\vec{r}_2, \vec{\omega}_2) \\ &\times g_{12}^{\text{rep}}(\vec{r}_1, \vec{\omega}_1, \vec{r}_2, \vec{\omega}_2) d\vec{r}_1 d\vec{\omega}_1 d\vec{r}_2 d\vec{\omega}_2, \quad (39) \end{aligned}$$

noting again that in our particular case the average is performed over the purely repulsive reference system, rather than the full system [cf. Equation (13)]. In the second form of the expression, the average is written in terms of the pair-correlation function  $g_{12}^{\text{rep}}(\vec{r}_1, \vec{\omega}_1, \vec{r}_2, \vec{\omega}_2) = \rho_{12}^{\text{rep}}(\vec{r}_1, \vec{\omega}_1, \vec{r}_2, \vec{\omega}_2) / [\rho_1^{\text{rep}}(\vec{r}_1, \vec{\omega}_1) \rho_1^{\text{rep}}(\vec{r}_2, \vec{\omega}_2)]$  of the reference system. To first order in the perturbation expansion [Equation (34)] the free energy of the anisotropic (and at this point inhomogeneous) system can thus be written in terms of the pair-correlation function as

$$\begin{aligned} A^{\text{att}} &= \langle U^{\text{att}} \rangle_{\text{rep}} \\ &= \frac{1}{2} \iiint \int u_{12}^{\text{att}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) \\ &\times \rho_1^{\text{rep}}(\vec{r}_1, \vec{\omega}_1) \rho_1^{\text{rep}}(\vec{r}_2, \vec{\omega}_2) \\ &\times g_{12}^{\text{rep}}(\vec{r}_1, \vec{\omega}_1, \vec{r}_2, \vec{\omega}_2) d\vec{r}_1 d\vec{\omega}_1 d\vec{r}_2 d\vec{\omega}_2. \quad (40) \end{aligned}$$

In the case of nematic phases which possess orientational but no positional order we have a homogeneous but anisotropic system, and the single-particle densities simplify to  $\rho_i^{\text{rep}}(\vec{r}_i, \vec{\omega}_i) = \rho f_{\text{eq}}^{\text{rep}}(\vec{\omega}_i)$ . The attractive contribution to the configurational free energy is thus a functional of  $f_{\text{eq}}^{\text{rep}}(\vec{\omega})$ :

$$\begin{aligned} A^{\text{att}} &= \mathcal{F}_{\text{conf}}^{\text{att}}[f_{\text{eq}}^{\text{rep}}(\vec{\omega})] \\ &= \frac{\rho^2 V}{2} \iiint \int u_{12}^{\text{att}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) \\ &\times f_{\text{eq}}^{\text{rep}}(\vec{\omega}_1) f_{\text{eq}}^{\text{rep}}(\vec{\omega}_2) \\ &\times g_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) d\vec{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2. \quad (41) \end{aligned}$$

One can take the centre of one of the particles as the origin of the coordinate system, and integrate it out of the expression leaving only a dependence of the relative centre-to-centre vector,  $\vec{r}_{12} = \vec{r}_2 - \vec{r}_1$ . It is important to reiterate that in developing a standard perturbative approach for the nematic phase, the averages must be taken over the equilibrium structure of the repulsive reference system. We emphasise this by expressing the free-energy perturbation in terms of the equilibrium single-particle orientation function of the reference system  $f_{\text{eq}}^{\text{rep}}(\vec{\omega})$  which is obtained by solving Equation (29).

Strictly the use of the term ‘‘perturbation theory’’ to describe approaches for systems of attracting mesogens must involve the equilibrium structure of the reference system as in Equation (41); the reader is directed to the related work on dipolar systems<sup>83</sup> as an example of the application of such a perturbative approach to dipolar hard spherocylinders. Clearly the incorporation of attractive interactions between the particles will mean that the equilibrium orientational distribution of the repulsive reference will no longer correspond to the state with the minimum total free energy; the attractions will often enhance the orientationally ordering of the particles. As in standard perturbative density functional theories of inhomogeneous fluids<sup>28</sup>, the equilibrium single particle density (orientational distribution in the case of a nematic state) is not represented by that of the repulsive reference system but by the form which corresponds to the minimum of the perturbed free energy functional.

### C. Equilibrium free energy

In order to allow the orientational distribution function to ‘‘relax’’ to that corresponding to the state of minimum free energy for the system with the full potential, we first write the total Helmholtz free energy [Equation (18)] as a functional of  $f(\vec{\omega})$  (instead of  $f_{\text{eq}}^{\text{rep}}(\vec{\omega})$  for the repulsive reference):

$$\begin{aligned}
\frac{A[f(\vec{\omega})]}{NkT} &= \frac{A^{\text{iso}}}{NkT} + \mathcal{F}_{\text{orient}}[f(\vec{\omega})] + G(\rho)\mathcal{F}_{\text{conf}}^{\text{rep}}[f(\vec{\omega})] + \mathcal{F}_{\text{conf}}^{\text{att}}[f(\vec{\omega})] \\
&= \frac{A^{\text{iso}}}{NkT} + \int f(\vec{\omega}) \ln \Omega f(\vec{\omega}) d\vec{\omega} + \frac{G(\rho)}{V_m} \iint V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2 \\
&\quad + \frac{\rho}{2kT} \iiint u_{12}^{\text{att}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) g_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) d\vec{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2, \quad (42)
\end{aligned}$$

where the contribution due to the orientational entropy is now a functional of  $f(\vec{\omega})$ ,

$$\mathcal{F}_{\text{orient}}[f(\vec{\omega})] = \int f(\vec{\omega}) \ln \Omega f(\vec{\omega}) d\vec{\omega}, \quad (43)$$

and the repulsive and attractive configurational functionals are defined respectively as

$$\mathcal{F}_{\text{conf}}^{\text{rep}}[f(\vec{\omega})] = \frac{G(\rho)}{V_m} \iint V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2 \quad (44)$$

and

$$\begin{aligned}
\mathcal{F}_{\text{conf}}^{\text{att}}[f(\vec{\omega})] &= \frac{\rho}{2kT} \iiint u_{12}^{\text{att}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) \\
&\quad \times g_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) d\vec{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2. \quad (45)
\end{aligned}$$

In the language of molecular-field theories<sup>12,137-140</sup>, it is convenient to define a dimensionless field  $\Psi[f(\vec{\omega})]$  (pseudo potential) acting on a particle with a certain orientation  $\vec{\omega} \equiv \vec{\omega}_1$  as an integrated interaction due to the presence of the particles with all other orientations  $\vec{\omega}_2$ :

$$\Psi[f(\vec{\omega})] = \int \left\{ \frac{G(\rho)}{V_m} V_{\text{exc}}(\vec{\omega}, \vec{\omega}_2) + \frac{\rho}{2kT} \int u_{12}^{\text{att}}(\vec{r}_{12}, \vec{\omega}, \vec{\omega}_2) g_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}, \vec{\omega}_2) d\vec{r}_{12} \right\} f(\vec{\omega}_2) d\vec{\omega}_2. \quad (46)$$

The contributions due to the repulsive and attractive interactions can also be treated separately:

$$\Psi[f(\vec{\omega})] = \Psi^{\text{rep}}[f(\vec{\omega})] + \Psi^{\text{att}}[f(\vec{\omega})], \quad (47)$$

where the repulsive pseudo-potential is

$$\Psi^{\text{rep}}[f(\vec{\omega})] = \frac{G(\rho)}{V_m} \int V_{\text{exc}}(\vec{\omega}, \vec{\omega}_2) f(\vec{\omega}_2) d\vec{\omega}_2, \quad (48)$$

and the attractive pseudo-potential is

$$\begin{aligned}
\Psi^{\text{att}}[f(\vec{\omega})] &= \frac{\rho}{2kT} \iint u_{12}^{\text{att}}(\vec{r}_{12}, \vec{\omega}, \vec{\omega}_2) f(\vec{\omega}_2) \\
&\quad \times g_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}, \vec{\omega}_2) d\vec{r}_{12} d\vec{\omega}_2. \quad (49)
\end{aligned}$$

After substituting Equation(46) [or Equations (48) and (49)] into Equation (42) we can express the Helmholtz

free-energy functional as

$$\begin{aligned}
\frac{A[f(\vec{\omega})]}{NkT} &= \frac{A^{\text{iso}}}{NkT} + \int f(\vec{\omega}) \ln \Omega f(\vec{\omega}) d\vec{\omega} \\
&\quad + \int f(\vec{\omega}) \Psi[f(\vec{\omega})] d\vec{\omega} \\
&= \frac{A^{\text{iso}}}{NkT} + \int f(\vec{\omega}) \{ \ln \Omega f(\vec{\omega}) \\
&\quad + \Psi^{\text{rep}}[f(\vec{\omega})] + \Psi^{\text{att}}[f(\vec{\omega})] \} d\vec{\omega}. \quad (50)
\end{aligned}$$

One must now examine the variation of the full free energy (42) with respect to  $f(\vec{\omega})$  (at constant  $N$ ,  $V$ , and  $T$ ) subject to the constraint that  $\int f(\vec{\omega}) d\omega = 1$ :

$$\begin{aligned}
\left. \frac{\delta \{ A[f(\vec{\omega})]/NkT + \lambda' (1 - \int f(\vec{\omega}) d\vec{\omega}) \}}{\delta f(\vec{\omega})} \right|_{\text{eq}} &= \frac{\delta A[f(\vec{\omega})]/NkT}{\delta f(\vec{\omega})} - \lambda' \\
&= \frac{\delta \mathcal{F}_{\text{orient}}[f(\vec{\omega})]}{\delta f(\vec{\omega})} + \frac{\delta \mathcal{F}_{\text{conf}}^{\text{rep}}[f(\vec{\omega})]}{\delta f(\vec{\omega})} + \frac{\delta \mathcal{F}_{\text{conf}}^{\text{att}}[f(\vec{\omega})]}{\delta f(\vec{\omega})} - \lambda' = 0. \quad (51)
\end{aligned}$$

After performing the variation for the functionals  $\mathcal{F}_{\text{orient}}[f(\vec{\omega})]$ ,  $\mathcal{F}_{\text{conf}}^{\text{rep}}[f(\vec{\omega})]$ , and  $\mathcal{F}_{\text{conf}}^{\text{att}}[f(\vec{\omega})]$  the following Euler-Lagrange expression is obtained for the equilibrium

value of the single particle orientational distribution function,  $f_{\text{eq}}$ :

$$\begin{aligned} \frac{\delta A[f(\vec{\omega})] / NkT}{\delta f(\vec{\omega})} &= \ln[\Omega f_{\text{eq}}(\vec{\omega})] + \lambda^* + 2 \frac{G(\rho)}{V_m} \int V_{\text{exc}}(\vec{\omega}, \vec{\omega}_2) f_{\text{eq}}(\vec{\omega}_2) d\vec{\omega}_2 \\ &+ \frac{\rho}{kT} \iint u_{12}(\vec{r}_{12}, \vec{\omega}, \vec{\omega}_2) g_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}, \vec{\omega}_2) f_{\text{eq}}(\vec{\omega}_2) d\vec{r}_{12} d\vec{\omega}_2 \\ &+ \frac{\rho}{kT} \iint u_{12}(\vec{r}_{12}, \vec{\omega}, \vec{\omega}_2) \frac{\delta g_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}, \vec{\omega}_2)}{\delta f_{\text{eq}}(\vec{\omega})} f_{\text{eq}}(\vec{\omega}) f_{\text{eq}}(\vec{\omega}_2) d\vec{r}_{12} d\vec{\omega}_2 = 0. \end{aligned} \quad (52)$$

The Euler-Lagrange expression can be written in a more compact manner in terms of the molecular fields defined earlier:

$$\begin{aligned} \frac{\delta A[f(\vec{\omega})] / NkT}{\delta f(\vec{\omega})} &= \ln[\Omega f_{\text{eq}}(\vec{\omega})] + \lambda^* + 2\Psi_{\text{eq}}^{\text{rep}}[f_{\text{eq}}(\vec{\omega})] \\ &+ 2\Psi_{\text{eq}}^{\text{att}}[f_{\text{eq}}(\vec{\omega})] + \Psi_{\text{eq}}^{\text{att}}[f_{\text{eq}}(\vec{\omega})]' = 0, \end{aligned} \quad (53)$$

where  $\Psi_{\text{eq}}^{\text{att}}[f_{\text{eq}}(\vec{\omega})]'$  represents the last term of Equation (52). The constant  $\lambda^* = \lambda' - 1$  is eliminated in a similar fashion to that for the repulsive system [cf. Equation (28)], i.e., exponentiating the expression, then integrating over  $\vec{\omega}$ , and finally making use of the normalisation condition, which leads to the final expression  $f_{\text{eq}}(\vec{\omega})$ :

$$\begin{aligned} f_{\text{eq}}(\vec{\omega}) &= \frac{\exp\left(-\frac{\delta \mathcal{F}_{\text{conf}}^{\text{rep}}[f_{\text{eq}}(\vec{\omega})]}{\delta f(\vec{\omega})} - \frac{\delta \mathcal{F}_{\text{conf}}^{\text{att}}[f_{\text{eq}}(\vec{\omega})]}{\delta f(\vec{\omega})}\right)}{\int \exp\left(-\frac{\delta \mathcal{F}_{\text{conf}}^{\text{rep}}[f_{\text{eq}}(\vec{\omega})]}{\delta f(\vec{\omega})} - \frac{\delta \mathcal{F}_{\text{conf}}^{\text{att}}[f_{\text{eq}}(\vec{\omega})]}{\delta f(\vec{\omega})}\right) d\vec{\omega}} \\ &= \frac{\exp(-2\Psi_{\text{eq}}^{\text{rep}}[f_{\text{eq}}(\vec{\omega})] - 2\Psi_{\text{eq}}^{\text{att}}[f_{\text{eq}}(\vec{\omega})] - \Psi_{\text{eq}}^{\text{att}}[f_{\text{eq}}(\vec{\omega})]')}{\int \exp(-2\Psi_{\text{eq}}^{\text{rep}}[f_{\text{eq}}(\vec{\omega})] - 2\Psi_{\text{eq}}^{\text{att}}[f_{\text{eq}}(\vec{\omega})] - \Psi_{\text{eq}}^{\text{att}}[f_{\text{eq}}(\vec{\omega})]') d\vec{\omega}}. \end{aligned} \quad (54)$$

The equilibrium orientational distribution satisfying this relation gives the state with the minimum free energy. Once the equilibrium Helmholtz free energy is known, the other thermodynamic quantities such as the pressure  $P$  (i.e., the equation of state) and chemical potential  $\mu$  can be obtained through the standard thermodynamic relations  $P = -(\partial A / \partial V)_{N,T}$  and  $\mu = (\partial A / \partial N)_{V,T}$ .

Together with the expression (50) for the Helmholtz free energy in terms of the molecular fields, the general relation (54) provides a unified form from which to cast the common approaches that are used to represent the thermodynamics of nematic liquid crystals. In the case of a system interacting only through repulsive interactions,

$\Psi_{\text{eq}}[f_{\text{eq}}(\vec{\omega})] = \Psi_{\text{eq}}^{\text{rep}}[f_{\text{eq}}(\vec{\omega})]$  with  $\Psi_{\text{eq}}^{\text{att}}[f_{\text{eq}}(\vec{\omega})] = 0$ , expression (50) reduces to the Onsager free-energy functional with the Parsons<sup>141</sup> and Lee<sup>142,143</sup> scaling to include the higher-order terms; the original expression of Onsager<sup>1</sup> is obtained if a simple linear dependence in density is assumed for the two-body term, i.e.,  $G(\rho) = \rho/2$ .

When one approximates the structure of the reference repulsive system by its low-density limit<sup>28</sup>,

$$\lim_{\rho \rightarrow 0} g_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) = \exp\left(-\frac{u_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)}{kT}\right), \quad (55)$$

the attractive contribution to the pseudo-potential is simply

$$\begin{aligned}
\Psi_{\text{GVDW}}^{\text{att}}[f(\vec{\omega})] &= \frac{\rho}{2kT} \iint u_{12}^{\text{att}}(\vec{r}_{12}, \vec{\omega}, \vec{\omega}_2) f(\vec{\omega}_2) \exp\left(-\frac{u_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}, \vec{\omega}_2)}{kT}\right) d\vec{r}_{12} d\vec{\omega}_2 \\
&= \frac{\rho}{2kT} \iint u_{12}^{\text{att}}(\vec{r}_{12}, \vec{\omega}, \vec{\omega}_2) f(\vec{\omega}_2) H[r_{12} - \sigma(\hat{r}_{12}, \vec{\omega}, \vec{\omega}_2)] d\vec{r}_{12} d\vec{\omega}_2 \\
&= \frac{\rho}{2kT} \iint \int_{\sigma}^{\infty} u_{12}^{\text{att}}(\vec{r}_{12}, \vec{\omega}, \vec{\omega}_2) f(\vec{\omega}_2) r_{12}^2 dr_{12} d\hat{r}_{12} d\vec{\omega}_2. \tag{56}
\end{aligned}$$

In the last form of the expression, the integral is written equivalently over the limits of the hard-core reference interaction [cf. Equation (2)]; the lower-limit corresponds to the contact distance  $\sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)$  and  $H[r_{12} - \sigma(\hat{r}_{12}, \vec{\omega}, \vec{\omega}_2)]$  is the heaviside function which ensures that one integrates the attractive potential only for configurations outside the excluded-volume region. The use of this approximation leads to the generalised van der Waals (GVDW) theory introduced by Kimura, Gelbart, Cotter, Vertogen and co-workers<sup>29–47</sup>; differences arise from the various ways of treating the reference hard-core system (e.g., scaled particle theory,  $\gamma$ -expansion, etc.). Though often referred to as a mean-field perturbation theory, one should take care to distinguish such an approach from the Zwanzig high-temperature perturbation theory where, as discussed earlier, one retains the equilibrium structure (in this case the single-particle orientational distribution function) of the repulsive reference system. Mean-field theories of type are of course commonly used in the description of isotropic fluids and are commonly referred to as augmented van der Waals approaches<sup>152–155</sup>.

The Maier-Saupe<sup>6</sup> theory, one of the most widespread approaches used to describe phase transitions in liquid crystals, can be obtained from our general expression for the free energy if one neglects the repulsive field  $\Psi^{\text{rep}}[f(\vec{\omega})] \approx 0$  (or assumes that it is constant and does not depend on density as in the case of a fully occupied lattice), and then assumes that the attractive field  $\Psi^{\text{att}}[f(\vec{\omega})] \propto S_2 P_2(\cos \gamma)$ ; the latter is equivalent to truncating the expansion of the attractive pair potential [Equation (8)] after the second Legendre term. The molecular-field theories of Chandrasekhar and co-workers<sup>137,138</sup>, and Luckhurst and co-workers<sup>12,139,140</sup> essentially amount to retaining higher-order terms in the Legendre expansion:  $\Psi^{\text{att}}[f(\vec{\omega})] \propto \sum_L S_{2L} P_{2L}(\cos \gamma)$ . Continuum versions of the Maier-Saupe theory have also been formulated (e.g., see references<sup>52,80</sup>), and correspond to using a hard-sphere repulsive reference

system  $\Psi^{\text{rep}}[f(\vec{\omega})] \approx \Psi^{\text{hs}}(\rho)$  with  $g_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}, \vec{\omega}_2) \approx \exp(-u_{12}^{\text{hs}}(r_{12})/kT)$  in  $\Psi^{\text{att}}[f(\vec{\omega})] \propto S_2 P_2(\cos \gamma)$  as with the GVDW approach; an analogous description (albeit with a different underlying significance of the temperature) results from the so-called L2 leading-order truncation of the Legendre polynomial series of the excluded volume of hard particles<sup>156–160</sup>.

For consistency with the decoupling approximation employed by Parsons<sup>141</sup> for the pair distribution function, one can approximate the pair distribution function of the reference repulsive system of anisotropic molecules required in the evaluation of the mean-attractive energy by that of an equivalent system of hard spheres with the same molecular volume:

$$g_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}, \vec{\omega}_2) \approx g_{12}^{\text{hs}}(r_{12}/\sigma). \tag{57}$$

This type of approximation has been used by Williamson and co-workers<sup>92,95</sup> and by García-Sánchez *et al.*<sup>102</sup> within a second-order perturbation theory of mesogens with repulsive and attractive interactions; as will be shown in the next section, the further use of the mean-value theorem can be employed to factorise the radial distribution function out of the expression, thus simplifying the integration of the mean-attractive energy.<sup>161,162</sup>

It is now clear that our general notation is appropriate to the most common approaches developed to deal with orientational ordering in liquid crystals. We now develop explicit expressions for the Helmholtz free energy of hard particles with specific centre-to-centre attractive interactions. In the first example, square-well anisotropic particles are examined; this is the system for which the fluid phase behaviour is investigated in detail. As a second example we give the specific expressions for the free energy of particles with Lennard-Jones interactions. The free energy of hard particles interacting through and attractive potential of the form defined in Equations (4)–(8) can be obtained from the general expression (42):

$$\begin{aligned}
\frac{A[f(\vec{\omega})]}{NkT} &= \frac{A^{\text{iso}}}{NkT} + \int f(\vec{\omega}) \ln \Omega f(\vec{\omega}) d\vec{\omega} + \frac{G(\rho)}{V_m} \iint V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2 \\
&\quad - \frac{\rho}{2kT} \iiint [\epsilon_0 + \epsilon_2 P_2(\cos \gamma) + \epsilon_4 P_4(\cos \gamma) + \dots] s(r_{12}) f(\vec{\omega}_1) f(\vec{\omega}_2) g_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) d\vec{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2. \tag{58}
\end{aligned}$$

If one approximates the pair distribution function by its low-density limit [Equation (55)], the free-energy can be written as

$$\begin{aligned} \frac{A[f(\vec{\omega})]}{NkT} &= \frac{A^{\text{iso}}}{NkT} + \int f(\vec{\omega}) \ln \Omega f(\vec{\omega}) d\vec{\omega} + \frac{G(\rho)}{V_m} \iint V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2 \\ &- \frac{\rho}{2kT} \iiint \int_{\sigma}^{\infty} [\epsilon_0 + \epsilon_2 P_2(\cos \gamma) + \epsilon_4 P_4(\cos \gamma)] s(r_{12}) f(\vec{\omega}_1) f(\vec{\omega}_2) r_{12}^2 dr_{12} d\hat{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2. \end{aligned} \quad (59)$$

This free-energy corresponds to a generalised van der Waals – Onsager description of the nematic phase. Here, the specific dependence of the contact distance  $\sigma(\hat{r}_{12}, \vec{\omega}, \vec{\omega}_2)$  on orientation is omitted for compactness; note that we will frequently omit this dependency in the text that follows.

#### D. Nonspherical molecules with orientationally dependent SW interactions

In the case of a centre-to-centre anisotropic square-well interaction defined in Equation (7), the shape function is simply  $s(r_{12}) = 1$  over the range of the attraction, and the mean-field Helmholtz free energy (59) simplifies to

$$\begin{aligned} \frac{A[f(\vec{\omega})]}{NkT} &= \frac{A^{\text{iso}}}{NkT} + \int f(\vec{\omega}) \ln \Omega f(\vec{\omega}) d\vec{\omega} + \frac{G(\rho)}{V_m} \iint V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2 \\ &- \frac{\rho}{2kT} \iiint \int_{\sigma}^{\lambda D} [\epsilon_0 + \epsilon_2 P_2(\cos \gamma) + \epsilon_4 P_4(\cos \gamma)] f(\vec{\omega}_1) f(\vec{\omega}_2) r_{12}^2 dr_{12} d\hat{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2 \\ &= \frac{A^{\text{iso}}}{NkT} + \int f(\vec{\omega}) \ln \Omega f(\vec{\omega}) d\vec{\omega} + \frac{G(\rho)}{V_m} \iint V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2 \\ &- \frac{\rho}{2kT} \iiint \int_{\sigma}^{\lambda D} \left[ \frac{r_{12}^3}{3} \right] [\epsilon_0 + \epsilon_2 P_2(\cos \gamma) + \epsilon_4 P_4(\cos \gamma)] f(\vec{\omega}_1) f(\vec{\omega}_2) d\hat{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2 \\ &= \frac{A^{\text{iso}}}{NkT} + \int f(\vec{\omega}) \ln \Omega f(\vec{\omega}) d\vec{\omega} + \frac{G(\rho)}{V_m} \iint V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2 \\ &- \frac{\rho}{2kT} \iiint \int \left( \frac{\lambda^3 D^3 - \sigma^3}{3} \right) [\epsilon_0 + \epsilon_2 P_2(\cos \gamma) + \epsilon_4 P_4(\cos \gamma)] f(\vec{\omega}_1) f(\vec{\omega}_2) d\hat{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2. \end{aligned} \quad (60)$$

In order for the upper limit of the integral in the distance  $r_{12}$  to be identified with the square-well range  $\lambda D$  for all relative orientations, the range has to be larger than the long dimension of the particle; when this is not the case the upper limit becomes a complicated function of orientation. If care is not employed, this can lead to an incorrect evaluation of the mean-attractive energy (e.g., see reference<sup>84</sup>) as has been pointed by García *et al.*<sup>99</sup>. It is now convenient to express the free energy in terms of angle averages of the individual configurational contributions as

$$\begin{aligned} \frac{A[f(\vec{\omega})]}{NkT} &= \frac{A^{\text{id}}_{\text{iso}}}{NkT} + \int f(\vec{\omega}) \ln \Omega f(\vec{\omega}) d\vec{\omega} + \frac{G(\rho)}{V_m} \langle V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) \rangle_{\vec{\omega}_1, \vec{\omega}_2} \\ &- \frac{\rho}{2kT} \left( \frac{4\pi\lambda^3 D^3}{3} \right) \epsilon_0 + \frac{\rho}{2kT} \langle V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) \rangle_{\vec{\omega}_1, \vec{\omega}_2} \epsilon_0 \\ &- \frac{\rho}{2kT} \left( \frac{4\pi\lambda^3 D^3}{3} \right) \langle P_2(\cos \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} \epsilon_2 + \frac{\rho}{2kT} \langle V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) P_2(\cos \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} \epsilon_2 \\ &- \frac{\rho}{2kT} \left( \frac{4\pi\lambda^3 D^3}{3} \right) \langle P_4(\cos \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} \epsilon_4 + \frac{\rho}{2kT} \langle V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) P_4(\cos \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} \epsilon_4. \end{aligned} \quad (61)$$

In general the orientational averages of a function  $J(\vec{\omega}_1, \vec{\omega}_2)$  are defined as

$$\langle J(\vec{\omega}_1, \vec{\omega}_2) \rangle_{\vec{\omega}_1, \vec{\omega}_2} = \iint J(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2. \quad (62)$$

Specific expressions for the orientational averages will be obtained by using the trial function of Onsager<sup>1</sup>, as will be shown in Section III F.



An inspection of Equations (61) highlights a tight coupling of the repulsive and attractive contributions to the free energy in such systems (cf. References<sup>30,31</sup>); the average excluded volume of the molecular hard core multiplies the isotropic mean-field dispersion contribution, and there are coupled averages of the excluded volume and the anisotropic part of the attractive interactions (e.g., of Maier-Saupe form) represented by the Legendre polynomial terms. The same type of coupling will also become apparent from an analysis of the expressions that we develop for the systems with Lennard-Jonesium attractive interactions in the next subsection. As a consequence one can not just simply add an uncoupled Maier-Saupe attractive contribution to the free energy of an isotropic hard-core reference in order to develop an equation of state of the nematic state. An inconsistent treatment of this kind has nevertheless been reported for the perturbed hard sphere chain theory (PHSCT)<sup>85</sup> and the statistical associating fluid theory (SAFT)<sup>106,107</sup> of chain-like mesogens.

### E. Nonspherical molecules with orientationally dependent LJ interactions

Another commonly employed centre-to-centre attractive interaction has the Lennard-Jones (Sutherland) form of Equation (6). For example, in the early work of Baron and Gelbart<sup>31</sup> an attractive potential of this form was used, though instead of the  $P_2(\cos \gamma)$  orientational dependence they used the essentially equivalent  $\cos^2 \gamma$  form. Attractive interactions of the Sutherland and Maier-Saupe  $\sim r_{12}^{-6} P_2(\cos \gamma)$  form have been examined by Telo da Gama and co-workers<sup>52,80</sup>, but in this case

for spherically symmetric molecules with hard spherical cores; Teixeira<sup>94</sup> later refined this model to include a hard ellipsoidal core, and a similar pair potential has also been studied by Simões *et al.*<sup>101</sup>. In this context it is also important to mention the Gay-Berne (GB) model<sup>163</sup>, an anisotropic (ellipsoidal) version of the Lennard-Jones potential, has been used extensively in simulation studies of liquid crystals<sup>164,165</sup> (see references<sup>103,166</sup> for recent reviews). Mean-field perturbation theories for the isotropic fluid and nematic phases of GB particles have thus also been developed<sup>79,88,103</sup>.

As a general example of the use of our approach for interactions of this form, we develop the free energy for a Lennard-Jonesium potential which conforms to the scaling proposed by Parsons<sup>141</sup>. In this case the potential is assumed to depend on the intermolecular distance  $r_{12}$  scaled by the orientationally dependent contact distance  $\sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)$ , rather than the molecular diameter  $D$ ,  $r^* = r_{12}/\sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)$ :

$$s(r^*) = \left[ \frac{\sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)}{r_{12}} \right]^6 = \frac{1}{r^{*6}} \quad \text{when} \quad r_{12} \geq \sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2). \quad (63)$$

In line with the Parsons<sup>141</sup> approach, the pair correlation function of the reference system of non-spherical molecules  $g_{12}^{\text{rep}}(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)$  can then be approximated by that of an effective system of hard-spheres with the same molecular volume [Equation 57]. The Helmholtz free energy for the system of nonspherical hard-core particles with Lennard-Jonesium attractive interactions can be obtained from Equation (58) as

$$\begin{aligned} \frac{A[f(\vec{\omega})]}{NkT} &= \frac{A_{\text{iso}}^{\text{id}}}{NkT} + \int f(\vec{\omega}) \ln \Omega f(\vec{\omega}) d\vec{\omega} + \frac{G(\rho)}{V_m} \iint V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2 \\ &- \frac{\rho}{2kT} \iiint \int_{\sigma}^{\infty} \left[ \frac{\sigma}{r_{12}} \right]^6 [\epsilon_0 + \epsilon_2 P_2(\cos \gamma) + \epsilon_4 P_4(\cos \gamma)] g_{12}^{\text{hs}}(r_{12}/\sigma) f(\vec{\omega}_1) f(\vec{\omega}_2) r_{12}^2 dr_{12} d\hat{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2 \quad (64) \end{aligned}$$

After changing variables from  $r_{12}$  to  $r^* = r_{12}/\sigma(\hat{r}_{12})$  we obtain

$$\begin{aligned} \frac{A[f(\vec{\omega})]}{NkT} &= \frac{A_{\text{iso}}^{\text{id}}}{NkT} + \int f(\vec{\omega}) \ln \Omega f(\vec{\omega}) d\vec{\omega} + \frac{G(\rho)}{V_m} \iint V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2 \\ &- \frac{\rho}{2kT} \iiint \int_1^{\infty} \left[ \frac{1}{r^*} \right]^6 [\epsilon_0 + \epsilon_2 P_2(\cos \gamma) + \epsilon_4 P_4(\cos \gamma)] g_{12}^{\text{hs}}(r^*) \sigma^3 r^{*2} dr^* f(\vec{\omega}_1) f(\vec{\omega}_2) r_{12}^2 dr_{12} d\hat{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2. \quad (65) \end{aligned}$$

We can make use of the mean-value theorem to factorise out the contact value of the hard-sphere distribution function  $g_{12}^{\text{hs}}(1; \rho^{\text{eff}})$  of a system at an effective density  $\rho^{\text{eff}}$  when integrating over  $dr^*$  (see the work by Gil-Villegas and co-

workers<sup>161,162</sup> for isotropic fluids of chain molecules):

$$\begin{aligned} \frac{A[f(\vec{\omega})]}{NkT} &= \frac{A_{\text{iso}}^{\text{id}}}{NkT} + \int f(\vec{\omega}) \ln \Omega f(\vec{\omega}) d\vec{\omega} + \frac{G(\rho)}{V_m} \iint V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2 \\ &\quad - \frac{\rho}{2kT} G^{\text{eff}}(\rho) \iiint \frac{\sigma^3}{3} d\hat{r}_{12} [\epsilon_0 + \epsilon_2 P_2(\cos \gamma) + \epsilon_4 P_4(\cos \gamma)] f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2, \end{aligned} \quad (66)$$

where we have defined the simple function of density as  $G^{\text{eff}}(\rho) = \rho g_{12}^{\text{hs}}(1; \rho^{\text{eff}})$ . As for the square-well potential the expression can now be written in terms of the orientational averages of the separate configurational contributions:

$$\begin{aligned} \frac{A[f(\vec{\omega})]}{NkT} &= \frac{A_{\text{iso}}^{\text{id}}}{NkT} + \int f(\vec{\omega}) \ln \Omega f(\vec{\omega}) d\vec{\omega} + \frac{G(\rho)}{V_m} \langle V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) \rangle_{\vec{\omega}_1, \vec{\omega}_2} - \frac{\rho}{2kT} G^{\text{eff}}(\rho) \left\{ \epsilon_0 \langle V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) \rangle_{\vec{\omega}_1, \vec{\omega}_2} \right. \\ &\quad \left. + \epsilon_2 \langle V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) P_2(\cos \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} + \epsilon_4 \langle V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) P_4(\cos \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} \right\}. \end{aligned} \quad (67)$$

We have again expressed the orientational average of the contact distance in terms of the excluded volume. This represents a generalised Onsager Helmholtz free-energy for a first-order perturbation theory of non-spherical molecules with Lennard-Jonesium anisotropic attractive interactions. The expression reduces to our generalised van der Waals – Onsager free energy when the pair-correlations are neglected in the attractive contribution, i.e.,  $g_{12}^{\text{hs}}(1; \rho^{\text{eff}}) = 1$ ; the corresponding expression for the square-well system was given in Equation (61).

It may now be apparent to the reader that the free energy of a nematic phase of non-spherical molecules with square-well or Lennard-Jonesium attractive interactions can be expressed in terms of orientational averages of the configurational contributions. These averages can be evaluated numerically and the equilibrium free energy obtained by solving the appropriate Euler-Lagrange equation [cf. Equation (54)]. As with the purely repulsive system examined in our previous work<sup>2</sup>, adopting this procedure is computationally intensive, particularly if one is interested in solving for the conditions of phase equilibria and treating mixtures, therefore we seek to develop more-convenient analytical expressions for the averages in terms of a parameter that characterises the degree of orientational order in the system. The representation of the orientational distribution function in terms of the Onsager<sup>1</sup> trial function provides an accurate and convenient method of obtaining a tractable expression for the free energy.<sup>2</sup>

## F. The Onsager trial function

In his seminal paper, Onsager<sup>1</sup> chose to represent the orientational distribution function  $f(\vec{\omega})$  by the simple form

$$f_{\text{OTF}}(\theta) = \frac{\alpha \cosh[\alpha \cos(\theta)]}{4\pi \sinh(\alpha)}, \quad (68)$$

This trial function depends on the azimuthal angle  $\theta = \arccos(\vec{\omega} \cdot \vec{\omega}_n)$ , defined with respect to a reference vector

$\vec{\omega}_n$  which corresponds to the director in a nematic phase, and on the parameter  $\alpha$  which describes the degree of orientational order. When  $\alpha = 0$  there is no preferential orientational ordering and the trial function takes on the isotropic value of  $f_{\text{OTF}} = 1/(4\pi)$ .

The use of the Onsager trial function to obtain analytical expressions for the orientational averages such as those described in the previous section has already been discussed in detail<sup>2</sup>. It is relatively straight forward to evaluate the functional corresponding to the ideal orientational entropic contribution to the free energy. In this case one obtains the following analytical function of the orientational parameter:

$$\begin{aligned} \mathcal{F}_{\text{orient}}[f_{\text{OTF}}] &= \int f_{\text{OTF}}(\theta) \{\ln \Omega f_{\text{OTF}}(\theta)\} d\vec{\omega} \\ &= \ln(\alpha \coth \alpha) - 1 + \frac{\arctan(\sinh \alpha)}{\sinh \alpha} \end{aligned} \quad (69)$$

The evaluation of the orientational averages of the configurational contributions due to the repulsive (excluded volume) and attractive interactions is less trivial. We have already demonstrated<sup>2</sup> the relevance and general applicability of the Onsager trial function in evaluating the angle average  $\langle J(\vec{\omega}_1, \vec{\omega}_2) \rangle_{\vec{\omega}_1, \vec{\omega}_2} \equiv \langle J(\gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2}$  of functionals that depend on the relative orientation  $\gamma = \arccos(\vec{\omega}_1 \cdot \vec{\omega}_2)$  of a given pair of anisotropic molecules. The method has broad applicability to any functional of the orientational distribution function  $f(\vec{\omega})$ . It is important to recall that the only requirement to implement Onsager's approach to a specific system is the feature of cylindrical symmetry such that

$$J(\gamma) = J(\pi - \gamma). \quad (70)$$

The specific functional form chosen by Onsager<sup>1</sup> was  $J(\gamma) = \sin \gamma$ , which corresponds to the leading contribution of the excluded volume for a system of hard rod-like molecules.

Going beyond the original treatment of Onsager, one can generalise the theory and express the configurational contributions as functions of terms in  $\sin^i \gamma$  (where

$i \geq 0$ ), to obtain analytical expressions for the functionals<sup>2</sup>. Each term of the configurational free energy thus satisfies the Onsager condition given by Equation (70). The excluded volume (second virial coefficient for a fixed relative orientation) of cylindrically symmetrical molecules can be expressed as such a series in  $\sin \gamma$ :

$$V_{\text{exc}}(\gamma) = 2B_2(\gamma) = \sum_{i=0}^{\infty} C_i \sin^i \gamma, \quad (71)$$

where the coefficients  $C_i$  depend on the specific form of the repulsive interactions (shape of the molecule). It should be noticed that in his original treatment, Onsager<sup>1</sup> considered only an excluded volume which was a linear function of  $\sin \gamma$  (appropriate for hard spherocylinders). In the case of linear chains formed from tangent hard-sphere segments the excluded volume can be captured by the first three terms ( $C_0$ ,  $C_1 \sin \gamma$ , and  $C_2 \sin^2 \gamma$ ) to very high accuracy<sup>167,168</sup>. When one represents the excluded volume as a series in  $\sin \gamma$ , it is clear from Equation (71) that, neglecting terms beyond  $\mathcal{O}(\sin^4 \gamma)$ , we can write its orientational average as

$$\begin{aligned} \langle V_{\text{exc}}(\gamma) \rangle_{\bar{\omega}_1, \bar{\omega}_2} &= C_0 + C_1 \langle \sin \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} + C_2 \langle \sin^2 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} \\ &+ C_3 \langle \sin^3 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} + C_4 \langle \sin^4 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2}. \end{aligned} \quad (72)$$

$$\begin{aligned} \langle V_{\text{exc}}(\gamma) P_2(\cos \gamma) \rangle_{\bar{\omega}_1, \bar{\omega}_2} &= C_0 + C_1 \langle \sin \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} + \left( C_2 - \frac{3C_0}{2} \right) \langle \sin^2 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} \\ &+ \left( C_3 - \frac{3C_1}{2} \right) \langle \sin^3 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} + \left( C_4 - \frac{3C_2}{2} \right) \langle \sin^4 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} \end{aligned} \quad (75)$$

where we again disregard terms beyond  $\mathcal{O}(\sin^4 \gamma)$  in the excluded volume. An examination of Equation (75) suggests the following recurrence formula:

$$\langle V_{\text{exc}}(\gamma) P_2(\cos \gamma) \rangle_{\bar{\omega}_1, \bar{\omega}_2} = \sum_{i=0}^n \left( C_i - \frac{3C_{i-2}}{2} \right) \langle \sin^i \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2}, \quad (76)$$

$$\begin{aligned} \langle V_{\text{exc}}(\gamma) P_4(\cos \gamma) \rangle_{\bar{\omega}_1, \bar{\omega}_2} &= C_0 + C_1 \langle \sin \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} + (C_2 - 5C_0) \langle \sin^2 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} \\ &+ (C_3 - 5C_1) \langle \sin^3 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} + \left( \frac{35C_0}{8} - 5C_2 + C_4 \right) \langle \sin^4 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2}, \end{aligned} \quad (77)$$

which can also be expressed in the more compact form

$$\langle V_{\text{exc}}(\gamma) P_4(\cos \gamma) \rangle_{\bar{\omega}_1, \bar{\omega}_2} = \sum_{i=0}^n \left( \frac{35}{8} C_{i-4} - 5C_{i-2} + C_i \right) \langle \sin^i \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2}. \quad (78)$$

In the case of the configurational free energy of systems with orientationally dependent attractions [e.g., Equation (61) and (67)] one has to evaluate the orientational averages of the Legendre polynomials, and of products of these with the excluded volume. If one uses the identity  $\cos^2 \gamma \equiv 1 - \sin^2 \gamma$ , then the terms in  $P_2(\cos \gamma)$ ,  $P_4(\cos \gamma)$ ,  $V_{\text{exc}}(\gamma) P_2(\cos \gamma)$ , and  $V_{\text{exc}}(\gamma) P_4(\cos \gamma)$  can also be expressed as a series in  $\sin \gamma$ . The orientational averages of the Legendre polynomials can be expressed simply as<sup>2</sup>

$$\langle P_2(\cos \gamma) \rangle_{\bar{\omega}_1, \bar{\omega}_2} = 1 - \frac{3}{2} \langle \sin^2 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} = S_2^2 \quad (73)$$

and

$$\begin{aligned} \langle P_4(\cos \gamma) \rangle_{\bar{\omega}_1, \bar{\omega}_2} &= \frac{35}{8} \langle \sin^4 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} - 5 \langle \sin^2 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} + 1 \\ &= S_4^2. \end{aligned} \quad (74)$$

The angle average of the mixed term  $V_{\text{exc}}(\gamma) P_2(\cos \gamma)$  can be written as

All of the configurational contributions to the free energy can therefore be evaluated by determining the appropriate orientational averages of powers of  $\sin \gamma$ . The use of the Onsager trial function to describe the orientational distribution function  $f(\vec{\omega})$  greatly simplifies the task of evaluating these contributions.<sup>2</sup> The orientational averages of the general function  $J(\gamma)$  are obtained by means of the following integral:

$$\langle J(\gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} = \frac{1}{2 \sinh^2 \alpha} \int_{\gamma=0}^{\pi} \cosh \left\{ \alpha \sqrt{2(1 + \cos \gamma)} \right\} dJ(\gamma) + J(0). \quad (79)$$

By employing this generic formula, the various terms in  $\langle \sin^i \gamma \rangle_{\vec{\omega}_1, \vec{\omega}_2}$  can now be expressed as relatively simple functions of the Onsager orientational parameter  $\alpha$  appearing in Equation (68) which characterises the extent of orientational order (sharpness of the orientational distribution function):

$$\langle \sin \gamma \rangle_{\vec{\omega}_1, \vec{\omega}_2} = \frac{\pi}{2 \sinh^2 \alpha} I_2(2\alpha); \quad (80)$$

$$\begin{aligned} \langle \sin^2 \gamma \rangle_{\vec{\omega}_1, \vec{\omega}_2} &= \frac{2}{3} (1 - S_2^2) \\ &= \frac{4 \coth \alpha}{\alpha} - \frac{4 + 6 \coth^2 \alpha}{\alpha^2} \\ &+ \frac{12 \coth \alpha}{\alpha^3} - \frac{6}{\alpha^4}; \end{aligned} \quad (81)$$

$$\langle \sin^3 \gamma \rangle_{\vec{\omega}_1, \vec{\omega}_2} = \frac{3}{2 \sinh^2 \alpha} \left\{ \frac{\pi}{4} [I_2(2\alpha) - I_6(2\alpha)] \right\}; \quad (82)$$

$$\begin{aligned} \langle \sin^4 \gamma \rangle_{\vec{\omega}_1, \vec{\omega}_2} &= \frac{8}{35} \left( -1 + \frac{10}{3} - \frac{10}{3} S_2^2 + S_4^2 \right) \\ &= 8 \left\{ \frac{2}{\alpha^2} + \frac{63}{\alpha^4} + \frac{270}{\alpha^6} + \frac{315}{\alpha^8} \right. \\ &- 2 \coth \alpha \left[ \frac{15}{\alpha^3} + \frac{165}{\alpha^5} + \frac{315}{\alpha^7} \right] \\ &\left. + \coth^2 \alpha \left[ \frac{2}{\alpha^2} + \frac{60}{\alpha^4} + \frac{315}{\alpha^6} \right] \right\}. \end{aligned} \quad (83)$$

We have introduced modified Bessel functions, which can be represented in the standard integral form<sup>169</sup>:

$$I_{2j}(2\alpha) = \frac{1}{\pi} \int_{u=0}^{\pi} \exp(2\alpha \cos u) \cos(2ju) du. \quad (84)$$

It is worth mentioning that modified Bessel functions are particularly useful in that they can be expressed as asymptotic expansions. In the context of moderately ordered nematic states an accurate representation of the configurational terms can be achieved when only the first few terms of the expansion in the orientational parameter

$\alpha$  are retained. The angle averages of Equation (80) and (82) can thus be accurately represented as relatively simple algebraic expressions in  $\alpha$ . We can now see how each of the angle averages required for the evaluation of the free energy depends only on the parameters  $C_i$  characterising the geometry of the molecule, and the variational parameter  $\alpha$  introduced in the definition of the trial function proposed by Onsager.

Once the separate orientational contributions have been determined these can be combined as in Equations (61) or (67) (depending on the particular molecular model) to express the Helmholtz free energy  $A(\alpha)$  of the system as a function of the parameter  $\alpha$ . The equilibrium free energy of the nematic phase is then obtained by determining the value of  $\alpha_{\text{eq}}$  that minimises the free energy, corresponding to the condition:

$$\left. \frac{\partial A(\alpha)}{\partial \alpha} \right|_{\text{eq}} = 0. \quad (85)$$

This expression is clearly much easier to solve than the Euler-Lagrange integral equation [see Equation (54)] that has to be evaluated numerically when the free energy  $A[f(\vec{\omega})]$  is described as the more general functional of the orientational distribution function  $f(\vec{\omega})$ . The other thermodynamic properties such as the pressure (equation of state) and chemical potential are also obtained from the equilibrium free energy as analytical functions of  $\alpha$  by employing the standard thermodynamic relations:  $\mu = (\partial A / \partial N)_{VT}$  and  $P = -(\partial A / \partial V)_{NT}$ . An additional advantage of using the Onsager trial-function method is that, by re-arranging Equations (81) and (83), one can express the nematic order parameter  $S_2$  (and the higher order parameters  $S_{2i}$ ) as an algebraic expression in the orientation parameter:<sup>2</sup>

$$S_2 = 1 - \frac{3 \coth \alpha_{\text{eq}}}{\alpha_{\text{eq}}} + \frac{3}{\alpha_{\text{eq}}^2}; \quad (86)$$

$$S_4 = 1 + \frac{45}{\alpha_{\text{eq}}^2} + \frac{105}{\alpha_{\text{eq}}^4} - \left( \frac{10}{\alpha_{\text{eq}}} + \frac{105}{\alpha_{\text{eq}}^3} \right) \coth \alpha_{\text{eq}}. \quad (87)$$

As an example of the usefulness and versatility of the theory developed here, we make use of the Onsager trial function with our free energy (Equation 61) to derive an analytical (algebraic) equation of state for hard spherocylindrical molecules interacting through orientationally dependent (Maier-Saupe,  $P_2(\cos \gamma)$ ) square-well attractive potential in the following subsection. This algebraic description represents the key highlight of our methodology for using the Onsager trial function within the generalised van der Waals formalism for nematic liquid crystals developed in the previous sections.

### G. Algebraic equation of state for SW spherocylinders.

The equation of state of hard spherocylinders with orientationally dependent (anisotropic) square-well attrac-

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tive interactions can be constructed from the general expressions for the angle averages of the configurational free energy given in the previous section. The main physical features of real mesogenic molecules (a hard anisotropic core with dispersive interactions that depend on the relative molecular orientation) are taken into account in the model. The equation of state can be represented in algebraic form for such a model system. Such a representation is particularly appropriate for use in engineering applications when a description of liquid-crystalline phases is required. The approach that we follow here is to examine the leading terms of the free energy obtained with the Onsager trial function for moderately ordered nematic states (large values of  $\alpha$ ). As we show in this section it is possible to obtain a cubic solution for the orientational parameter  $\alpha$  of the equilibrium nematic state by an appropriate truncation of the free energy.

The total free energy of nonspherical hard-core molecules with isotropic and anisotropic square-well attractive interactions was given in Equation (61). For the sake of simplicity, we have chosen to assume a Maier-Saupe form where the higher-order Legendre contributions to the attractive part of the free energy are not present (i.e.,  $\epsilon_4 = 0$ ):

$$\begin{aligned} \frac{A[f(\vec{\omega})]}{NkT} &= \frac{A_{\text{iso}}^{\text{id}}}{NkT} + \mathcal{F}_{\text{orient}}[f(\vec{\omega})] + \frac{G(\rho)}{V_{\text{m}}} \langle V_{\text{exc}}(\gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} \\ &- \frac{\rho}{2} \frac{\epsilon_0}{kT} \left\{ \frac{4\pi D^3}{3} \lambda^3 \left[ 1 + \frac{\epsilon_2}{\epsilon_0} \langle P_2(\sin \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} \right] \right. \\ &\left. - \left[ \langle V_{\text{exc}}(\gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} + \frac{\epsilon_2}{\epsilon_0} \langle V_{\text{exc}}(\gamma) P_2(\sin \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} \right] \right\}. \end{aligned} \quad (88)$$

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The ideal isotropic contribution to the free energy  $A_{\text{iso}}^{\text{id}}$  is simply proportional to  $\ln \rho$  [Equation 20] and does not depend on the orientational parameter  $\alpha$ .

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On describing the free energy of the anisotropic system with the Onsager trial function, the contribution due to the ideal orientational entropy  $\mathcal{F}_{\text{orient}}[f(\vec{\omega})]$  can be expressed in terms of orientational parameter  $\alpha$  as [Equation (69)]

$$\begin{aligned} \mathcal{F}_{\text{orient}}[f_{\text{OTF}}] &= \ln(\alpha \coth \alpha) - 1 + \frac{\arctan(\sinh \alpha)}{\sinh \alpha} \\ &\approx \ln \alpha - 1 + \mathcal{O}(\exp[-\alpha]). \end{aligned} \quad (89)$$

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The approximate form of the ideal orientational entropy is obtained for moderately ordered nematic states where  $\alpha \gg 1$ . In order to determine the configurational contributions to the free energy that arise from the repulsive and attractive intermolecular interactions it is necessary to specify the features of the molecular model. In this example we develop the theory for hard spherocylinders with central square-well interactions [see Figure (1)]. As has been already mentioned, the hard spherocylinders comprise a cylinder of length  $L$  with hemispherical caps of diameter  $D$  at each end. The square-well interaction [cf. Equation (7)] acts from the centre of mass of the

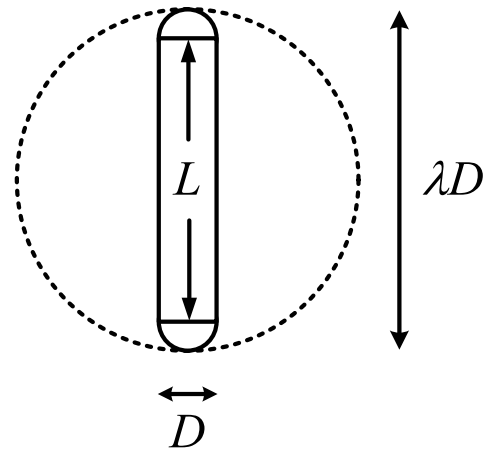


FIG. 1: Our model for the attractive rod-like molecules constitutes a hard spherocylinder core of aspect ratio  $(L + 1)/D$  and a spherical square-well (SW) potential characterised by isotropic and anisotropic interactions of strengths  $\epsilon_0$  and  $\epsilon_2$ , and range  $\lambda D$ . In the figure we have depicted the shortest range (dotted line) that circumscribes the hard core characterised by  $\lambda D = L + D$  (the so-called “square peg in a round hole” model)

hard rods and has a range  $\lambda D \geq L + D$  so that one can obtain analytical expressions for the appropriate integrals [see Section (III D)]; the attractive square-well is assumed to consist of an isotropic part of depth  $-\epsilon_0$  and an anisotropic Maier-Saupe part (second Legendre form) of depth  $-\epsilon_2 P_2(\cos \gamma)$ . The excluded volume of a pair of spherocylinders is given by<sup>1</sup>

$$V_{\text{exc}}(\gamma) = C_0 + C_1 \sin \gamma, \quad (90)$$

where the constants  $C_0 = \frac{4}{3} \pi D^3 + 2\pi LD^2$  and  $C_1 = 2L^2D$  depend on the molecular dimensions. It is clear from Equation (88) that the orientational averages  $\langle V_{\text{exc}}(\gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2}$ ,  $\langle P_2(\sin \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2}$ , and  $\langle V_{\text{exc}}(\gamma) P_2(\sin \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2}$  have to be evaluated to give the free-energy of the nematic state. The orientational average of the excluded volume can be determined from  $\langle \sin \gamma \rangle_{\vec{\omega}_1, \vec{\omega}_2}$  [see Equations (72) and (80)], the average of the second Legendre polynomial  $\langle P_2(\sin \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2}$  can be determined from  $\langle \sin^2 \gamma \rangle_{\vec{\omega}_1, \vec{\omega}_2}$  [see Equations (73) and (81)], and the mixed average  $\langle V_{\text{exc}}(\gamma) P_2(\sin \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2}$  is a function of  $\langle \sin \gamma \rangle_{\vec{\omega}_1, \vec{\omega}_2}$ ,  $\langle \sin^2 \gamma \rangle_{\vec{\omega}_1, \vec{\omega}_2}$ ,  $\langle \sin^3 \gamma \rangle_{\vec{\omega}_1, \vec{\omega}_2}$  [see Equations (75) and (82)], and with  $C_2 = C_3 = C_4 = 0$ . This means that the free-energy of our model can be evaluated from the average of the first three moments of  $\sin \gamma$ . For large  $\alpha$  the average of the moments given in Equations (80) to (83) can be approximated by retaining



terms up to  $1/\alpha^{3/2}$ :

$$\langle \sin \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} \approx \sqrt{\pi} \left( \frac{1}{\alpha^{1/2}} - \frac{15}{16\alpha^{3/2}} \right) + \mathcal{O} \left( \frac{1}{\alpha^{5/2}} \right) \quad (91)$$

$$\langle \sin^2 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} \approx \frac{4}{\alpha} + \mathcal{O} \left( \frac{1}{\alpha^2} \right) \quad (92)$$

$$\langle \sin^3 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} \approx \sqrt{\pi} \frac{6}{\alpha^{3/2}} + \mathcal{O} \left( \frac{1}{\alpha^{5/2}} \right) \quad (93)$$

$$\langle \sin^4 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} \approx 0 + \mathcal{O} \left( \frac{1}{\alpha^2} \right). \quad (94)$$

These expressions are generalisations of the simpler linear expressions for the orientational averages of the configurational functionals of hard-core molecules presented by Odijk<sup>130</sup> with the Gaussian trial function. For Equations (91) and (93) we have made use of the asymptotic expansion<sup>169</sup>

$$\frac{\pi}{2 \sinh^2 \alpha} I_\nu(2\alpha) \approx \sqrt{\pi} \left\{ \frac{1}{\alpha^{1/2}} + \sum_{i=1}^{\infty} \left[ (-1)^i \frac{\prod_{j=1}^i 4\nu^2 - (2j-1)^2}{i!(16)^i \alpha^{(2i+1)/2}} \right] \right\} \quad (95)$$

to represent the modified Bessel function  $I_\nu(2\alpha)$  (where here  $\nu = 2, 6$ ). The orientational averages of the configurational contributions can thus be approximated by

$$\langle V_{\text{exc}}(\gamma) \rangle_{\bar{\omega}_1, \bar{\omega}_2} = C_0 + C_1 \langle \sin \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} \approx C_0 + C_1 \sqrt{\pi} \left[ \frac{1}{\alpha^{1/2}} - \frac{15}{16} \frac{1}{\alpha^{3/2}} + \mathcal{O} \left( \frac{1}{\alpha^{5/2}} \right) \right] \quad (96)$$

$$\langle P_2(\sin \gamma) \rangle_{\bar{\omega}_1, \bar{\omega}_2} = 1 - \frac{3}{2} \langle \sin^2 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} = S_2^2 \approx 1 - \frac{6}{\alpha} + \mathcal{O} \left( \frac{1}{\alpha^2} \right) \quad (97)$$

$$\begin{aligned} \langle V_{\text{exc}}(\gamma) P_2(\sin \gamma) \rangle_{\bar{\omega}_1, \bar{\omega}_2} &= C_0 + C_1 \langle \sin \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} - \frac{3}{2} \{ C_0 \langle \sin^2 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} + C_1 \langle \sin^3 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} \} \\ &\approx C_0 + C_1 \sqrt{\pi} \frac{1}{\alpha^{1/2}} - 6 C_0 \frac{1}{\alpha} + \frac{159 C_1 \sqrt{\pi}}{16} \frac{1}{\alpha^{3/2}} + \mathcal{O} \left( \frac{1}{\alpha^{5/2}} \right) \end{aligned} \quad (98)$$

$$\langle P_4(\sin \gamma) \rangle_{\bar{\omega}_1, \bar{\omega}_2} = \frac{35}{8} \langle \sin^4 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} - 5 \langle \sin^2 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2} + 1 = S_4^2 \approx 1 - \frac{20}{\alpha} + \mathcal{O} \left( \frac{1}{\alpha^2} \right). \quad (99)$$

Note that though not necessary in this particular case we have included the expression for  $\langle \sin^4 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2}$  and  $\langle P_4(\sin \gamma) \rangle_{\bar{\omega}_1, \bar{\omega}_2}$  for the sake of completeness; in the case of systems with more complex forms of the excluded volume interaction or with attractive interaction including

higher order Legendre terms these contributions would have to be included.

The total Helmholtz free energy of the nematic phase [Equation (88)] can now be expressed as an algebraic function of the Onsager orientational parameter  $\alpha$  as

$$\begin{aligned} \frac{A(\alpha)}{NkT} &= \frac{A_{\text{iso}}^{\text{id}}}{NkT} + \ln \alpha - 1 + \frac{G(\rho)}{V_m} \left[ C_0 + C_1 \sqrt{\pi} \left( \frac{1}{\alpha^{1/2}} - \frac{15}{16} \frac{1}{\alpha^{3/2}} \right) \right] \\ &\quad - \frac{\rho}{2} \frac{\epsilon_0}{kT} \left\{ \left[ \frac{4\pi}{3} (\lambda D)^3 - C_0 \right] \left( 1 + \frac{\epsilon_2}{\epsilon_0} \right) - C_1 \sqrt{\pi} \left( 1 + \frac{\epsilon_2}{\epsilon_0} \right) \frac{1}{\alpha^{1/2}} \right. \\ &\quad \left. + \frac{\epsilon_2}{\epsilon_0} \left[ C_0 - \frac{4\pi}{3} (\lambda D)^3 \right] \frac{6}{\alpha} + \frac{15}{16} C_1 \sqrt{\pi} \left( 1 + \frac{53}{5} \frac{\epsilon_2}{\epsilon_0} \right) \frac{1}{\alpha^{3/2}} \right\}. \end{aligned} \quad (100)$$

This expression is much more tractable than the full func-

tional form of Equation (88), and, as we will show, pro-

vides one with a simple and accurate algebraic equation of state which is ideal for the modelling of the nematic phase in engineering applications.

The numerical advantage of such an approach becomes apparent when one determines the equilibrium nematic

state. In this case instead of having to solve a Euler-Lagrange integral equation [cf. Equation (54)], the free energy is simply minimised with respect to the Onsager parameter  $\alpha$  (by equating its derivative to zero):

$$\begin{aligned} \frac{\partial}{\partial \alpha} \left[ \frac{A(\alpha)}{NkT} \right] &= \frac{1}{\alpha} - \frac{1}{2} C_1 \sqrt{\pi} \left[ \frac{\rho}{2} \frac{\epsilon_0}{kT} \left( 1 + \frac{\epsilon_2}{\epsilon_0} \right) + \frac{G(\rho)}{V_m} \right] \frac{1}{\alpha^{3/2}} + 6\rho \frac{\epsilon_2}{kT} \left[ C_0 - \frac{4\pi}{3} (\lambda D)^3 \right] \frac{1}{\alpha^2} \\ &+ \frac{45}{32} C_1 \sqrt{\pi} \left[ \frac{\rho}{2} \frac{\epsilon_0}{kT} \left( 1 + \frac{53}{5} \frac{\epsilon_2}{\epsilon_0} \right) + \frac{G(\rho)}{V_m} \right] \frac{1}{\alpha^{5/2}} = 0. \end{aligned} \quad (101)$$

In order to express the solution for the equilibrium orientational parameter  $\alpha_{\text{eq}}$  in a compact cubic form we define the parameter  $\chi = \alpha^{1/2}$  which leads to

$$\frac{\partial}{\partial \alpha} \left[ \frac{A(\alpha)}{NkT} \right] = \frac{1}{\chi^5} \{ a_0 + a_1 \chi + a_2 \chi^2 + \chi^3 \} = 0, \quad (102)$$

where the state/molecule dependent coefficients are defined as

$$a_0 = \frac{45}{32} C_1 \sqrt{\pi} \left[ \frac{\rho}{2} \frac{\epsilon_0}{kT} \left( 1 + \frac{53}{5} \frac{\epsilon_2}{\epsilon_0} \right) + \frac{G(\rho)}{V_m} \right] \quad (103)$$

$$a_1 = 6\rho \frac{\epsilon_2}{kT} \left[ C_0 - \frac{4\pi}{3} (\lambda D)^3 \right] \quad (104)$$

$$a_2 = -\frac{1}{2} C_1 \sqrt{\pi} \left[ \frac{\rho}{2} \frac{\epsilon_0}{kT} \left( 1 + \frac{\epsilon_2}{\epsilon_0} \right) + \frac{G(\rho)}{V_m} \right]. \quad (105)$$

It is immediately clear that the equilibrium value for  $\chi$  and therefore  $\alpha$  can be evaluated after solving the cubic polynomial that appears within curly brackets in Equation (102). We use the relatively simple trigonometric formulation of Nickalls<sup>170</sup> to solve the cubic polynomial for the value of  $\alpha$  at equilibrium:

$$\alpha_j = \frac{1}{9} \left\{ a_2 - 2\sqrt{a_2^2 - 3a_1} \cos \left( \frac{2j\pi}{3} + \frac{1}{3} \arccos \frac{-27[a_0 - \frac{1}{3}a_1a_2 + \frac{2}{27}a_2^3]}{2[a_2^2 - 3a_1]^{3/2}} \right) \right\}^2, \quad (106)$$

where  $j = \{0, 1, 2\}$ . As in the case of the purely repulsive system,<sup>2</sup> the largest root  $\alpha_2 = \alpha_{\text{eq}}$  corresponds to the equilibrium value of the orientational parameter. The roots  $\alpha_0$  and  $\alpha_1$  correspond to the ‘‘isotropic’’ and unstable solutions. One should note that the expressions do not provide a good approximation of the thermodynamics of the system for these lower values of  $\alpha$  as the free energy expansion involves a truncated series. The correct expression with  $\alpha = 0$  is used to represent the isotropic phase; the specific expressions for the Helmholtz free-energy, chemical potential and pressure (equation of state) will be given at the end of this section.

The phase coexistence between the isotropic and anisotropic (nematic) states is established by ensuring that the phases are in chemical and mechanical equilibrium, i.e., the equality of chemical potential and pressure.

The expression for the chemical potential is given by

$$\begin{aligned} \frac{\mu}{kT} &= \left( \frac{\partial(A/kT)}{\partial N} \right)_V \\ &= \frac{\mu^0}{kT} + \ln \rho - 1 + \ln \alpha_{\text{eq}} \\ &+ \frac{1}{8V_m} \frac{\mu^{\text{hs}}}{kT} \left[ C_0 + C_1 \sqrt{\pi} \left( \frac{1}{\alpha_{\text{eq}}^{1/2}} - \frac{15}{16} \frac{1}{\alpha_{\text{eq}}^{3/2}} \right) \right] \\ &- \frac{\rho}{2} \frac{\epsilon_0}{kT} \left\{ \frac{4\pi}{3} (\lambda D)^3 \left[ 1 + \frac{\epsilon_2}{\epsilon_0} \left( 1 - \frac{6}{\alpha_{\text{eq}}} \right) \right] \right. \\ &- C_0 \left( 1 + \frac{\epsilon_2}{\epsilon_0} \right) - C_1 \sqrt{\pi} \left( 1 + \frac{\epsilon_2}{\epsilon_0} \right) \frac{1}{\alpha_{\text{eq}}^{1/2}} \\ &\left. + \frac{\epsilon_2}{\epsilon_0} C_0 \frac{6}{\alpha_{\text{eq}}} + \frac{15}{16} C_1 \sqrt{\pi} \left( 1 - \frac{53}{5} \frac{\epsilon_2}{\epsilon_0} \right) \frac{1}{\alpha_{\text{eq}}^{3/2}} \right\}. \end{aligned} \quad (107)$$

where the reference chemical potential is

$$\frac{\mu^0}{kT} = \ln \left( \frac{\mathcal{V}}{4\pi} \right), \quad (108)$$

and the term in  $\mu^{\text{hs}}$  corresponds to the chemical potential of the effective hard-sphere system which is obtained from the Carnahan and Starling expression (cf. Equation (23)):

$$\frac{\mu^{\text{hs}}}{kT} = \frac{3\eta^3 - 9\eta^2 + 8\eta}{(1 - \eta)^3}. \quad (109)$$

It is more usual to express the density dependence in terms of the packing fraction  $\eta = \rho V_{\text{m}}$ , where in this case the volume of the hard spherocylinder is given by  $V_{\text{m}} = V_{\text{HSC}} = \pi/6 D^3 + \pi/4 LD^2$ .

Once expressions for the Helmholtz free energy and chemical potential are known, the pressure can be obtained from the thermodynamic relationship

$$\begin{aligned} A &= N\mu - pV \\ \frac{A}{NkT} &= \frac{\mu}{kT} - \frac{pV}{NkT}. \end{aligned} \quad (110)$$

The compressibility factor of the nematic phase of attractive hard-spherocylinders can thus be written as

$$\begin{aligned} Z &= \frac{pV}{NkT} = \frac{\mu}{kT} - \frac{A}{NkT} \\ &= 1 + \frac{Z^{\text{hs}} - 1}{8V_{\text{m}}} \left[ C_0 + C_1 \sqrt{\pi} \left( \frac{1}{\alpha_{\text{eq}}^{1/2}} - \frac{15}{16} \frac{1}{\alpha_{\text{eq}}^{3/2}} \right) \right] \\ &\quad - \frac{\rho}{4} \frac{\epsilon_0}{kT} \left\{ \frac{4\pi}{3} (\lambda D)^3 \left[ 1 + \frac{\epsilon_2}{\epsilon_0} \left( 1 - \frac{6}{\alpha_{\text{eq}}} \right) \right] \right. \\ &\quad - C_0 \left( 1 + \frac{\epsilon_2}{\epsilon_0} \right) - C_1 \sqrt{\pi} \left( 1 + \frac{\epsilon_2}{\epsilon_0} \right) \frac{1}{\alpha_{\text{eq}}^{1/2}} \\ &\quad \left. + \frac{\epsilon_2}{\epsilon_0} C_0 \frac{6}{\alpha_{\text{eq}}} + \frac{15}{16} C_1 \sqrt{\pi} \left( 1 - \frac{53}{5} \frac{\epsilon_2}{\epsilon_0} \right) \frac{1}{\alpha_{\text{eq}}^{3/2}} \right\}. \end{aligned} \quad (111)$$

where  $Z^{\text{hs}}$  is the Carnahan and Starling<sup>145</sup> hard-sphere compressibility factor:

$$Z^{\text{hs}} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}. \quad (112)$$

In essence this is a generalisation of the van der Waals<sup>26</sup> (or augmented van der Waals<sup>152-154</sup>) equation of state to deal with anisotropic (nematic) phases of non-spherical molecules with orientationally dependent attractive interactions; it goes beyond the van der Waals treatment in that the Parsons-Lee scaling applied to the Onsager theory is used to give an accurate representation of the anisotropic repulsive cores, and furthermore orientationally dependent attractive pair interactions are treated. The cubic equation for the parameter  $\alpha_{\text{eq}}$  that characterises the degree of orientation order of the equilibrium

state [cf. Equation (106)] provides a fully algebraic equation of state of the system. This is the first analytical equation of state of its kind that has been developed to describe anisotropic phases at the microscopic level of specific molecular interactions. We feel that such an equation is of particular relevance to the description of fluid phase equilibria of orientationally ordered states in practical applications where fast and reliable computations are required.

Before our examination of the phase equilibria is presented for specific systems it only remains to provide the corresponding expressions for the Helmholtz free energy, chemical potential, and pressure (compressibility factor) of the isotropic state of hard-spherocylinders with orientationally dependent attractive interactions. In the case of isotropic phases the single particle orientational distribution function is constant for all orientations:  $f(\vec{\omega}) = f_{\text{OTF}}(\vec{\omega}) = 1/4\pi$ . When this value of  $f(\vec{\omega})$  for the isotropic phase is substituted in the free energy of the nematic [Equation (61)] the contribution due to the ideal orientational entropy [Equation (43)] disappears, i.e.,  $\mathcal{F}_{\text{orient}}[1/4\pi] = 0$ , and the respective configurational contributions can easily be integrated to give  $\langle V_{\text{exc}}(\gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} = C_0 + C_1 \pi/4$ ,  $\langle P_2(\sin \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} = S_2^2 = 0$ ,  $\langle P_4(\sin \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} = S_4^2 = 0$ , and  $\langle V_{\text{exc}}(\gamma) P_2(\sin \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} = -C_1 \pi/32$ . The Helmholtz free energy, chemical potential, and compressibility factor of the isotropic phase of our model mesogen can thus be expressed as

$$\begin{aligned} \frac{A[f(\vec{\omega})]}{NkT} &= \frac{A_{\text{iso}}^{\text{id}}}{NkT} + \mathcal{F}_{\text{orient}}[f(\vec{\omega})] + \frac{G(\rho)}{V_{\text{m}}} \left( C_0 + \frac{\pi}{4} C_1 \right) \\ &\quad - \frac{\rho}{2} \frac{\epsilon_0}{kT} \left[ \frac{4\pi}{3} (\lambda D)^3 - C_0 + \frac{\pi}{4} C_1 \left( \frac{1}{8} \frac{\epsilon_2}{\epsilon_0} - 1 \right) \right], \end{aligned} \quad (113)$$

$$\begin{aligned} \frac{\mu}{kT} &= \frac{\mu^0}{kT} + \ln \rho + \frac{1}{8V_{\text{m}}} \frac{\mu^{\text{hs}}}{kT} \left( C_0 + \frac{\pi}{4} C_1 \right) \\ &\quad - \frac{\rho}{2} \frac{\epsilon_0}{kT} \left[ \frac{4\pi}{3} (\lambda D)^3 - C_0 + \frac{\pi}{4} C_1 \left( \frac{1}{8} \frac{\epsilon_2}{\epsilon_0} - 1 \right) \right], \end{aligned} \quad (114)$$

and

$$\begin{aligned} Z &= \frac{pV}{NkT} = 1 + \frac{Z^{\text{hs}} - 1}{8V_{\text{m}}} \left( C_0 + \frac{\pi}{4} C_1 \right) \\ &\quad - \frac{\rho}{4} \frac{\epsilon_0}{kT} \left[ \frac{4\pi}{3} (\lambda D)^3 - C_0 + \frac{\pi}{4} C_1 \left( \frac{1}{8} \frac{\epsilon_2}{\epsilon_0} - 1 \right) \right]. \end{aligned} \quad (115)$$

From these expressions one can readily obtain the vapour-liquid coexistence branches for the isotropic fluid, and together with the corresponding relations (106), (107) and (111) for the anisotropic fluid one can also determine the boundaries of vapour-nematic and liquid-nematic equilibria.

## IV. RESULTS

The liquid-crystalline phase transitions of model mesogens with attractive interactions have been studied with numerous theoretical approaches, including the Flory lattice treatments<sup>109–117</sup>, the Maier-Saupe and other molecular field theories<sup>5,6,12,137–140</sup>, and a host of numerical studies with generalised van der Waals (perturbative), integral equation and density functional theories<sup>29–108</sup>. In this section we present the fluid phase equilibria and orientational ordering for molecules with anisotropic repulsive and attractive and interactions determined using the compact algebraic equation of state developed in the previous section. As we have seen, a generalised van der Waals – Onsager Helmholtz free energy for the nematic phase of hard spherocylinders with square-well attractive interactions can be expressed as Equation (61). Here, a Parsons-Lee scaling of the Onsager free energy is used to determine the repulsive contribution, and a first-order perturbation theory (described at the mean-field level) is employed to determine the effect of the attractive interactions. We employ an Onsager trial function to simplify the treatment of the orientational order by expressing the free energy as a function of an orientational parameter  $\alpha$  (see Section III F). When only the leading terms in the orientational parameter  $\alpha$  are retained, a cubic equation (106) can be solved to give algebraic equations for the free energy [Equation (100)], chemical potential [Equation (107)], and pressure (compressibility factor) [Equation (111)]. To assess the adequacy of our algebraic equation of state, the phase behaviour obtained with the analytical expressions is first compared with the results obtained with the numerical solution of the full Bessel integrals involved in the Onsager trial-function description. It is important to point out that positionally ordered states such as smectic and solid phases are not considered in our current study. As a consequence it is possible that some of the high-density states examined in our calculations may be metastable with respect to smectic or solid ordering.

We start by examining a system of hard spherocylinders of length  $L$  and diameter  $D$  with isotropic square-well interactions of range  $\lambda D$  and well depth  $-\epsilon_0$  (see Figure 1); the higher-order orientationally dependent contributions are all zero in the first instance, i.e.,  $\epsilon_2 = \epsilon_4 = 0$ . Although the attractive interactions do not in this case depend on the relative orientations of the particles for this simple model, it is important to stress that the inclusion of purely isotropic attractive pair interactions still gives rise to a free-energy contribution with an appreciable angular dependence as a result of a coupling with the anisotropic hard-core interactions<sup>30,31</sup>. The shape of the model mesogen is characterised by the length-to-breadth ratio  $L/D$  (corresponding to an aspect ratio of  $L/D+1$ ). In the theory developed in the previous section we have assumed that the range is always  $\lambda \geq L/D + 1$  to ensure the proper decomposition of the repulsive and attractive parts of the integrals<sup>99</sup>. It is convenient to ex-

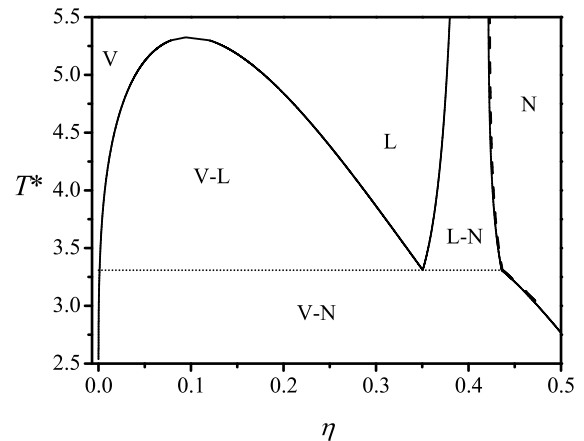


FIG. 2: The temperature-density fluid phase diagram ( $T^* = kT/\epsilon_0$  and  $\eta = \rho V_{HSC}$ ) for attractive spherocylinders with a length-to-breadth ratio of  $L/D = 5$  and an attractive range of  $\lambda = 6$ . The scaled Onsager free energy functional (section III F) is used to describe the system with the Onsager trial function; the representation with the full modified Bessel function [cf. Equation (61)] is represented by the continuous curve, and the truncated algebraic solution [cf. Equation (100)] by the dashed curve; there is virtually no difference between the results obtained with the truncated and the full Bessel functions. The dotted line corresponds to the vapour-liquid-nematic three phase coexistence separating the vapour-liquid ( $V - L$ ), liquid-nematic ( $L - N$ ), and vapour-nematic ( $V - N$ ) regions.

amine the phase behaviour in terms of a reduced temperature defined as  $T^* = kT/\epsilon_0$ , a reduced pressure  $P^* = PV_m/\epsilon_0$ , and a reduced density (packing fraction)  $\eta = \rho V_m$ , where the volume of the hard spherocylinder is  $V_m = V_{HSC} = \pi D^3/6 + \pi LD^2/4$ .

The fluid phase behaviour for the system of  $L/D = 5$  hard spherocylinders with isotropic square-well attractions of range  $\lambda = 6$  is presented as a temperature-density projection of the phase diagram in Figure 2. In keeping with the previous theoretical studies for this type of model (see References<sup>48,49,52,53,68,70,72,73,79,80,95,96,99,109</sup> as typical examples), three-regions of fluid phase equilibria are apparent. This type of vapour-liquid-nematic ( $V-L-N$ ) phase behaviour has also been observed in simulations of Gay-Berne particles<sup>165</sup>, and of hard spherocylinders with isotropic (depletion)<sup>171</sup> and anisotropic<sup>93</sup> attractive interactions for appropriate choices of the molecular aspect ratio and attractions. Note that in these studies, high-density coexistence regions involving positionally ordered phases are also determined; for the original parametrisation of the Gay-Berne potential simulated by de Miguel *et al.*<sup>164</sup>, both vapour-liquid-smectic and liquid-nematic-smectic triple points are exhibited by the system. The phase equilibria between vapour ( $V$ ) and isotropic liquid ( $L$ ) states determined with the isotropic



equation of state [cf. Equations (113), (114), and (115)] is seen at low and intermediate densities; as with other equations of state of the general van der Waals form, the vapour-liquid equilibrium is bounded at higher temperature by a critical point ( $T_c^* = 5.32$  and  $\eta_c = 0.105$ ). The coexistence region between isotropic liquid (L) and anisotropic nematic (N) states can be seen at higher densities (packing fractions of  $\sim 40\%$ ). In the high-temperature limit the thermodynamic properties of the system are dominated by the repulsive interactions, and the L-N transition rapidly tends to that of the hard-core system<sup>2</sup>, with limiting coexisting packing fractions of  $\eta_L = 0.406$  and  $\eta_N = 0.427$ . As the temperature is lowered the L-N region gets broader, which is in line with the well accepted view that even isotropic attractive interactions enhance the degree of alignment of the system and the first-order character of the phase transition (e.g., see References<sup>31,35,40,45,52,58,59,68,99</sup>). At sufficiently low temperatures, the L-N region merges into the vapour-liquid curve at the vapour-liquid-nematic (V-L-N) triple point corresponding to  $T_t^* = 3.31$ ,  $\eta_V = 0.001$ ,  $\eta_L = 0.351$  and  $\eta_N = 0.436$ . Below the triple-point temperature, only vapour-nematic (V-N) coexistence is seen. The L-N and V-N phase boundaries determined with the full numerical description of the Bessel function [cf. Equation (61) in Section III F] are compared with those determined with the algebraic expression [cf. Equation (100)] in Figure 2. It is very gratifying to see that the algebraic solution obtained from a truncated free-energy provides an essentially identical description to the full numerical solution of the configurational contributions as described with the Onsager trial function; only a very slight deviation in the density of the coexisting nematic state is found. In view of the positive endorsement of the accuracy of the algebraic description, this simplified form of the equation of state will be used exclusively from now on to describe the fluid phase equilibria of the other model systems.

The effect of varying the range of the isotropic attractive interaction ( $\epsilon_0 \neq 0$  and  $\epsilon_2 = 0$ ) for hard spherocylinders with a fixed length-to-breadth ratio of  $L/D = 5$  is now examined. The temperature-density projection of the fluid phase equilibria is shown in Figure 3 for attractive ranges of  $\lambda = 6, 10$  and  $15$ . The vapour-liquid phase equilibrium is much more sensitive to the range of the isotropic attractive interaction than the liquid-nematic coexistence. The vapour-liquid critical temperature is seen to rapidly increase with increasing range; a corresponding increase in the vapour-liquid-nematic triple point temperature is also found. The extent of the liquid-nematic coexistence does not vary much with the range of the attractive potential, though a slight shift in the coexistence boundaries to higher density is apparent. Does the phase behaviour of such a model conform to the van der Waals principle of corresponding states<sup>172</sup>? In order to answer this question we have replotted the fluid phase equilibria in terms of a temperature which is reduced in a van der Waals dimensionless form in terms of the inte-

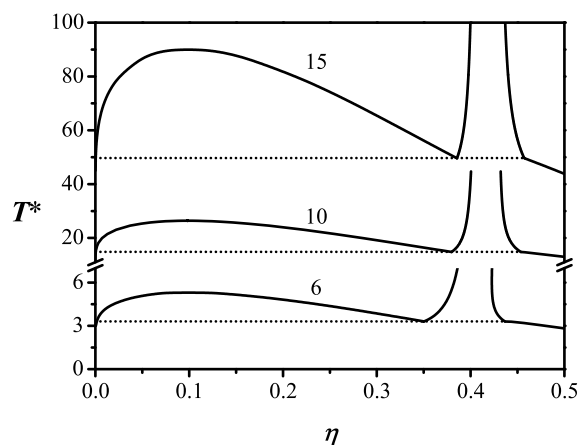


FIG. 3: The temperature-density fluid phase diagram ( $T^* = kT/\epsilon_0$  and  $\eta = \rho V_{HSC}$ ) for attractive hard spherocylinders with a length-to-breadth ratio of  $L/D = 5$  and a varying attractive range  $\lambda$  (denoted on the figure). Our generalised van der Waals – Onsager free energy functional is used to describe the system with the Onsager trial function [Equation (100)]. The dotted line corresponds to the vapour-liquid-nematic three phase coexistence.

grated attractive constant,  $T_{vdW}^* = kT/[\epsilon_0(\lambda^3 - 1)]$ . One can see from Figure 4, that as the range of the isotropic attraction is increased the vapour-liquid coexistence of the system converges onto a universal corresponding-states curve (also see the work by Williamson and Guevara<sup>96</sup>). This is expected as we are modelling the fluid phase equilibria with an augmented van der Waals equation of state; for large ranges of the attractive interactions one tends to the mean-field limit. More interestingly, the isotropic liquid-nematic (L-N) coexistence also appears to converge to a universal corresponding-states solution. The L-N coexistence region of the system with a range of  $\lambda = 6$  is seen to be shifted to lower densities, but those with  $\lambda = 10$  and  $15$  are almost indistinguishable. Though not apparent at the scale of Figure 4, the L-N coexistence densities of all of these systems approach the limiting values of the repulsive reference at sufficiently high temperatures (with corresponding packing fractions of  $\eta_L = 0.406$  and  $\eta_N = 0.427$ ). It is clear from these findings that the range of the attractive interactions does not qualitatively affect the type of fluid phase behaviour that is observed. Teixeira<sup>84</sup> has reported the possibility of an additional region of nematic-nematic coexistence when the range of the spherical-well is made significantly smaller than the aspect ratio of the particle, but this finding has been brought into question<sup>99</sup>. We should also add that solid-solid phase behaviour is possible for spherical molecules with very short ranged attractions<sup>173,174</sup>; a study of this type of behaviour is omitted from our current work as the focus is on nematic liquid-crystalline phases.



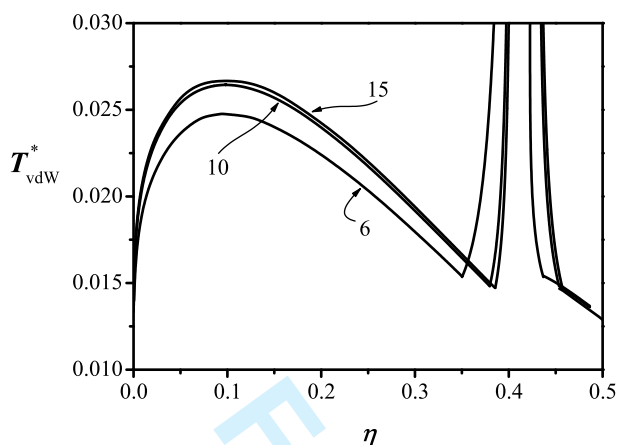


FIG. 4: Corresponding states representation of the temperature-density fluid phase diagram ( $T_{\text{vdW}}^* = kT / [\epsilon_0(\lambda^3 - 1)]$  and  $\eta = \rho V_{\text{HSC}}$ ) for attractive hard spherocylinders with a length-to-breadth ratio of  $L/D = 5$  and a varying attractive range  $\lambda$  (denoted on the figure). The generalised van der Waals - Onsager free energy functional is used to describe the system with the Onsager trial function [Equation (100)].

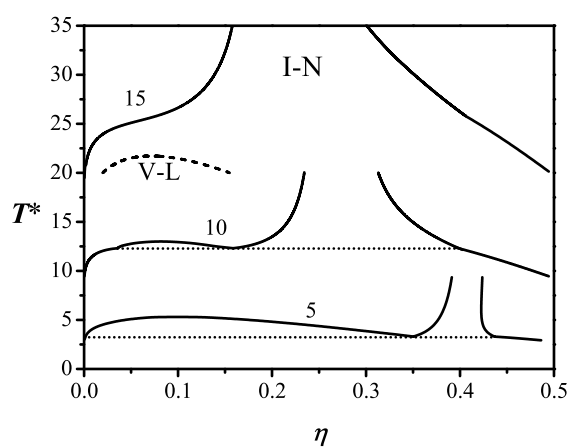


FIG. 5: The temperature-density fluid phase diagram ( $T^* = kT / \epsilon$  and  $\eta = \rho V_{\text{HSC}}$ ) for attractive hard spherocylinders of varying length-to-breadth ratio  $L/D$  (labelled on the figure) and attractive range  $\lambda = L/D + 1$ . The generalised van der Waals - Onsager free-energy functional is used to describe the system with the Onsager trial function [Equation (100)]. The dotted line corresponds to the vapour-liquid-nematic three-phase coexistence line. The vapour-liquid coexistence becomes metastable for large values of the aspect ratio (e.g., dashed curve  $L/D = 15$ ).

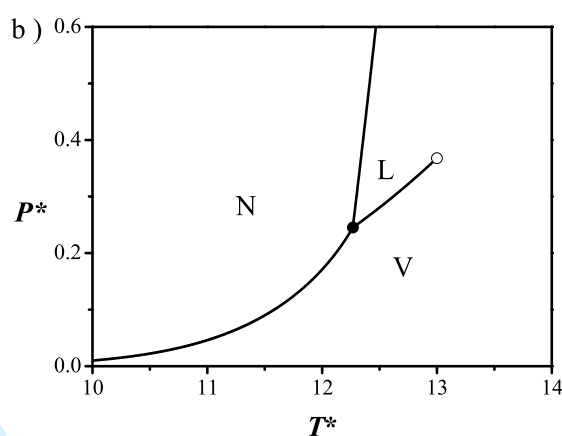
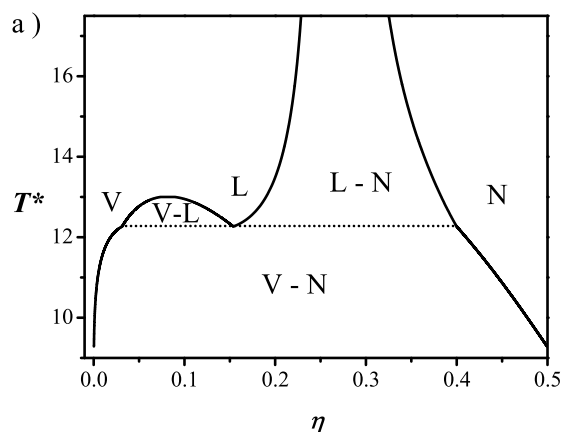


FIG. 6: (a) The temperature-density ( $T^* = kT / \epsilon_0$  and  $\eta = \rho V_{\text{HSC}}$ ), and (b) the corresponding pressure-temperature ( $P^* = PV_{\text{HSC}} / \epsilon_0$ ) fluid phase diagrams for attractive hard-spherocylinders with a length-to-breadth ratio of  $L/D = 10$  and an attractive range  $\lambda = L/D + 1 = 11$ . The generalised van der Waals - Onsager free-energy functional is used to describe the system with the Onsager trial function [Equation (100)]. The dotted line corresponds to the vapour-liquid-nematic three phase coexistence separating the vapour-liquid ( $V-L$ ), liquid-nematic ( $L-N$ ), and vapour-nematic ( $V-N$ ) regions.

We now examine the effect of varying the molecular length-to-breadth ratio  $L/D$  on the fluid phase behaviour of hard spherocylinders with enveloping isotropic square wells of range  $\lambda = L/D + 1$  (“square peg in a round hole” model<sup>68,70</sup>). Qualitatively different types of behaviour are exhibited by the system in this case depending on the asymmetry of the molecule. The effect of the aspect ratio on the fluid phase equilibria and orientational ordering for models of this type has already been investigated

in some detail (e.g., see References<sup>53,80,84,92,95,102</sup>). The findings obtained with Flory lattice models for solutions of rigid rod-like polymers<sup>109,116</sup> are also particularly relevant to our study because a direct analogy can be made between a solvent-rod mixture and a lattice-gas system of purely attractive rods in vacuum. Similarly, the work on models of ideal polymers and rod-like colloids<sup>73,175</sup> is relevant as the effect of the polymer components can be averaged out to provide the behaviour of pure rod-like molecules with effective attractions (Asakura-Oosawa depletion interactions).

The phase diagram of the system with  $L/D = 5$  and  $\lambda = 6$  is re-plotted in Figure 5 together with that of the longer molecule with  $L/D = 10$  and  $\lambda = 11$ . As expected the liquid-nematic region becomes much more extensive as the aspect ratio is increased: the vapour-liquid region is seen to have shrunk considerably with respect to that of the  $L/D = 5$  system (when measured relative to the triple point), while the liquid-nematic region covers a wide range of densities. There is also a corresponding increase in vapour-liquid-nematic triple-point temperature. Quantitatively, however, the phase behaviour of the models with  $L/D = 5$  and  $L/D = 10$  is the same. An enlargement of the fluid phase diagram and the corresponding pressure-temperature projection for the system with  $L/D = 10$  and  $\lambda = 11$  are shown in Figures 6 a) and b): the stable vapour, liquid, and nematic  $PT$  regions are clearly visible as are the V-L critical and the V-L-N triple points. Following the classification scheme of Varga *et al.*<sup>95</sup> this type of fluid phase behaviour is referred to as type I behaviour.

Flory and co-workers<sup>109,116</sup>, and Khokhlov and Semenov<sup>53</sup> showed early on that as the aspect ratio of the molecules is increased, there is a transition to a different type of fluid phase diagram, classified as type II behaviour<sup>95</sup>. Type II phase behaviour is exhibited by the system of  $L/D = 15$  hard-spherocylinders with an enveloping isotropic square well of range  $\lambda = 16$  as can be seen in Figure 5. In this case the vapour-nematic and liquid-nematic phase boundaries found for type I behaviour have merged into a single isotropic-nematic (I-N) region; the vapour-liquid coexistence curve is now metastable with respect to the I-N coexistence. As a consequence type II systems do not exhibit a vapour-liquid-nematic triple point. The existence of type II behaviour has been reported experimentally for solutions of the polypeptide polycarbobenzoxylysine (PCBL) in dimethylformamide (DMF)<sup>176</sup>, which can effectively be thought of as a pseudo one-component suspension of rod-like macro particles, and has now also been confirmed by simulation for a related model<sup>171</sup>.

We display the phase behaviour of molecules with large aspect ratios specifically in Figure 7. The systems of hard spherocylinders with a length-to-breadth ratio of  $L/D = 40$  and a attractive range of  $\lambda = 41$  are still seen to exhibit type II phase behaviour. As the aspect ratio is increased further a new region of nematic-nematic coexistence is found at densities above those of the I-N

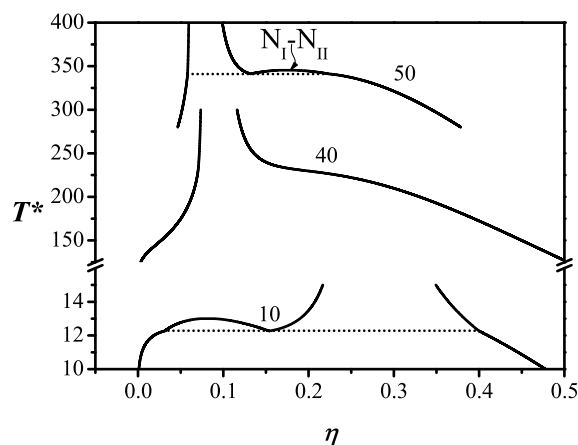


FIG. 7: The temperature-density fluid phase diagram ( $T^* = kT/\epsilon_0$  and  $\eta = \rho V_{HSC}$ ) for attractive hard spherocylinders of varying length-to-breadth ratio  $L/D$  (labelled on the figure) and attractive range  $\lambda = L/D + 1$ . The generalised van der Waals - Onsager free energy functional is used to describe the system with the Onsager trial function [Equation (100)]. For large aspect ratio above  $L/D \sim 45$  a new region of nematic-nematic ( $N_I$ - $N_{II}$ ) coexistence develops, and in this case the dotted line represents a vapour-nematic-nematic three-phase line.

boundary, as can be seen for the system with  $L/D = 50$  and  $\lambda = 51$  in Figure 7. A narrow V-N region is now found at relatively low densities at higher temperatures, and below a vapour-nematic-nematic triple-point temperature there is a relative broad region of V-N coexistence. This can be seen more clearly in the enlarged representation of the temperature-density phase diagram shown in Figure 8 a). The corresponding pressure-temperature projection for this system is given in Figure 8 b): in this case the N-N coexistence is bounded by the N-N critical and the V-N-N triple points. This type of nematic-nematic coexistence, classified by Varga *et al.*<sup>95</sup> as type III behaviour, was already predicted in the early lattice calculations solutions of rigid polymers by Flory and co-workers<sup>109,116</sup>). In their very interesting paper, Khokhlov and Semenov<sup>53</sup> re-examined this type of N-N behaviour using an Onsager-like theory for a system of pure rods with attractive interactions, showing the transitions between type I, II, and III phase behaviour with increasing molecular aspect ratio. We should also mention that coexistence between nematic phases has also been found in mixtures of hard rods of different length or thickness (e.g., see References<sup>158-160,177-182</sup>). It is pleasing to see that our simple algebraic equation of state (obtained from a generalised van der Waals - Onsager free energy with a cubic solution of the orientational parameter) also predicts the three possible types of fluid phase behaviour exhibited by such systems.

Type III behaviour with the characteristic feature of

coexistence between two nematic phases has been identified in solutions of the polypeptide poly( $\gamma$ -benzyl-L-glutamate) (PBLG) in DMF<sup>176,183</sup> or benzyl alcohol<sup>184</sup>, and in aqueous solutions of the rod-like polysaccharide schizophyllan<sup>185,186</sup>. Interestingly, the complete phase diagram obtained for PBLG rods (with a molecular weight of 310,000 g/mol) dispersed in DMF<sup>176</sup> is qualitatively very similar to the type III behaviour shown in 8 a); the apparent aspect ratio of the PBLG rods<sup>176</sup> is expected to be somewhere between 50 and 130 which is above the threshold of  $\sim 45$  where we predict the transition from type II to III. We should note in this case that the PBLG rods form cholesteric (chiral nematic) phases<sup>187,188</sup>, though the difference in free energy between the nematic and cholesteric states (and as a consequence the main features of the fluid phase behaviour) are expected to be very small<sup>108</sup>.

In the last part of our work we focus on the effect of including anisotropic attractive interactions on the fluid phase behaviour of such systems. The model in question is a hard spherocylinder with both isotropic and anisotropic ( $\epsilon_0 \neq 0$  and  $\epsilon_2 \neq 0$ ) square-well interactions of range  $\lambda = L/D + 1$  (see Section III D). As with the studies of Gelbart<sup>30-33,33</sup>, Cotter<sup>35-41</sup>, and Vertogen<sup>42-47</sup> and Telo da Gama<sup>52,80</sup> and co-workers, the anisotropic interaction is assumed to be of the Maier-Saupe (second Legendre polynomial) form. It is now convenient to introduce an additional reduced parameter  $\epsilon^* = \epsilon_2/\epsilon_0$  to characterise the strength of the anisotropic interaction relative to the isotropic interaction; a value of  $\epsilon^* = 0$  would correspond to the systems studied earlier in this section.

The temperature-density projection of the fluid phase behaviour for  $L/D = 5$  hard spherocylinders with isotropic and anisotropic square-well interactions of range  $\lambda = 6$  is depicted for different values of the relative strength  $\epsilon^*$  in Figure 9. As expected the introduction of the anisotropic attractive interactions of the Maier-Saupe form enhances the propensity of the system to form orientationally ordered states. The liquid-nematic region broadens significantly as  $\epsilon^*$  is increased, while the vapour-liquid coexistence curve remains unaltered (in an isotropic phase the orientational average of the Maier-Saupe attractive interaction is zero). As a consequence, the vapour-liquid-nematic triple point is seen to increase. For sufficiently large anisotropies in the attractions (above  $\epsilon^* \sim 0.25$ ), the vapour-liquid region becomes metastable relative to the isotropic-nematic region. This type of behaviour was also reported by Telo da Gama<sup>52</sup> for hard spheres with isotropic and anisotropic (Maier-Saupe) attractions of the Lennard-Jones form, where the orientational ordering is driven solely by the attractive interactions. In the case of our square-well hard-spherocylinder model, anisotropies in both the repulsive (molecular shape) and attractive interactions stabilise the formation of the liquid-crystalline states. In contrast to the hard-sphere Maier-Saupe model of Telo da Gama, our attractive rods still exhibit orientationally ordered

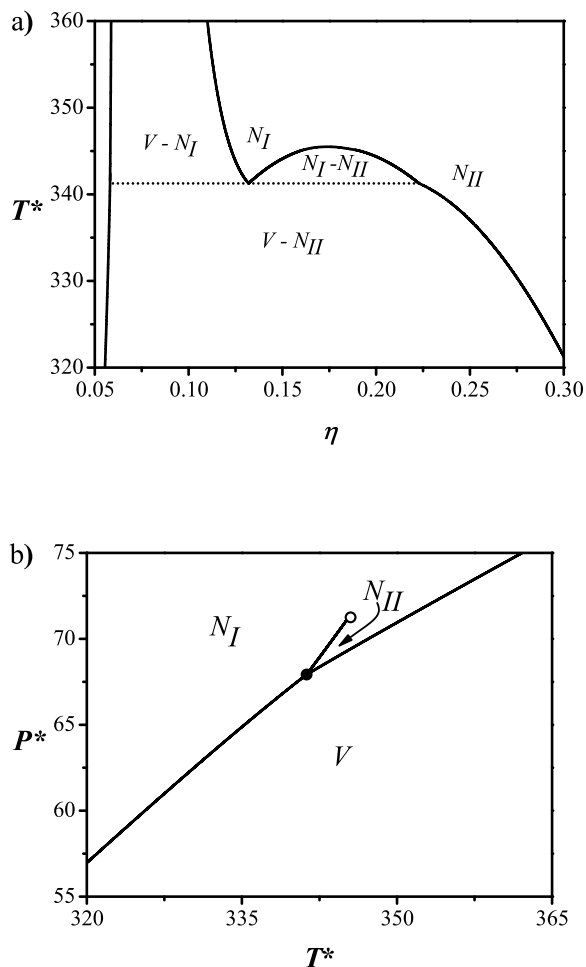


FIG. 8: (a) The temperature-density ( $T^* = kT/\epsilon_0$  and  $\eta = \rho V_{HSC}$ ), and (b) the corresponding pressure-temperature ( $P^* = PV_{HSC}/\epsilon_0$ ) fluid phase diagrams for attractive hard-spherocylinders with a length-to-breadth ratio of  $L/D = 50$  and an attractive range of  $\lambda = L/D + 1 = 11$ . The generalised van der Waals - Onsager free-energy functional is used to describe the system with the Onsager trial function [Equation (100)]. In this case the dotted line corresponds to a new coexistence three-phase line corresponding to a vapour-nematic-nematic equilibria.

states at high temperature as the system approaches the limiting behaviour of the repulsive hard-core fluid. Furthermore, the slope of the liquid-nematic coexistence densities with temperature found for the spherical models (see Figure 3 in Reference<sup>52</sup>) is much less marked than that depicted in Figure 9, and the L-N coexistence densities of the Maier-Saupe spheres are seen to rapidly extend into the region where one would expect solid phases to be stable.

The separate effect on the fluid phase behaviour of changing the anisotropy in the molecular shape for a

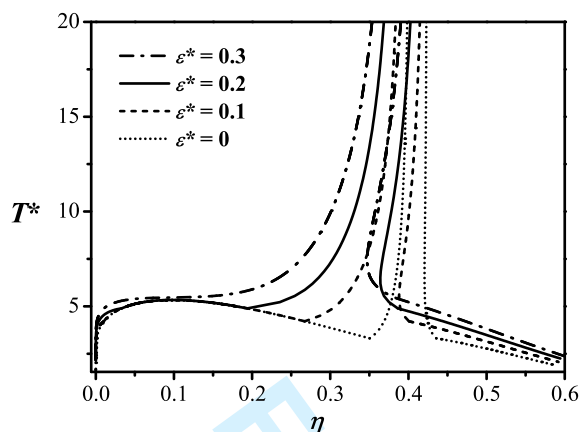


FIG. 9: The temperature-density fluid phase diagram ( $T^* = kT/\epsilon_0$  and  $\eta = \rho V_{HSC}$ ) for hard spherocylinders of length-to-breadth ratio  $L/D = 5$  with isotropic ( $\epsilon_0$ ) and anisotropic ( $\epsilon_2$ ) attractive interactions of range  $\lambda = 6$ . The types of phase diagrams obtained for different values of the relative attractive strength  $\epsilon^* = \epsilon_2/\epsilon_0$  (denoted on the figure) are shown. The generalised van der Waals - Onsager free-energy functional is used to describe the system with the Onsager trial function [Equation (100)]. The difference between Onsager-like ( $\epsilon^* = 0$ ) and Maier-Saupe-like ( $\epsilon^* > 0$ ) phase behaviour can be seen.

fixed anisotropy in the attractive interactions is shown in Figure 10. We examine hard spherocylinders of varying aspect ratio with isotropic and anisotropic square-well interactions of relative strength  $\epsilon^* = \epsilon_2/\epsilon_0 = 0.3$ , but now for an attractive range described by  $\lambda = L/D + 1.5$ . This choice will enable us to include the important limiting system corresponding to spherical molecules ( $L/D = 0$ ) with square-well interactions of range  $\lambda = 1.5$ . This model is equivalent to the Lennard-Jonesium system examined by Telo da Gama<sup>52</sup> at the level of the mean-field theory employed in both of our studies. It is evident from Figure 10 that the system of attracting hard-spherocylinders with  $L/D = 5$ ,  $\epsilon^* = 0.3$  and  $\lambda = 6.5$  exhibits only isotropic-nematic phase equilibria; the vapour-liquid coexistence is metastable in this case. When the length-to-breadth ratio is reduced to  $L/D = 4$  (with a corresponding decrease in the square-well range to  $\lambda = 5.5$ ), the vapour-liquid coexistence becomes stable, and separate liquid-nematic and vapour-nematic regions are seen. As expected the isotropic states are stabilised with respect to the anisotropic states as the aspect ratio is decreased: the density of the nematic phase at the V-L-N triple point is seen to increase with decreasing  $L/D$ , the first-order character of L-N transition decreases, and the slope of the L-N coexistence boundaries with temperature decreases markedly. In the case of hard spheres with isotropic and anisotropic square-well attractions of relative strength  $\epsilon^* = 0.3$  and range

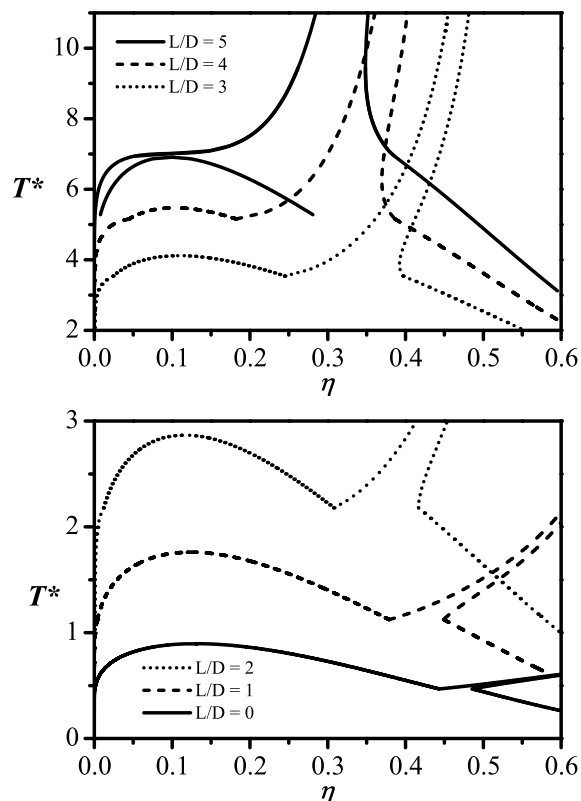


FIG. 10: The temperature-density fluid phase diagram ( $T^* = kT/\epsilon_0$  and  $\eta = \rho V_{HSC}$ ) for hard spherocylinders of varying length-to-breadth ratio  $L/D$  (denoted on the figure) with isotropic and anisotropic attractive interactions of relative strength  $\epsilon^* = \epsilon_2/\epsilon_0 = 0.3$  and range  $\lambda = L/D + 1.5$ . The generalised van der Waals - Onsager free-energy functional is used to describe the system with the Onsager trial function [Equation (100)].

$\lambda = 1.5$ , the L-N transition is weakly first order, and the nematic states are stable only for packing fractions above about  $\sim 50\%$ , where positionally ordered phases are expected to be stable. The phase diagram for the spherical system with  $L/D = 0$  is essentially same as the Lennard-Jonesium-Maier-Saupe model of Telo da Gama<sup>52</sup> when examined in terms of the appropriate reduced variables; the marked temperature dependence of the liquid and nematic densities at coexistence becomes apparent from Figure 10.

The reduced pressure-temperature projection of the fluid phase behaviour for the hard spherocylinders of varying length-to-breadth ratio  $L/D$  with isotropic and anisotropic square-well attractions of relative strength  $\epsilon^* = 0.3$  and range  $\lambda = L/D + 1$  are shown in Figure 11. Separate V-L, L-N and V-N boundaries are seen for the systems with  $L/D = 0$  to 4, while a continuous I-N curve is seen for  $L/D = 5$ . The L-N boundary is found to be very steep as expected from a Clausius relation



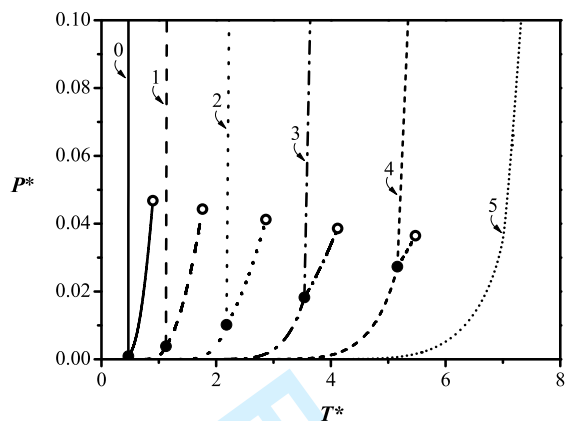


FIG. 11: The pressure-temperature fluid phase diagram ( $P^* = P V_{\text{HSC}}/\epsilon_0$  and  $T^* = kT/\epsilon_0$ ) for hard spherocylinders of varying length-to-breadth ratio  $L/D$  (denoted on the figure) with isotropic and anisotropic attractive interactions of relative strength  $\epsilon^* = \epsilon_2/\epsilon_0 = 0.3$  and range  $\lambda = L/D + 1.5$ . The generalised van der Waals - Onsager free-energy functional is used to describe the system with the Onsager trial function [Equation (100)].

for transitions with a small change in density<sup>172</sup>. The critical temperature is seen to increase rapidly with increasing aspect ratio, while the critical pressure remains relatively insensitive to changes in the aspect ratio. On the other hand, the pressure and temperature of the V-L-N triple point both increase noticeably as the anisotropy in the molecular shape is increased. For sufficiently large anisotropies the triple and critical points merge and only I-N phase behaviour is found (e.g., see the system with  $L/D = 5$ ). An important practical implication of using a model such as the one that is proposed here is that one can easily control the slopes of the  $P - T$  boundaries by varying the molecular shape and/or the anisotropy in the attractive interactions. This turns out to be particularly useful in controlling the form of the temperature dependence of the order parameter  $S_2$ .

We have analysed the temperature dependence of  $S_2$  at a fixed pressure ( $P^* = P V_{\text{HSC}}/\epsilon_0 = 0.1$ ) for the systems of  $L/D$  hard spherocylinders with a fixed relative strength of anisotropic and isotropic attractions of  $\epsilon^* = 0.3$  and a range  $\lambda = L/D + 1.5$ . The effect of changing the molecular aspect ratio on the temperature dependence of the degree of orientational order obtained with the algebraic equation of state [cf. Equation (100)] is apparent from Figure 12. The slope of the curves can be controlled by varying the molecular shape, a clear advantage from the original Maier-Saupe model. The same effect can be found if the strength of the anisotropic attraction is varied, providing a means of describing the temperature dependence of the order parameter found in different mesogenic systems. This will allow one to deter-

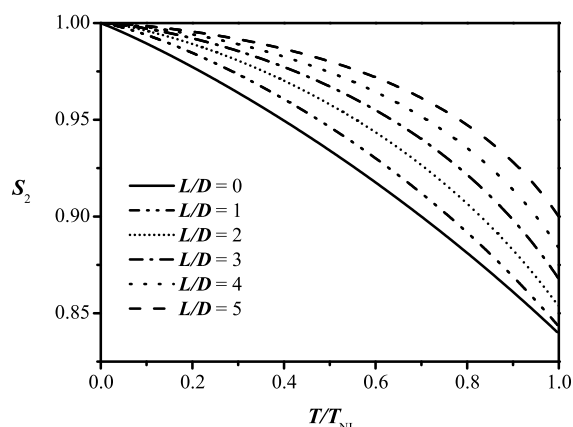


FIG. 12: The nematic order parameter  $S_2$  as a function of the temperature relative to that of the I-N transition ( $T_{\text{NI}}$ ) for hard spherocylinders of varying length-to-breadth ratio  $L/D$  (denoted on the figure) with isotropic and anisotropic attractive interactions of relative strength  $\epsilon^* = \epsilon_2/\epsilon_0 = 0.3$  and range  $\lambda = L/D + 1.5$ . The generalised van der Waals - Onsager free-energy functional is used to describe the system with the Onsager trial function [Equation (100)]. The calculations are for a fixed pressure of  $P^* = P V_{\text{HSC}}/\epsilon_0 = 0.1$ , which corresponding to a relatively high pressure state (cf. Figure 11).

mine the optimal set of molecular parameters (e.g.,  $L/D$  and  $\epsilon^*$ ) for a given system in a relatively straightforward manner.

## V. CONCLUSIONS

We consider the main achievement of this study to be the development of an algebraic theory that includes the effect of isotropic and anisotropic attractive interactions as well as molecular shape. It is recognised that anisotropic phases may appear as a consequence of only the competition between the repulsive entropic contributions as confirmed by molecular simulation<sup>21-25</sup>. Nonetheless, in order to model real thermotropic mesogens the effect of dispersive forces cannot be neglected and its contribution to the development and stabilisation of the anisotropic phase should be thoroughly studied. This is certainly facilitated if one has a reliable, theoretically well-founded and easy-to-use equation of state at hand. A free energy of closed analytical form in terms of the Onsager orientational parameter  $\alpha$  is provided for systems with nematic ordering. The algebraic solution of the equilibrium value  $\alpha_{\text{eq}}$  given through a cubic polynomial represents a real advantage, since it leads to an algebraic expression for the generalised Onsager free energy, and correspondingly any other thermodynamic function. In essence, this algebraic equation of state corresponds to



a extension of a van der Waals treatment of fluid phase behaviour to systems exhibiting orientational order; the determination of the isotropic-nematic (vapour-nematic and liquid-nematic) with our approach is no more difficult than obtaining vapour-liquid phase behaviour using van der Waals-like equations of state to describe isotropic fluids.

The adequacy of our algebraic equation of state is assessed by determining the phase equilibria of systems comprising square-well hard spherocylinders, and comparing it with that obtained from a numerical solution of the generalised Onsager free energy, where the configurational functionals are evaluated in terms of modified Bessel functions  $I_\nu(2\alpha)$  of the orientational parameter  $\alpha$ . It is confirmed that the approximate solution (cubic expression for  $\alpha$ ) of the model provides a description which is certainly in good agreement with the numerical evaluation of the Bessel functions. It is also very rewarding to observe that with the algebraic equation of state in  $\alpha$  one obtains a qualitatively (and in most cases quantitatively) correct description of the different classes of phase diagram that have been described in systems of this type with fully numerical approaches (see for example references<sup>84,94,95</sup>); in the latter the contributions to the free energy, which are functionals of the orientational distribution function  $f(\vec{\omega})$ , were evaluated using (essentially exact) numerical methods.

Finally, we would like to emphasise the generality of the method and the ease of implementation when more-complex anisotropic forms of attractive interactions are

required to accurately describe the phase behaviour of real liquid crystals. In Section III F we laid out a set of expressions that can easily be added to the description when the attractive interactions contain higher-order Legendre contributions, such as the spherical harmonic expansion of the anisotropic pair potential first proposed by Pople<sup>134</sup>. The methodology developed here can be extended to enable a quantitative treatment of real mesogenic systems by coupling it with an accurate description of the isotropic phase such as that provided by the statistical associating fluid theory (SAFT)<sup>189–192</sup>.

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