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A generalisation of the Onsager trial-function approach: Describing nematic liquid crystals with an algebraic equation of state.

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The molecular theory of Onsager [L. Onsager, *Ann. N.Y. Acad. Sci.* **51**, 627 (1949)] for liquid crystals is developed and extended to describe ordering transitions in systems of generic cylindrically symmetrical molecules. A number of new analytical results are discussed for particles characterised by a general form of the excluded-volume interaction. Our description makes use of the Onsager trial function (OTF) to represent the orientational distribution and degree of anisotropy. Algebraic expressions for the thermodynamic properties, which provide a particularly tractable description of the isotropic-nematic equilibria, are also presented. The degree of orientational order can be represented by a simple cubic equation in the molecular parameters (molecular diameter and aspect ratio) and thermodynamic variables (temperature and number density). Onsager's theory was originally developed at the level of the second virial coefficient; here the Parsons-Lee decoupling approximation is used to describe the higher body contributions in a straightforward manner. The adequacy of treating the scaled Onsager (Parsons-Lee) free-energy functional within the OTF formalism to describe anisotropic states is illustrated by examining systems of hard spherocylinders. An excellent representation of the equation of state of the isotropic and nematic phases and the ordering transition is demonstrated for molecules of moderate aspect ratio ($L/D = 5$). Algebraic equations of state of the type developed here are suitable for practical engineering applications involving anisotropic fluids particularly in the case of multicomponent systems; our general analytical results for the averages of orientational functions will turn out to be useful in the development of a description of molecules with more realistic attractive and Maier-Saupe interactions.

Keywords: Onsager trial function, Onsager free energy, mean-field theory, Landau-de Gennes theory, liquid crystals, mesogens, nematics, cholesterics, cubic equations of state, fluid phase equilibria.

I. INTRODUCTION

The simplest liquid crystal phase is the nematic, in which the constituent molecules (mesogens) are distributed uniformly within the sample (there is no long-range positional order and the phase is homogeneous as for an isotropic liquid) while there is a degree of orientational order whereby the molecules tend to align along a preferred direction (the director). The nematic state is therefore anisotropic and possesses long-range (macroscopic) orientational order [1–3]. A wide variety of low molecular weight organic compounds are found to exhibit liquid crystalline phases (e.g., the reader is directed to the book by Chandrasekhar [1] and a compilation dedicated to nematics [4]); these compounds tend to be referred to as thermotropic liquid crystals owing to the leading role that temperature plays as a variable in the transformations between the various states. Liquid crystal phases are also found with solutions of amphiphilic molecules, and in dispersions of higher molecular weight molecules such as polymers, and colloidal suspensions of inorganic and biological particles (e.g., cellulose, V_2O_5 , DNA, and viruses).

The unique thermodynamic, structural, rheological, and optical properties of liquid crystalline materials make

them suitable for a wide range of applications [1–3]. Since the first electronic calculators with a liquid crystal display (LCD) came on to the market in the early 1980s, systems comprising liquid crystal molecules (mesogens) have increasingly been used for the development of new devices in the opto-electronic industry (from standard LCDs, mobile handsets, laptops, to the now ubiquitous flat screen televisions). Liquid crystalline materials are also widespread in the formulation of cosmetics, food products, and pharmaceuticals, and form part of the biological structures such as DNA and cell membranes that are essential to life itself. There is thus a clear need for a fundamental understanding and accurate theoretical description of the physical properties of such systems.

There is a vast body of work on the development of molecular theories for liquid crystals and associated computer simulation studies which has been collected and discussed from various perspectives in review literature [1, 2, 5–15]. It is not our intention here to go through the different approaches in any detail but to highlight features which are relevant to our study. The most commonly used macroscopic theory of liquid crystals is the phenomenological approach of Landau and de Gennes [2, 16–19] in which the free energy of the system is expressed as appropriate contributions in powers of the order parameters (which characterise the degree of anisotropy) and their gradients, chosen according to the symmetry of the phase; the prefactors of each term are treated as adjustable parameters to be determined

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1 from experimental information. The approach certainly
2 has physical appeal, is mathematically tractable, and can
3 easily be extended and generalised to broad classes of
4 phase transitions. The main drawback of this type of
5 macroscopic treatment is that it does not provide a pre-
6 dictive capability as one can not make a direct link be-
7 tween the molecular interactions and the parameters in
8 the theory which characterise the properties of the ma-
9 terial.

10
11 In the development of molecular theories of liquid crys-
12 talline fluids there are, broadly speaking, two seemingly
13 opposing views. One has its roots the early suggestion by
14 Born [20, 21] that dipolar (attractive) interactions are re-
15 sponsible for the anisotropy in liquid crystalline phases.
16 Born was the first to apply the mean-field approxima-
17 tion to the isotropic-nematic (I-N) transition, although
18 within his approach the anisotropic phase is ferroelec-
19 tric, the experimental confirmation of which is inconclu-
20 sive. In their mean-field treatment, Maier and Saupe [22–
21 24] also make the assumption that orientationally de-
22 pendent attractive interactions are the molecular feature
23 that give rise to liquid crystalline order. The Maier-
24 Saupe approach and its extensions [1, 6, 25–28], now re-
25 present a very popular mean-field treatment of anisotropic
26 phases. The analytical description of the order param-
27 eter (but not the free energy) within the Maier-Saupe
28 theory means that this has been the method of choice
29 for comparison/correlation with experiment. It is clear
30 from the rich variety of phase behaviour exhibited by
31 thermotropic mesogens [4] that the specific features of
32 the attractive interactions play an important role in de-
33 termining the types of liquid crystalline phases that are
34 observed. The relationship between dipolar interactions
35 and the stabilisation of anisotropic phases has been ex-
36 amined in detailed computer simulation studies of model
37 dipolar rod-like molecules, where the isotropic-nematic
38 and nematic-smectic A (layering) phase transitions are
39 found to be very sensitive to the position and orientation
40 of the dipole within the molecular core [29–32]. Though
41 mesogenic molecules often possess flexible side chains and
42 groups which mediate anisotropic attractive interactions
43 (such as the $\pi - \pi$ interactions between phenyl cores,
44 dipole-dipole interactions, and hydrogen bonding) that
45 affect the stability of the anisotropic phase, it is now
46 widely accepted that shape anisotropy (a rigid nonspher-
47 ical core) is the molecular attribute that is primarily re-
48 sponsible for the formation of liquid crystals. The ne-
49 glect of anisotropy in the shape of the molecules (which
50 give rise to anisotropic repulsive interactions) is the main
51 criticism often directed at the Maier-Saupe theory [33].
52 As is well known, the structure of isotropic fluid phases
53 is dominated by the repulsive forces between molecules,
54 and a description of the thermophysical properties of a
55 repulsive reference fluid is at the heart of the develop-
56 ment of perturbative approaches for fluids of molecules
57 with attractive interactions [34, 35]. The treatment of re-
58 pulsive interactions as the key feature in the description
59 liquid crystalline fluids leads to the alternative approach

originally due to Onsager [36, 37].

One of the major driving forces behind the formation
of anisotropic phases is the reduction of the excluded vol-
ume (repulsive interactions) between pair of particles: at
higher densities when the particles are (on average) closer
to each other, the rigid molecular cores align in order to
increase the free volume, and the gain in entropy from
the increase in accessible volume more than compensates
for the loss of orientational disorder. The idea that the
isotropic-nematic transition is entropically driven is the
basic one that Onsager introduced [36] and developed [37]
in his seminal papers of the 1940s. By 1957 Alder and
Wainwright [38] had already highlighted the importance
of entropy in ordering transitions by showing that a sys-
tem of purely repulsive spheres can form a solid phase,
without the need to invoke attractive interactions. Sur-
prisingly, one had to wait more than a third of a century
for Onsager's clairvoyant hypothesis of the entropic role
in liquid crystalline ordering to be confirmed by the es-
sentially exact findings of molecular simulation. Contin-
uum simulation studies of hard disks [39, 40], ellipsoids of
revolution [41, 42] and hard spherocylinders [11, 43–45]
support the fact that repulsive interactions alone are suf-
ficient to stabilise an orientationally ordered (nematic)
state, and additionally, in the case of hard disks and
hard spherocylinders, positionally ordered columnar and
smectic A states, respectively. One should note that sim-
ulations of ordering transitions in lattice models had been
reported earlier (see the work of Lebwohl and Lasher [46]
for particles on a cubic lattice interacting via a Maier-
Saupe attractive term, and Chapter 9 of reference [6]);
these lattice models artificially omit the essential fluid
nature of the structure of liquid crystals, and hence can
not be used to explore the nature of the stabilisation of
anisotropic phases in a conclusive manner.

Onsager [37] constructed a free energy for the nematic
phase (at the level of the second virial coefficient) as a
functional of the single-particle orientational distribution
function $f(\theta)$, which is proportional to the probability
that the principal axes of the molecules are at an an-
gle θ relative to the nematic director. In the case of an
isotropic liquid $f(\theta)$ is a constant and the molecules do
not point in a preferred direction but are randomly ori-
ented. The theory of Onsager can be considered as one
of the first classical density functional theories (DFTs)
of the fluid state; the earliest DFT of all is arguably
the square-gradient approach of van der Waals [47] for
the vapour-liquid interface in which the free energy is
a functional of the now inhomogeneous number density
 $\rho(\vec{r})$. The precise equilibrium form of the orientational
distribution function that corresponds to the minimum
of the Onsager free-energy functional can be obtained by
numerically determining the coefficients of a series ex-
pansion [48–52], by direct iteration [53, 54], or by Monte
Carlo annealing [55].

In his original theory, Onsager [37] truncated the free
energy at the level of the second virial coefficient. This
limits the applicability to the low-density region; as the

1 aspect ratio of the rod-like particles increases, the system
2 will exhibit an isotropic-nematic at progressively lower
3 densities so the Onsager second-virial approach is exact
4 in the limit of infinitely long and thin particles. A num-
5 ber of alternative approaches are available to incorpo-
6 rate the effect of higher-body contributions (which are
7 important for molecules with more moderate aspect ra-
8 tios) in an Onsager-like treatment: higher virial coeffi-
9 cients can be included in the density series of the free
10 energy (often represented as a Padé approximant) [56–
11 60]; the Onsager free energy can be reformulated as a
12 scaled-particle theory [49, 61–63]; more-rigorous integral
13 equation and density functional approaches can be used
14 (see for example [10, 12, 64–80]); scaling arguments and
15 the decoupling approximation can be employed to ex-
16 press the free energy of the system in terms of that of
17 an effective hard-sphere system (or of an isotropic fluid
18 of the non-spherical particles) [81–84]. In our work we
19 opt for a decoupling approximation of this type, as these
20 have been shown to provide a very accurate representa-
21 tion of the isotropic-nematic transition for hard-core par-
22 ticles of moderate size asymmetry (e.g., [11, 42]); further
23 details of the methodology are presented in the follow-
24 ing section. Related theories for repulsive lattice mod-
25 els [7, 85–87], for models with restricted orientations [88],
26 and for semi-flexible liquid crystalline polymers [89–91]
27 are also in common use. It is not possible to mention
28 all of the applications and extensions of the Onsager the-
29 ory for liquid crystals here; to date of publication there
30 are over two thousand citations to Onsager’s 1949 pa-
31 per since 1970, and the approach is still very popular.
32 Recent examples of studies which make use of his un-
33 derlying treatment of anisotropic phases include an ex-
34 amination of: worm-like polymers confined between nar-
35 row slits [92]; layering transitions in systems of charged
36 rods [93]; phase separation in mixtures of mesogenic par-
37 ticle particles [94, 95]; inhomogeneous systems of disk-
38 like particles [96, 97]; confined DNA in ionic media [98];
39 chirality in biological suspensions [99, 100]; the addition
40 of polymer to suspensions of rod-like particles [101]; the
41 cholesteric-smectic transition of viral suspensions [102];
42 and of the original Onsager expressions for the excluded
43 volume of hard cylinders [103]. It is clear from an inspec-
44 tion of this short selection of papers that the Onsager
45 theory of liquid crystals is applicable to an astonishingly
46 broad variety of systems.

47 The main theme of our study concerns the use of the
48 Onsager trial function $f_{\text{OTF}}(\theta)$ (OTF) to represent the
49 single-particle orientational distribution function. The
50 last three (concise) pages of Onsager’s long paper [37]
51 are dedicated to the use of a single-parameter hyperbolic
52 trial function to develop an analytical representation of
53 the free energy for the nematic phase of hard rod-like par-
54 ticles. Considering the large number of studies that have
55 made use of the generic form of the Onsager free-energy
56 functional for anisotropic phases, it is surprising that his
57 trial function has been employed far less frequently (see,
58 for example, references [52, 104–119]). As far as we are

aware only the explicit analytical forms of the free en-
ergy derived by Onsager for the leading term of the sec-
ond virial coefficient of rod-like particles have been used
thus far; no attempt has been made to generalise the
treatment to more complicated mathematical forms of
the excluded volume. One should note that other related
trial functions of the Gaussian form have also been em-
ployed to provide analytical forms of the free energy to
determine the phase behaviour of a variety of anisotropic
fluids and mixtures (e.g., [84, 91, 120–136]). Though the
use of Gaussian trial functions (GTFs) leads to a sim-
pler algebraic treatment, the resulting expressions for the
free energy generally provide a less adequate description
of the free energy and ordering phase transitions than
those obtained with the OTF. In some cases qualitative
differences in the types of phase behaviour are seen when
compared with the full numerical solution particularly for
mixtures (see the studies on mixtures of rod and disk-like
particles [137–140]). The simple model of Zwanzig [88]
(in which only the three cartesian orientations of the ori-
entational distribution function are considered) have also
found popular use owing to the tractable nature of the
free energy [141–154]. As a final remark on the general
use of trial functions, one should mention that in addition
to being a useful ingredient in providing a representation
of the thermodynamic properties of the isotropic-nematic
transition, the Onsager, Gaussian and related trial func-
tions have been used to analyse and describe the degree of
orientational order determined experimentally [155–160].

In the current work we aim to develop an equation
of state for nematic fluids that is suitable for the intensive
calculations routinely required in engineering applica-
tions. To this end, the specific question we shall answer
is: Can one use Onsager’s trial function to obtain accu-
rate yet analytical expressions for the free energy in the
case of a general form of the excluded volume (not just
the extreme aspect ratio limit examined by Onsager)?
An accurate analytical description of the thermodynamic
properties of hard anisotropic fluids is the key to the
development of a perturbative platform for an algebraic
equation of state of real mesogens (treating both attrac-
tive and repulsive interactions). This would certainly
enhance the general applicability of the Onsager trial-
function approach for anisotropic order.

An updated view of the derivation of Onsager’s free-
energy functionals is given in Section II. In this paper
we focus on model systems of nematogens with purely
repulsive potentials. In Section II A we take as a starting
point the second-virial theory originally proposed by On-
sager [37]. Later in Section II B we review how Onsager’s
theory can be extended by means of the decoupling ap-
proximation due to Parsons and Lee [81–83] to account
for higher virial-coefficients. The seminal Appendix B of
Onsager [37], in which he introduces his trial function,
is rather difficult to follow, which probably explains why
the OFT approach has not found a more widespread use
even though (as we will show) it is well suited to describe
orientationally ordered systems with a high degree of ac-

curacy. Particular effort is taken to shed light on the separate contributions to the free energy (Section II C) when the orientational distribution is described with the OTF: an *orientational entropy* term (Section II E), which can be seen as an entropy of mixing when one assumes that every particle with any given orientation represents a different species in the fluid; and a term which is proportional to the second virial coefficient B_2 , which can be seen as a packing or *configurational entropy* as it accounts for the volume restricted to the centre of any given molecule within the fluid due to the presence of a second (Section II F). We examine the form these functionals take when using the OTF for a general excluded volume interaction. In Section II G we compare the use of the OTF and a full numerical solution of the equilibrium free energy to locate the I-N transition for a fluid of hard spherocylinders. We then show in Section IV how a comparatively accurate, but compact cubic representation of the orientational order can be formulated. We point out that our approach is very general and can be used to describe systems with generic excluded volume interactions and orientationally dependent attractive interactions. The method described by Onsager [37] for the evaluation of the configurational functional is applied more generally to evaluate other angle averages of similar (mathematical) form. This is illustrated in Section III by showing how our approach can be used to provide closed-form expressions for the order parameters, S_n , which when applied to the nematic order parameter S_2 concurs with the expression commonly obtained via the addition theorem for spherical harmonics [108, 161].

II. ONSAGER MOLECULAR THEORY OF THE NEMATIC FLUID

A. Onsager Free Energy (Second Virial Theory)

The first term of the Onsager [37] free-energy functional for the nematic phase represents the ideal free energy of orientationally ordered rod-like particles, including the contributions due to the translational and rotational entropy. Onsager obtained an expression for the rotational entropy by considering each orientation of the particle as a separate component in a mixture.

The ideal part of the Helmholtz free energy of an inhomogeneous system of spherically symmetric molecules is given by [35]

$$A_{\text{sph}}^{\text{id}} = kT \int \rho(\vec{r}) \{ \ln \mathcal{V}_{\text{sph}} \rho(\vec{r}) - 1 \} d\vec{r}, \quad (1)$$

which is expressed as a functional of $\rho(\vec{r})$, the single-particle number density at position \vec{r} , which is normalised such that $\int \rho(\vec{r}) d\vec{r} = N$, the total number of particles; T is the temperature and k is the Boltzmann constant. The de Broglie volume \mathcal{V}_{sph} is defined in terms of the thermal de Broglie wavelength, $\Lambda = \sqrt{h^2/(2\pi mkT)}$, where m

is the molecular mass and h is the Planck constant, so that, in Equation (1) $\mathcal{V}_{\text{sph}} = \Lambda^3$, which arises from the partition function of a system of spherical particles that has only translational contributions.

The partition function for a system of non-spherical particles also contains rotational contributions [162]. The de Broglie volume in the ideal free energy for non-spherically symmetric particles is denoted by \mathcal{V} . Further, the density ρ becomes a function not only of position but also of orientation $\vec{\omega}$. The analogue of Equation (1) for non-spherical molecules is then written as an integral over position and orientation:

$$A^{\text{id}} = kT \int \rho(\vec{r}, \vec{\omega}) \{ \ln \mathcal{V} \rho(\vec{r}, \vec{\omega}) - 1 \} d\vec{r} d\vec{\omega}. \quad (2)$$

Here, the free energy is a functional of the density $\rho(\vec{r}, \vec{\omega})$ which is normalised such that $\int \rho(\vec{r}, \vec{\omega}) d\vec{r} d\vec{\omega} = N$. As a consequence, $\rho(\vec{r}, \vec{\omega})$ has the units of ρ/Ω , where $\rho = N/V$ is the number density, V is the volume, and $\Omega = \int d\vec{\omega} = 4\pi$ for molecules with cylindrical symmetry. The de Broglie volume of rod-like particles is given by $\mathcal{V} = \mathcal{V}_t \mathcal{V}_r$ where the subscripts t and r represent the translational and rotational contributions. As for spherical particles, the translational contribution is $\mathcal{V}_t = \Lambda^3$. The rotational contribution is defined as $\mathcal{V}_r = s \prod_i^{n_{\text{axes}}} \sqrt{(h^2/(2\pi I_i kT))}$, where I_i is the moment of inertia about the rotation axis i , n_{axes} is the number of rotation axes, and s is a symmetry number. For cylindrically-symmetric, rod-shaped molecules, $n_{\text{axes}} = 2$ with $I_1 = I_2 = I$, so that $\mathcal{V}_r = h^2/(\pi I kT)$; in this case the symmetry number $s = 2$.

The liquid crystalline state relevant to this work is the nematic, which is characterised by long-range orientational order but no long-range positional order. The density $\rho(\vec{r}, \vec{\omega})$ can be factorised into a well-defined single-particle orientational distribution function $f(\vec{\omega})$ and a positionally homogeneous density $\rho(\vec{r}) = \rho = N/V$, so that $\rho(\vec{r}, \vec{\omega}) = \rho f(\vec{\omega})$. The orientational distribution function describes the probability of finding a molecule at a certain orientation $\vec{\omega}$ (defined relative to the nematic director), and is normalised such that $\int f(\vec{\omega}) d\vec{\omega} = 1$. The ideal contribution to the free energy of a nematic state of rod-like particles can thus be expressed as

$$\frac{A^{\text{id}}}{NkT} = \ln(\mathcal{V}\rho) - 1 + \int f(\vec{\omega}) \ln \{ \Omega f(\vec{\omega}) \} d\vec{\omega}. \quad (3)$$

For an isotropic fluid $f(\vec{\omega}) = 1/(4\pi)$, so the free energy simplifies to

$$\frac{A_{\text{iso}}^{\text{id}}}{NkT} = \ln(\mathcal{V}\rho) - 1. \quad (4)$$

The ideal contribution to the free energy of the anisotropic nematic phase can be written as a sum of the isotropic and anisotropic contributions,

$$\frac{A^{\text{id}}}{NkT} = \frac{A_{\text{iso}}^{\text{id}}}{NkT} + \mathcal{F}_{\text{orient}}[f]. \quad (5)$$

The functional of the orientational distribution function $f(\vec{\omega})$, defined as

$$\mathcal{F}_{\text{orient}}[f] \equiv \int f(\vec{\omega}) \ln \{\Omega f(\vec{\omega})\} d\vec{\omega}, \quad (6)$$

denotes the so-called ideal orientational entropy which was derived by Onsager [37]. At this stage we have described the ideal contribution of the Onsager free-energy functional for a nematic state.

The full Onsager free energy is obtained by taking into account the intermolecular interactions. The total free energy A can be written as $A = A^{\text{id}} + A^{\text{res}}$, where the residual contribution due to intermolecular interactions is collected in A^{res} . If one assumes a pairwise-additive intermolecular potential, the residual contribution can be derived by integrating the virial equation (for the pressure p , or equivalently the compressibility factor Z) of an inhomogeneous system of non-spherical particles [162]:

$$Z = \frac{p}{\rho kT} = 1 - \frac{1}{6\rho kT} \iiint r_{12} \frac{\partial \phi(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)}{\partial r_{12}} \times g(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) \rho(\vec{r}_1, \vec{\omega}_1) \rho(\vec{r}_2, \vec{\omega}_2) d\vec{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2. \quad (7)$$

Here, $\phi(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)$ is the pairwise-additive potential between particles 1 and 2 with intermolecular vector \vec{r}_{12} (of magnitude r_{12}) and orientations $\vec{\omega}_1$ and $\vec{\omega}_2$, $g(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)$ is the corresponding pair distribution function, $\rho(\vec{r}_1, \vec{\omega}_1)$ is the density of particle 1 at position \vec{r}_1 and orientation $\vec{\omega}_1$, and $\rho(\vec{r}_2, \vec{\omega}_2)$ that of particle 2 at position \vec{r}_2 and orientation $\vec{\omega}_2$. Purely repulsive rods were considered by Onsager, and his free energy may be obtained as a special case of expression (7). For a homogenous system, the distribution function may be written as an expansion in powers of the number density ρ [35]. The Onsager free energy involves a second-virial approximation, and therefore corresponds to the low-density limit $\rho \rightarrow 0$. In this case the pair distribution function reduces to the Boltzmann factor of the pair potential,

$$\lim_{\rho \rightarrow 0} g(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) = \exp \left[\frac{-\phi(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)}{kT} \right], \quad (8)$$

which is valid for inhomogeneous systems as the limit is independent of density. If we focus on the nematic phase [where $\rho(\vec{r}, \vec{\omega}) = \rho f(\vec{\omega})$] and retain only the low-density limit of $g(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)$ in Equation (7) we have

$$\begin{aligned} Z &= 1 - \frac{\rho}{6kT} \iiint r_{12} f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2 \\ &\times \frac{\partial \phi(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)}{\partial r_{12}} \exp \left[\frac{-\phi(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)}{kT} \right] \\ &= 1 + \frac{\rho}{6} \iiint r_{12} f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2 \\ &\times \frac{\partial}{\partial r_{12}} \left\{ \exp \left[\frac{-\phi(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)}{kT} \right] \right\}. \quad (9) \end{aligned}$$

For a purely repulsive potential $\phi = \phi_{\text{rep}}$ of cylindrically symmetrical molecules, the Boltzmann factor can be represented by a Heaviside step function

$H(r_{12} - \sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2))$; here the particle 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 derivative of a Heaviside function is the corresponding Dirac delta function δ , so the compressibility factor can be written as

$$\begin{aligned} Z &= 1 + \frac{\rho}{6} \iiint r_{12}^2 dr_{12} d\hat{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2 \\ &\times r_{12} \delta[r_{12} - \sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)] f(\vec{\omega}_1) f(\vec{\omega}_2) \\ &= 1 + \frac{\rho}{6} \iiint f(\vec{\omega}_1) f(\vec{\omega}_2) d\hat{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2 \\ &\times \int r_{12}^3 \delta[r_{12} - \sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)] dr_{12} \\ &= 1 + \frac{\rho}{6} \iiint d\hat{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2 \\ &\times \sigma^3(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2). \quad (10) \end{aligned}$$

The second virial coefficient of an orientationally ordered system of cylindrically symmetrical molecules is defined as [37]

$$\begin{aligned} B_2 &= \frac{1}{2} \iiint f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2 \\ &\times \left\{ 1 - \exp \left[\frac{-\phi(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)}{kT} \right] \right\}. \quad (11) \end{aligned}$$

For hard-core interactions, B_2 is related to the angle average of the excluded volume $V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2)$ of a pair of molecules with orientations $\vec{\omega}_1$ and $\vec{\omega}_2$ via

$$\begin{aligned} B_2 &= \frac{1}{2} \langle V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) \rangle_{\vec{\omega}_1, \vec{\omega}_2} \\ &= \frac{1}{2} \int V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2, \quad (12) \end{aligned}$$

where

$$\begin{aligned} V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) &= \int \left(1 - \exp \left[\frac{-\phi(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)}{kT} \right] \right) d\vec{r}_{12} \\ &= \int \int r_{12}^2 dr_{12} d\hat{r}_{12} \\ &\times \left\{ 1 - \exp \left[\frac{-\phi(\vec{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)}{kT} \right] \right\} \\ &= \int_0^{\sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)} \int r_{12}^2 dr_{12} d\hat{r}_{12} \\ &= \frac{1}{3} \int \sigma^3(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2) d\hat{r}_{12}. \quad (13) \end{aligned}$$

It is clear from the preceding discussion that the excluded volume so defined corresponds to the space inaccessible to a particle with orientation $\vec{\omega}_2$ due to another particle with orientation $\vec{\omega}_1$. From Equation (10), it follows that

$$Z = 1 + \frac{\rho}{2} \iint V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2. \quad (14)$$

The residual free energy can be obtained by integration from the thermodynamic identity $[\partial A/\partial V]_{N,T} = -p$, or correspondingly $[\partial(A/NkT)/\partial\rho]_{N,T} = Z/\rho$:

$$\begin{aligned} \frac{A^{\text{res}}}{NkT} &= \int_0^\rho \frac{Z(\rho) - 1}{\rho} d\rho \\ &= \frac{1}{2} \rho \int \int V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2 \\ &= \frac{1}{2} \rho V_m \mathcal{F}_{\text{conf}} [f], \end{aligned} \quad (15)$$

where V_m is the molecular volume and

$$\begin{aligned} \mathcal{F}_{\text{conf}} [f] &\equiv \frac{1}{V_m} \int \int V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2 \\ &\equiv \frac{2B_2}{V_m} \equiv 2B_2^*. \end{aligned} \quad (16)$$

The contribution $\mathcal{F}_{\text{conf}} [f]$, which is equivalent to the configurational functional defined by Onsager, incorporates all interactions between the molecules (in this case the repulsive interactions) and drives the transition to the orientationally ordered phase – the nematic liquid. It is effectively a weighted average of the excluded volume interaction between two particles, over all orientations; the corresponding dimensionless second virial coefficient is defined as $B_2^* = B_2/V_m$.

On combining the ideal (3) and residual (15) contributions we obtain the Onsager free-energy functional for an orientationally ordered phase [37], which lies at the heart of his molecular theory of the liquid crystalline state:

$$\begin{aligned} \frac{A}{NkT} &= \ln(\mathcal{V}\rho) - 1 + \int f(\vec{\omega}) \ln \{\Omega f(\vec{\omega})\} d\vec{\omega} \\ &+ \frac{\rho}{2} \int \int V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2 \\ &= \ln(\mathcal{V}\rho) - 1 + \mathcal{F}_{\text{orient}} [f] + \frac{\rho V_m}{2} \mathcal{F}_{\text{conf}} [f]. \end{aligned} \quad (17)$$

Clearly, then, the Onsager free energy is truncated at the level of the second virial coefficient and thus is expected to provide a good description of the system only in the low-density limit. Only molecules with extreme aspect ratios exhibit transitions at low densities; the Onsager description provides a good representation of the orientational ordering in such systems (e.g., see [9] and references therein). Higher-body contributions (third and higher virial coefficients) must also be included in the description of particles with the moderate aspect ratios characterising mesogens of practical interest.

B. Higher Body Terms (Parsons-Lee Scaling)

Improvements to Equation (17) are required to account for the omission of the higher virial terms. A popular method of including higher-body contributions is due to

Parsons [81] and Lee [82, 83] (also see reference [11]). The alternative approach due to Vega and Lago [84] can be employed if the equation of state of the isotropic fluid is known, but we opt for the more general Parsons-Lee approach as one requires a knowledge of the properties only of the hard-sphere fluid.

The Parsons-Lee extension of the Onsager second-virial free energy can be obtained following an approach similar to that discussed in the preceding section, but using an improved approximation for the pair distribution function $g(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)$ in Equation (7). The interparticle distance r_{12} is scaled in terms of the contact distance $\sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)$ to define a reduced variable $y = r_{12}/\sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)$ which takes the value $y = 1$ at contact, regardless of the relative orientation of the two particles. The distribution function $g(y)$ is then represented as a simple function such that the positional and orientational dependencies are decoupled and can be integrated separately. This type of decoupling approximation is commonly used to represent the structure of non-spherical molecules (e.g., see references [67, 163, 164]). Thereby, the compressibility factor (Equation (7)) becomes

$$\begin{aligned} Z &= 1 - \frac{\rho}{6kT} \iiint y \sigma \left(\frac{1}{\sigma} \right) \frac{du(y)}{dy} \\ &\times g(y) f(\vec{\omega}_1) f(\vec{\omega}_2) (y^2 \sigma^2) (\sigma dy) d\hat{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2 \\ &= 1 - \frac{\rho}{6kT} \left[\int y^3 \frac{du}{dy} g(y) dy \right] \\ &\times \left[\iiint \sigma^3 f(\vec{\omega}_1) f(\vec{\omega}_2) d\hat{r}_{12} d\vec{\omega}_1 d\vec{\omega}_2 \right] \\ &= 1 - \frac{\rho}{2kT} \left[\int y^3 \frac{du}{dy} g(y) dy \right] \\ &\times \left[\iint V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2 \right], \end{aligned} \quad (18)$$

where the angular dependence of $\sigma(\hat{r}_{12}, \vec{\omega}_1, \vec{\omega}_2)$ has been omitted from the expression for compactness. In terms of the scaled distance y , the pair potential of a cylindrically symmetric hard-body takes the form

$$u(y) = \begin{cases} \infty & y < 1 \\ 0 & y \geq 1. \end{cases}$$

Defining the cavity function $\mathcal{Y}(y) = g(y) \exp(u/kT)$ and replacing the double integral involving $V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2)$ by B_2 (Equation (12)), Z can be expressed as

$$\begin{aligned} Z &= 1 - \frac{\rho B_2}{kT} \left[\int y^3 \frac{du}{dy} \exp\left(-\frac{u}{kT}\right) \mathcal{Y}(y) dy \right] \\ &= 1 + \rho B_2 \mathcal{Y}(1) \\ &= Z = 1 + \rho B_2 g(1_+) \end{aligned} \quad (19)$$

via the introduction of a Heaviside step function (as in the development of Equation (10)). The orientational dependence of the distribution function has clearly been factored out into the second virial coefficient. At contact,

the value of the distribution function is discontinuous and the value $g(1)$ in Equation (19) is taken as the limit approaching contact from above, $g(1_+)$. For a system of non-spherical molecules this is generally unknown but can be approximated by the contact radial distribution function $g(1_+) \approx g_{\text{hs}}(\sigma_+)$ of an equivalent system of hard spheres of the same molecular volume ($V_m = V_{\text{hs}}$) at the same density. The advantage of this is that the Carnahan and Starling [165] relation provides an accurate description of the compressibility factor for hard spheres, and the corresponding contact value of the radial distribution function can be obtained directly from the pressure virial $Z_{\text{hs}}(\eta) = 1 + \rho B_{2,\text{hs}} g_{\text{hs}}(\sigma_+)$ [35]. Equation (19) thus becomes

$$Z = 1 + \left(\frac{Z_{\text{hs}} - 1}{B_{2,\text{hs}}} \right) B_2. \quad (20)$$

The hard-sphere compressibility factor Z_{hs} can also be expressed as a virial expansion, so that the factor pre-multiplying B_2 is actually a sum of virial coefficient terms $\rho^{n-1} B_{n,\text{hs}}/B_{2,\text{hs}}$:

$$Z = 1 + \left(\sum_{i=2}^n \frac{\rho^{i-1} B_{i,\text{hs}}}{B_{2,\text{hs}}} \right) B_2. \quad (21)$$

Clearly the Parsons-Lee approximation incorporates all of the higher virial coefficients B_i ($3 \leq i < \infty$) by effectively scaling the hard-sphere terms. The second virial coefficient of the equivalent hard-sphere system is simply $B_{2,\text{hs}} = 4V_m$. The compressibility factor [Equation (19)] of an orientationally ordered system of non-spherical molecules can thus be obtained simply from the second virial coefficient of the nematogen and the compressibility factor of the isotropic hard-sphere system as

$$\begin{aligned} Z &= 1 + \frac{(Z_{\text{hs}} - 1)}{4V_m} B_2 \\ &= 1 + \frac{(Z_{\text{hs}} - 1)}{8V_m} \\ &\quad \times \iint V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2. \end{aligned} \quad (22)$$

The last form of the expression, in terms of the excluded volume, provides an indication of dependence of the equation of state on the orientation of the molecules through the orientational distribution function $f(\vec{\omega})$.

As before, the residual free energy is obtained by integrating the equation of state:

$$\begin{aligned} \frac{A^{\text{res}}}{NkT} &= \int_0^\rho \frac{Z(\rho) - 1}{\rho} d\rho = \frac{B_2}{4V_m} \int_0^\rho \frac{Z_{\text{hs}}(\rho) - 1}{\rho} d\rho \\ &= \frac{1}{8V_m} \frac{A_{\text{hs}}^{\text{res}}}{NkT} \\ &\quad \times \iint V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2. \end{aligned} \quad (23)$$

The residual free energy for hard spheres $A_{\text{hs}}^{\text{res}}$ can be obtained from the Carnahan and Starling [165] compressibility factor as

$$\begin{aligned} \frac{A_{\text{hs}}^{\text{res}}}{NkT} &= \int_0^\eta \frac{Z_{\text{hs}}(\eta) - 1}{\eta} d\eta \\ &= \frac{V_m(4\rho - 3\rho^2 V_m)}{(1 - \rho V_m)^2} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2}, \end{aligned} \quad (24)$$

which is more conveniently expressed in terms of the packing fraction $\eta = \rho V_m \equiv \rho V_{\text{hs}}$.

Combining the ideal (3) and residual (23) contributions we obtain the Parsons-Lee Helmholtz free-energy functional for the nematic phase (Onsager free energy corrected to include the higher virial coefficients):

$$\begin{aligned} \frac{A}{NkT} &= \ln(\mathcal{V}\rho) - 1 + \int f(\vec{\omega}) \ln \{\Omega f(\vec{\omega})\} d\vec{\omega} \\ &\quad + \frac{1}{8V_m} \frac{A_{\text{hs}}^{\text{res}}}{NkT} \iint V_{\text{exc}}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_1) f(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2 \\ &= \frac{A_{\text{iso}}^{\text{id}}}{NkT} + \mathcal{F}_{\text{orient}}[f] + G(\rho) \mathcal{F}_{\text{conf}}[f], \end{aligned} \quad (25)$$

where the the density (packing fraction) dependence is contained in the function $G(\rho) = (A_{\text{hs}}^{\text{res}}/NkT)/8$. This is the final expression of the free energy that is used in the computations presented in this work. It reduces to the Onsager second virial theory when a linear density dependence $G(\rho) = \rho V_m/2 = \eta/2$ is assumed; in the limit of molecules with infinite aspect ratio the free energy takes the Onsager form as the isotropic-nematic transition occurs in the limit of vanishing density.

Common to Equations (17) and (25) there are two important terms $\mathcal{F}_{\text{orient}}[f]$ and $\mathcal{F}_{\text{conf}}[f]$, which are the competing contributions that give rise to the orientationally ordered nematic state. The first functional $\mathcal{F}_{\text{orient}}[f]$ of $f(\vec{\omega})$ describes the orientational entropy that the system loses by ordering its molecular axis. This term is at its maximum $\mathcal{F}_{\text{orient}}[f]^{\text{max}} = \mathcal{F}_{\text{orient}}[f_{\text{iso}}] = 0$ for the orientationally disordered isotropic state where $f_{\text{iso}}(\vec{\omega}) = 1/(4\pi)$; the orientational entropy of the isotropic fluid is contained in the rotational contribution to the de Broglie volume in $A_{\text{iso}}^{\text{id}}$. The second functional $\mathcal{F}_{\text{conf}}[f]$ is proportional to the second virial coefficient B_2 ; it effectively represents a weighted average of the excluded volume interaction between two particles over all relative orientations. This term is at a minimum for the perfectly aligned state, corresponding to a minimum in the excluded volume; in turn this maximises the free volume available to the particles (configurational entropy). As the density is increased [corresponding to an increase in $G(\rho)$] the configurational entropy starts to dominate over the orientational contribution, and the subsequent decrease in free energy drives the transition to a nematic phase. For the isotropic fluid $\mathcal{F}_{\text{conf}}[f] = 2B_{2,\text{iso}}/V_m = 2B_{2,\text{iso}}^*$, which can be evaluated once the explicit form of the excluded volume interaction is specified.

C. Equilibrium Orientational Distribution Function

It was clear from the preceding sections that the free energy $A[f(\vec{\omega})]$ of a system of orientationally ordered particles is a functional of the single-particle orientational distribution function $f(\vec{\omega})$. The equilibrium state corresponds to the function $f_{eq}(\vec{\omega})$ that minimises the free energy (Equation (17) in the case of the Onsager second-virial theory or Equation (25) in the case of the Parsons-Lee modification). The variation of the free energy with respect to $f(\vec{\omega})$ must fulfill the following condition [9]:

$$\left. \frac{\delta A[f(\vec{\omega})]}{\delta f(\vec{\omega})} \right|_{eq} - \lambda = 0, \quad (26)$$

where λ is a Lagrange undetermined multiplier. In essence this Euler-Lagrange equation is equivalent to requiring that the free-energy functional be a minimum subject to the additional normalisation constraint $\int f(\vec{\omega}) d\vec{\omega} = 1$. The integral equation for the equilibrium orientational distribution corresponding to the free energy given by Equation (25) is

$$f_{eq}(\vec{\omega}) = \frac{\Omega \exp \left[-\frac{2G(\rho)}{V_m} \int V_{exc}(\vec{\omega}, \vec{\omega}_2) f(\vec{\omega}_2) d\vec{\omega}_2 \right]}{\int \exp \left[-\frac{2G(\rho)}{V_m} \int V_{exc}(\vec{\omega}_1, \vec{\omega}_2) f(\vec{\omega}_2) d\vec{\omega}_2 \right] d\vec{\omega}_1}. \quad (27)$$

A variety of approaches have been applied to undertake this minimisation. As we alluded to earlier, these can be grouped into two classes: trial-function methods [37, 91, 120] and numerical methods [48–55].

In order to solve Equation (27) numerically, the orientational distribution function $f(\vec{\omega})$ (or its logarithm) and the excluded volume $V_{exc}(\vec{\omega}, \vec{\omega}_2)$ can be expanded as series of Legendre polynomials, and the resulting expression can then be minimised with respect to the unknown expansion coefficients [48–52]. Alternatively $f(\vec{\omega})$ can be described in discrete form and Equation (27) can then be solved by straightforward iteration [53, 54] or by using Monte Carlo annealing [55]. Though all of these numerical techniques provide the equilibrium orientational distribution function to the desired accuracy, it is clear that no analytical solution is available.

A well-chosen analytical description of $f(\vec{\omega})$ can make the solution of the equilibrium distribution much simpler and computationally efficient, without compromising too much of the numerical accuracy. In his seminal paper, Onsager [37] used a simple hyperbolic trial function to describe $f(\vec{\omega})$ in terms of single parameter α which characterises the degree or orientational order in the system; the precise form of the Onsager trial function (OTF) is given in the following section. Straley [120], and more recently Odijk [91], have used similar Gaussian trial functions which are also cast in terms of a single parameter, but as we hope to show it is difficult to improve on the simplicity and elegance of the Onsager approach. By using this type of trial function, the free energy becomes a function of the parameter α and the equilibrium orientational state of the system is determined from a simple

derivative of the free energy with respect to α rather than the variation described by Equation (26):

$$\left(\frac{\partial A(\alpha)}{\partial \alpha} \right)_{NVT} - \lambda = 0. \quad (28)$$

In this work we shall show that there are a number of general and novel results that can be obtained for the free energy of an orientationally ordered system in terms of the OTF, and show that the use of the trial function within a Parsons-Lee free energy provides an accurate description of the equation of state and ordering of repulsive particles such as hard spherocylinders.

Once the equilibrium orientational distribution function is known the free energy of the orientational ordered nematic state can be used to determine the isotropic-nematic equilibria in a straightforward fashion. The densities of the coexisting isotropic fluid and nematic phases at a fixed temperature are determined numerically by requiring equality of the pressure $p = -(\partial A/\partial V)_{NT}$, and chemical potential $\mu = (\partial A/\partial N)_{VT}$ of the two phases.

D. Onsager Trial Function

The advantage of describing the orientational distribution function and the free energy of the nematic state in terms of a simple function has been pointed out in the previous section. For the nematic fluid, evaluating the functionals $\mathcal{F}_{orient}[f]$ and $\mathcal{F}_{conf}[f]$ is not trivial even with a simple trial function. Here we describe the use of the original hyperbolic trial function of Onsager in some detail. As has already been pointed out the use of the OTF approach is comparatively rare compared with a full numerical solution of Onsager-like free energies. This is due in part to the lack of transparency in the description that Onsager provides in his well-known appendix [37]. In the majority of studies that have been made with the OTF [52, 104–119], the Onsager expressions are employed as originally quoted. Significant effort has to be expended to recognise the general aspects of the Onsager approach in describing the ordering transition of more-complex molecules and mixtures with simple algebraic equations. It is hoped that the analysis provided in this section will lift some of the obstacles encountered in the use of the OTF and reveal the truly generic nature of the approach.

Onsager chose the following form to represent the orientational distribution function $f(\vec{\omega})$ [37]:

$$f_{OTF}(\theta) = \frac{\alpha \cosh[\alpha \cos(\theta)]}{4\pi \sinh(\alpha)}. \quad (29)$$

The trial function depends on the azimuthal angle $\theta = \arccos(\vec{\omega} \cdot \vec{\omega}_0)$, defined with respect to a reference vector $\vec{\omega}_0$ which corresponds to the director in a nematic phase. It is clear from Figure 1 that the degree of orientational order in the system is determined by the parameter α . For an isotropic system $\alpha = 0$, this can be seen by

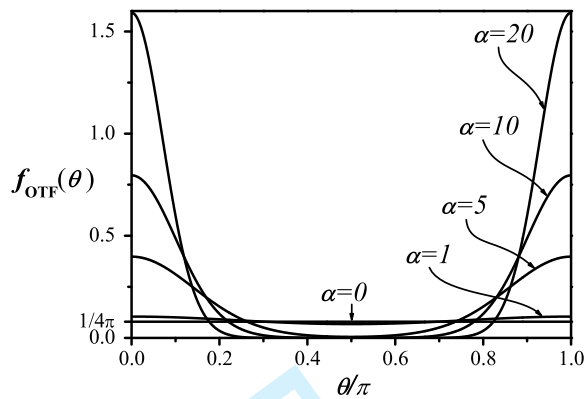


FIG. 1: The dependence of the Onsager trial function [Equation (29)] on the relative orientation θ of the principal molecular axis for a range of values of the orientational parameter α . The orientational distribution function becomes progressively more peaked around $\theta = 0$ and π as the value of α is increased, corresponding to states with increasing orientational order. In the case of the isotropic phase $\alpha = 0$ and $f_{\text{OTF}}(\theta) = 1/(4\pi)$.

taking the limit $\lim_{\alpha \rightarrow 0} (f_{\text{OTF}})$ using l'Hôpital's rule, giving $f_{\text{iso}} = f_{\text{OTF}}(\alpha = 0) = 1/(4\pi)$, whereas a large value of α (in practise, ~ 10 or higher) indicates a high degree of orientational order. As we show in the following sections the introduction of this trial function allows one to solve the integrals analytically giving the free energy as

a function of α . The equilibrium distribution function is obtained from the simple derivative $(\partial A/\partial \alpha)_{NVT} = 0$. There is no longer a need to specify the undetermined multiplier λ as Onsager's trial function is correctly normalised irrespective of the value of α :

$$\begin{aligned} \int_{\vec{\omega}} f_{\text{OTF}}(\theta) d\vec{\omega} &= \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} f_{\text{OTF}}(\theta) \sin \theta d\theta d\phi \\ &= \frac{\alpha}{2 \sinh \alpha} \int_{\theta=0}^{\pi} \cosh(\alpha \cos \theta) \sin \theta d\theta; \end{aligned}$$

substituting $u = \cos \theta$, $du = -\sin \theta d\theta$, this becomes

$$\int_{\vec{\omega}} f_{\text{OTF}}(\theta) d\vec{\omega} = \frac{\alpha}{2 \sinh \alpha} \int_{u=-1}^1 \cosh(\alpha u) du = 1. \quad (30)$$

By contrast the Gaussian trial function is not naturally normalised [9]; the normalisation constant is a more-complex function of the parameter α , though the integral involved can be expressed analytically in truncated form.

E. Orientational Entropy Functional

The importance of the simplification provided by the use of the OTF is revealed from an evaluation of the orientational entropy. The functional $\mathcal{F}_{\text{orient}}[f]$ [equation (6)] is integrated to give a simple function of α as follows (recall that $\Omega = 4\pi$ for cylindrically symmetric molecules):

$$\begin{aligned} \mathcal{F}_{\text{orient}}[f] &= \int \frac{\alpha \cosh(\alpha \cos \theta)}{4\pi \sinh \alpha} \ln \left\{ \frac{\alpha \cosh(\alpha \cos \theta)}{\sinh \alpha} \right\} d\vec{\omega} \\ &= \frac{\alpha}{4\pi \sinh \alpha} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \cosh(\alpha \cos \theta) \ln \left\{ \frac{\alpha \cosh(\alpha \cos \theta)}{\sinh \alpha} \right\} \sin \theta d\theta d\phi \\ &= \frac{-\alpha}{4\pi \sinh \alpha} \int_{\cos \theta=1}^{-1} \int_{\phi=0}^{2\pi} \cosh(\alpha \cos \theta) \ln \left\{ \frac{\alpha \cosh(\alpha \cos \theta)}{\sinh \alpha} \right\} d(\cos \theta) d\phi \\ &= \frac{\alpha}{2 \sinh \alpha} \int_{u=-1}^1 \cosh(\alpha u) du \left\{ \ln \left(\frac{\alpha}{\sinh \alpha} \right) + \ln [\cosh(\alpha u)] \right\} \\ &= \frac{\alpha}{2 \sinh \alpha} \left\{ \left[\frac{\sinh(\alpha u)}{\alpha} \ln \left(\frac{\alpha}{\sinh \alpha} \right) \right]_{u=-1}^1 + \int_{u=-1}^1 \cosh(\alpha u) \ln [\cosh(\alpha u)] du \right\}, \quad (31) \end{aligned}$$

where the substitution $u = \cos \theta$ has been made. The remaining integral in equation (31) can be solved by parts:

$$\begin{aligned}
 \mathcal{F}_{\text{orient}}[f] &= \frac{\alpha}{2 \sinh \alpha} \left\{ \left[\frac{\sinh(\alpha u)}{\alpha} \ln \left(\frac{\alpha}{\sinh \alpha} \right) \right]_{u=-1}^1 \right. \\
 &\quad \left. + \left[\frac{\sinh(\alpha u)}{\alpha} \ln (\cosh(\alpha u)) \right]_{u=-1}^1 - \int_{u=-1}^1 \frac{\cosh^2(\alpha u) - 1}{\cosh(\alpha u)} du \right\} \\
 &= \frac{\alpha}{2 \sinh \alpha} \left\{ \frac{2 \sinh \alpha}{\alpha} \left(\ln \frac{\alpha}{\sinh \alpha} + \ln \cosh \alpha - 1 \right) + \frac{2 \arctan(\sinh \alpha)}{\alpha} \right\} \\
 &= \ln(\alpha \coth \alpha) - 1 + \frac{\arctan(\sinh \alpha)}{\sinh \alpha}; \tag{32}
 \end{aligned}$$

Equation (32) is commonly approximated as $\mathcal{F}_{\text{orient}}[f] \approx \ln \alpha - 1 + \pi \exp(-\alpha)$, e.g., see references [91, 108]; Onsager himself used simply $\mathcal{F}_{\text{orient}}[f] \approx \ln \alpha - 1$ [37]. Whilst these approximations are not unacceptable, the full expression is calculated with no real effort on modern computers and therefore we retain this form. One should note that in the case of the Maier-Saupe [22–24] approach the orientational entropic term is not analytical and has to be evaluated numerically. A clear advantage of the use of the OTF is the analytical form that one obtains for $\mathcal{F}_{\text{orient}}[f]$.

F. Configurational Entropy Functional

A method for the evaluation of the configurational functional $\mathcal{F}_{\text{conf}}[f]$ is the subject of the seminal Appendix B of Onsager's paper [37]. The essential problem which Onsager overcame is that the excluded volume interaction V_{exc} is a function of the angle between two molecules, $\gamma = \arccos(\vec{\omega}_1 \cdot \vec{\omega}_2)$, whereas the integral is over $\vec{\omega}_1(\theta_1, \phi_1)$ and $\vec{\omega}_2(\theta_2, \phi_2)$, in terms of a cartesian reference frame where, as usual, θ and ϕ represent polar and azimuthal angles. By use of the trial function [Equation (29)], together with ingenious rotations of the coordinate frame (see Figure 2) and changes of variables, Onsager was able to reduce the problem to a single integration over γ , his only stipulation being the symmetry condition that the intermolecular interaction can be represented as a function F of $\sin \gamma$ with

$$F(\gamma) = F(\pi - \gamma). \tag{33}$$

This means that an ‘‘up-down’’ symmetry is imposed together with the implicit cylindrical symmetry. As we show here a particular strength of the Onsager trial-function method is that it may be applied to the average over all orientations of any function F for a pair of molecules (not just the simple excluded volume interaction that Onsager considered) provided that this symmetry condition is met.

The functional $\mathcal{F}_{\text{conf}}[f]$ is related to the average second virial coefficient and a specific form of the excluded

volume of a pair of particles for a fixed relative orientation now has to be specified. For purposes of illustration, we choose to represent the excluded volume in terms of the relative orientation γ of the main molecular axes of the two molecules with the following general form which is used throughout our paper:

$$V_{\text{exc}} = \sum_{i=0} C_i \sin^i \gamma. \tag{34}$$

This should not be confused with the representation of the excluded volume as a spherical-harmonic expansion, *i.e.*, a series in $\cos^i \theta$ (even i) which is commonly used to expand the leading term ($\sin \gamma$) of the excluded volume in order to perform the numerical integration. The hard spherocylinder (a cylinder of length L capped by two hemispheres of diameter D) is an example of a nematogen for which the excluded volume can be exactly represented in this form as $V_{\text{exc}} = C_0 + C_1 \sin \gamma$, where $C_0 = \frac{4}{3}\pi D^3 + 2\pi D^2 L$ and $C_1 = 2L^2 D$ [37]. The leading contribution in the excluded volume of two hard cylinders given by Onsager [37] is also proportional to $\sin \gamma$; Onsager chose to neglect all but this contribution, while the full expression also contains a term in $|\cos \gamma|$ and the complete elliptic integral of the second kind $E(\sin^2 \gamma) = \int_0^{\pi/2} (1 - \sin^2 \gamma \sin^2 \xi) d\xi$. The full expression could be given in the general form of Equation (34) since the former can be represented as a binomial series expansion of $(1 - \sin^2 \gamma)^{1/2} = 1 - \frac{1}{2} \sin^2 \gamma - \frac{1}{8} \sin^4 \gamma - \frac{1}{16} \sin^6 \gamma - \dots$, and the latter as the series expansion $E(\sin^2 \gamma) = \frac{\pi}{2} \left(1 - \frac{1}{4} \sin^2 \gamma - \frac{3}{64} \sin^4 \gamma - \frac{5}{256} \sin^6 \gamma - \dots \right)$. In either case only a few terms would be sufficient due to the rapidly decreasing nature of the high powers of $\sin \gamma$. In the case of linear chains formed from m tangent hard-sphere segments the excluded volume is also very accurately represented by a series of the form of Equation (34) [166]; a truncated form up to $\sin \gamma$ provides the second virial coefficient to an accuracy of better than 0.02% for a chain of length $m = 10$, and the inclusion of a term in $\sin^2 \gamma$ captures the excluded volume essentially completely. Even when the chains are flexible the excluded volume can be represented as a series in $\sin^i \gamma$ [112], confirming the usefulness of such an expansion. Our analysis is thus more general than that of Onsager, and will enable

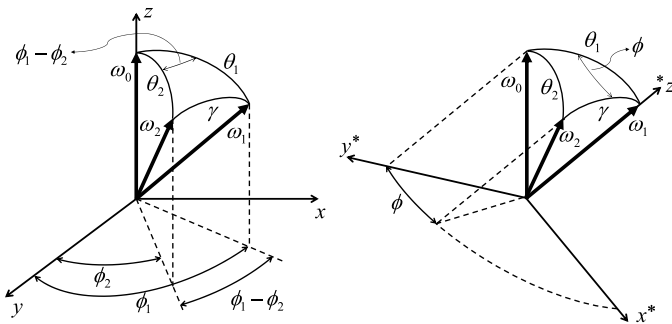


FIG. 2: The orientations $\vec{\omega}_1(\theta_1, \phi_1)$ and $\vec{\omega}_2(\theta_2, \phi_2)$ of a pair of cylindrically symmetrical molecules in terms of polar coordinates can be described in terms of the polar θ_1 and azimuthal $\phi = \phi_1 - \phi_2$ angles, and the angle γ between the two principal axes with a simple rotation of the cartesian axis. The key to the approach of Onsager [37] is that the configurational functional can be expressed uniquely in terms of γ by integrating out the variables θ and ϕ .

one to express the configurational functional in analytical form even for the full excluded volume contribution of hard cylinders, linear and flexible hard-sphere chains, and other such models, albeit as truncated series.

It is simple to evaluate $\mathcal{F}_{\text{conf}}[f]$ for the isotropic fluid. For a pair of molecules one is free to choose the orientation of one molecule (say $\vec{\omega}_1$) as the reference axis, so that $\gamma = \theta_2$ becomes the polar angle. Thus

$$\begin{aligned} \mathcal{F}_{\text{conf}}[f_{\text{iso}}] &= \frac{1}{(4\pi)^2 V_m} \int_{\vec{\omega}_1} d\vec{\omega}_1 \int_{\phi=0}^{2\pi} d\phi_2 \int_{\gamma=0}^{\pi} \sum_{i=0} C_i \sin^{i+1} \gamma d\gamma \\ &= \frac{1}{2} \sum_{i=0} C_i^* \int_{\gamma=0}^{\pi} \sin^{i+1} \gamma d\gamma = 2B_{2,\text{iso}}^*. \end{aligned} \quad (35)$$

where the coefficients of the series $C_i^* = C_i/V_m$ are expressed in reduced form for convenience, and $B_{2,\text{iso}}^* = B_{2,\text{iso}}/V_m$ is the reduced second virial coefficient of the isotropic fluid that depends on the precise form of the excluded volume interaction: the integrals involved are all

functions of the angle γ : $\int_0^\pi \sin \gamma d\gamma = 2$, $\int_0^\pi \sin^2 \gamma d\gamma = \pi/2$, $\int_0^\pi \sin^3 \gamma d\gamma = 4/3$, $\int_0^\pi \sin^4 \gamma d\gamma = 3\pi/8$, etc. For long rods the configurational functional of the isotropic phase can be approximated by $\mathcal{F}_{\text{conf}}[f] \approx \pi L^2 D / (2V_m)$ where the excluded volume is given by the leading term in $\sin \gamma$ [37].

We define a general functional \mathfrak{S} which represents the orientational average $\langle F(\gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2}$ of some function F which obeys the symmetry condition described earlier:

$$\mathfrak{S} = \int_{\vec{\omega}_1} \int_{\vec{\omega}_2} F(\gamma) f_1(\vec{\omega}_1) f_2(\vec{\omega}_2) d\vec{\omega}_1 d\vec{\omega}_2, \quad (36)$$

For complete generality at this stage, it is not assumed that the particles interacting are of the same type, so a different trial function is used to represent the orientational distribution function of each class of particle. In polar coordinates Equation (36) then becomes

$$\begin{aligned} \mathfrak{S} &= \int_{\phi_1} \int_{\phi_2} \int_{\theta_1} \int_{\theta_2} F(\gamma) f_{\text{OTF},1}(\theta_1) f_{\text{OTF},2}(\theta_2) \\ &\quad \times \sin \theta_1 d\theta_1 d\phi_1 \sin \theta_2 d\theta_2 d\phi_2 \\ &= K \int_{\phi_1} \int_{\phi_2} \int_{\theta_1} \int_{\theta_2} F(\gamma) \cosh(\alpha_1 \cos \theta_1) \cosh(\alpha_2 \cos \theta_2) \\ &\quad \times \sin \theta_1 d\theta_1 d\phi_1 \sin \theta_2 d\theta_2 d\phi_2, \end{aligned} \quad (37)$$

where the following constant has been defined

$$K \equiv K(\alpha_1, \alpha_2) = \frac{\alpha_1 \alpha_2}{(4\pi)^2 \sinh \alpha_1 \sinh \alpha_2} \quad (38)$$

The presence of the product $\cosh(\alpha_1 \cos \theta_1) \cosh(\alpha_2 \cos \theta_2)$ leads one naturally to think about the compound angle formulae for the cosh function, $\cosh(A+B)$ and $\cosh(A-B)$, $\cosh(A \pm B) = \cosh A \cosh B \pm \sinh A \sinh B$. The sum $\cosh(A+B) + \cosh(A-B)$ leads to the product of the cosh functions without introducing a complementary product of sinh functions. Therefore, for the case at hand:

$$\begin{aligned} \mathfrak{S} &= \frac{K}{2} \left\{ \int_{\phi_1} \int_{\phi_2} \int_{\theta_1} \int_{\theta_2} F(\gamma) \cosh(\alpha_1 \cos \theta_1 + \alpha_2 \cos \theta_2) \sin \theta_1 d\theta_1 d\phi_1 \sin \theta_2 d\theta_2 d\phi_2 \right. \\ &\quad \left. + \int_{\phi_1} \int_{\phi_2} \int_{\theta_1} \int_{\theta_2} F(\gamma) \cosh(\alpha_1 \cos \theta_1 - \alpha_2 \cos \theta_2) \sin \theta_1 d\theta_1 d\phi_1 \sin \theta_2 d\theta_2 d\phi_2 \right\}. \end{aligned} \quad (39)$$

Making the change of variables $\tau = \pi - \theta_2$, $d\tau = -d\theta_2$ in the second integral only

$$\mathfrak{S} = \frac{K}{2} \left\{ \int_{\phi_1} \int_{\phi_2} \int_{\theta_1} \int_{\theta_2=0}^{\pi} F(\gamma) \cosh(\alpha_1 \cos \theta_1 + \alpha_2 \cos \theta_2) \sin \theta_1 d\theta_1 d\phi_1 \sin \theta_2 d\theta_2 d\phi_2 \right. \\ \left. - \int_{\phi_1} \int_{\phi_2} \int_{\theta_1} \int_{\tau=\pi}^0 F(\gamma) \cosh(\alpha_1 \cos \theta_1 + \alpha_2 \cos \tau) \sin \theta_1 d\theta_1 d\phi_1 \sin \tau d\tau d\phi_2 \right\}. \quad (40)$$

The sign of the second integral is reversed by inverting the limits of the integration over τ , whence it can be seen that the two integrals differ only in a label and are therefore identical. Thus,

$$\mathfrak{S} = K \int_{\phi_1} \int_{\phi_2} \int_{\theta_1} \int_{\theta_2} \sin \theta_1 d\theta_1 d\phi_1 \sin \theta_2 d\theta_2 d\phi_2 \\ \times F(\gamma) \cosh(\alpha_1 \cos \theta_1 + \alpha_2 \cos \theta_2). \quad (41)$$

At this point the azimuthal angles ϕ_1 and ϕ_2 could be integrated out, however this would leave the integral in terms of the inconvenient variables θ_1 and θ_2 , instead of the convenient variable γ (in terms of which the function F is defined). Onsager rotates the coordinate frame as illustrated in Figure 2. In this new coordinate frame, the polar angles are θ_1 and γ , the latter of which becomes one of the integration variables (in place of the inconvenient θ_2). One of the new azimuthal angles is now integrated out to give 2π so that the remaining one is labelled simply $\phi = \phi_1 - \phi_2$ (with no suffix) and the expression becomes:

$$\mathfrak{S} = 2K\pi \int_{\phi} \int_{\theta_1} \int_{\gamma} F(\gamma) \cosh(\alpha_1 \cos \theta_1 + \alpha_2 \cos \theta_2) \\ \times \sin \theta_1 d\theta_1 \sin \gamma d\gamma d\phi. \quad (42)$$

This is Equation (B8) of Onsager's appendix [37]. Following this, Onsager transforms the integral with two complicated (and remarkably farsighted) substitutions which are not straightforward to illustrate. The first replaces the integration variables θ_1 and ϕ with new variables χ and ψ , defined through the relations:

$$\cos \theta_1 = \sin \chi \cos(\psi + \eta(\gamma)) \\ \sin \theta_1 \cos \phi = \sin \chi \sin(\psi + \eta(\gamma)) \\ \tan \eta(\gamma) = \frac{\alpha_2 \sin \gamma}{\alpha_1 + \alpha_2 \cos \gamma}; \quad (43)$$

after some algebra, omitted by Onsager, one finds the Jacobian,

$$\frac{\partial(\theta_1, \phi)}{\partial(\chi, \psi)} = \frac{\partial\theta_1}{\partial\chi} \frac{\partial\phi}{\partial\psi} - \frac{\partial\theta_1}{\partial\psi} \frac{\partial\phi}{\partial\chi} = \frac{\sin \chi}{\sin \theta_1}. \quad (44)$$

Following further algebra, one can show that the integral

is thus transformed as

$$\mathfrak{S} = 2K\pi \int_{\gamma=0}^{\pi} \int_{\chi=0}^{\pi} \int_{\psi=0}^{2\pi} F(\gamma) \sin \gamma d\gamma \sin \chi d\chi d\psi \\ \times \cosh \left[(\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos \gamma)^{\frac{1}{2}} \sin \chi \cos \psi \right]. \quad (45)$$

The advantage of this is not immediately clear, however the purpose becomes apparent following the final transformation,

$$\sin \chi \cos \psi = \cos \mu \\ \cos \chi = \sin \mu \cos \xi, \quad (46)$$

which replaces the integration variables χ and ψ with (new) variables μ and ξ . Invoking the symmetry condition on the function $F(\gamma)$, the Jacobian is derived as

$$\frac{\partial(\chi, \psi)}{\partial(\mu, \xi)} = \frac{\sin \mu}{\sin \chi}, \quad (47)$$

and after some rearrangement the integral becomes

$$\mathfrak{S} = 2K\pi \int_{\gamma=0}^{\pi} \int_{\mu=0}^{\pi} \int_{\xi=0}^{2\pi} F(\gamma) \sin \gamma d\gamma \sin \mu d\mu d\xi \\ \times \cosh \left[(\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos \gamma)^{\frac{1}{2}} \cos \mu \right]. \quad (48)$$

The remarkable result of this substitution is that it leads to a form in which the variables μ and ξ can be integrated out entirely, leaving only the dependence on the angle γ between the two principal molecular axes.

It is possible that some of the difficulty in following Onsager's method (and in generalising it) arises from the transformations he makes. Not only is it far from clear how the substitutions were chosen, but on reading Onsager's paper it is not immediately obvious that a very substantial amount of algebra has been omitted, firstly in obtaining the Jacobians and secondly in rearranging the integrals to the forms given - so much, indeed, that to include it all would create a distraction and we follow Onsager in its omission. Once this omission is pointed out, however, much of the opaqueness is lifted.

The integral over ξ can be carried out directly to yield another factor of 2π ; the integral remaining, considered as a function of μ , is of the form $\int_0^\pi \cosh(\kappa \cos \mu) \sin \mu \, d\mu$ which integrates out directly as $2 \sinh \kappa / \kappa$:

$$\mathfrak{S} = 4K\pi^2 \int_{\gamma=0}^{\pi} F(\gamma) \sin \gamma \, d\gamma \times \left\{ \frac{2 \sinh \left[(\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos \gamma)^{\frac{1}{2}} \right]}{(\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos \gamma)^{\frac{1}{2}}} \right\}. \quad (49)$$

The transformations have thus allowed all but the de-

pendence on γ to be integrated out directly. The only remaining integration variable is γ , as originally desired; this is the important point to understand from this part of the derivation. Equation (49) can be rewritten as

$$\mathfrak{S} = 8K\pi^2 \int_{\gamma=0}^{\pi} \frac{-1}{\alpha_1\alpha_2} F(\gamma) \, d\gamma \times \frac{d}{d\gamma} \left\{ \cosh \left[(\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos \gamma)^{\frac{1}{2}} \right] \right\}, \quad (50)$$

which can be integrated by parts to give

$$\begin{aligned} \mathfrak{S} &= \frac{8K\pi^2}{\alpha_1\alpha_2} \left\{ -\cosh \left[(\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos \gamma)^{\frac{1}{2}} \right] F(\gamma) \Big|_{\gamma=0}^{\pi} - \int_{\gamma=0}^{\pi} -\cosh \left[(\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos \gamma)^{\frac{1}{2}} \right] \, dF(\gamma) \right\} \\ &= \frac{8K\pi^2}{\alpha_1\alpha_2} \left\{ [-\cosh(\alpha_1 - \alpha_2) F(\pi)] - [-\cosh(\alpha_1 + \alpha_2) F(0)] + \int_{\gamma=0}^{\pi} \cosh \left[(\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos \gamma)^{\frac{1}{2}} \right] \, dF(\gamma) \right\}. \end{aligned} \quad (51)$$

The symmetry requirement $F(\gamma) = F(\pi - \gamma)$ means $F(\pi) = F(0)$, therefore

$$\begin{aligned} \mathfrak{S} &= \frac{8K\pi^2}{\alpha_1\alpha_2} \left\{ F(0) [\cosh(\alpha_1 + \alpha_2) - \cosh(\alpha_1 - \alpha_2)] \right. \\ &\quad \left. + \int_{\gamma=0}^{\pi} \cosh \left([\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos \gamma]^{\frac{1}{2}} \right) \, dF(\gamma) \right\} \\ &= \frac{8K\pi^2}{\alpha_1\alpha_2} \left\{ 2F(0) \sinh \alpha_1 \sinh \alpha_2 \right. \\ &\quad \left. + \int_{\gamma=0}^{\pi} \cosh \left([\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos \gamma]^{\frac{1}{2}} \right) \, dF(\gamma) \right\}. \end{aligned} \quad (52)$$

From the definition of K [see Equation (38)] we can write

$$\mathfrak{S} = \frac{1}{2 \sinh \alpha_1 \sinh \alpha_2} \times \int_{\gamma=0}^{\pi} \cosh \left[(\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos \gamma)^{\frac{1}{2}} \right] \, dF(\gamma) + F(0); \quad (53)$$

which is essentially Onsager's expression (B14) [37]. For identical particles $\alpha = \alpha_1 = \alpha_2$ the expression for the

configurational functional may be simplified to

$$\mathfrak{S} = \frac{1}{2 \sinh^2 \alpha} \int_{\gamma=0}^{\pi} \cosh \left\{ \alpha [2(1 + \cos \gamma)]^{\frac{1}{2}} \right\} \, dF(\gamma) + F(0) \quad (54)$$

$$= \frac{1}{2 \sinh^2 \alpha} \int_{\gamma=0}^{\pi} \cosh \left[2\alpha \cos \left(\frac{\gamma}{2} \right) \right] \, dF(\gamma) + F(0). \quad (55)$$

These two last expressions will become the workhorse for the evaluation of the orientational average for a general function of the relative orientation $F(\gamma)$ using Onsager's trial function, which provides a solution for the configurational functional $\mathcal{F}_{\text{conf}}[f]$. It is important to highlight that one is not restricted to the excluded volume form $F(\gamma) \propto \sin \gamma$ examined by Onsager. We use these expressions as the starting point for the illustrations that follow; depending on the problem at hand either of the forms given as Equations (54) and (55) may turn out to be more convenient.

We proceed to calculate $\mathcal{F}_{\text{conf}}[f]$ in which the excluded volume is given by the general expression (34), which is a polynomial in $\sin \gamma$. Each term in $\sin \gamma$ gives an integral which may be solved using Onsager's method. In order to illustrate the generality of the technique, we consider

the case for some $F(\gamma) = F_n$ defined by

$$F_0 = F_0(0) = C_0, \quad \therefore dF_0(0) = 0,$$

$$F_n = C_n \sin^n \gamma \quad \therefore d(F_n) = nC_n \sin^{n-1} \gamma \cos \gamma d\gamma.$$

The configurational functionals can be approximated by using the Onsager trial function $\mathcal{F}_{\text{conf}}[f_{\text{OTF}}]$ in terms of a sum over the corresponding integrals:

$$\mathcal{F}_{\text{conf}}[f_{\text{OTF}}] = \frac{1}{V_m} \sum_i \mathfrak{S}(F_i) \equiv \frac{1}{V_m} \sum_i \mathfrak{S}_i. \quad (56)$$

Using either of Equations (54) or (55) yields trivially $\mathfrak{S}_0 = C_0$, and the first four non-trivial such integrals for identical particles are given by

$$\mathfrak{S}_1 = \frac{C_1}{2 \sinh^2 \alpha} \int_{\gamma=0}^{\pi} \cosh \left(2\alpha \cos \left(\frac{\gamma}{2} \right) \right) \cos \gamma d\gamma \quad \propto \langle \sin \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2}; \quad (57)$$

$$\mathfrak{S}_2 = \frac{C_2}{\sinh^2 \alpha} \int_{\gamma=0}^{\pi} \cosh \left(\alpha [2(1 + \cos \gamma)]^{\frac{1}{2}} \right) \sin \gamma \cos \gamma d\gamma \quad \propto \langle \sin^2 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2}; \quad (58)$$

$$\mathfrak{S}_3 = \frac{3C_3}{2 \sinh^2 \alpha} \int_{\gamma=0}^{\pi} \cosh \left(2\alpha \cos \left(\frac{\gamma}{2} \right) \right) \sin^2 \gamma \cos \gamma d\gamma \quad \propto \langle \sin^3 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2}; \quad (59)$$

$$\mathfrak{S}_4 = \frac{2C_4}{\sinh^2 \alpha} \int_{\gamma=0}^{\pi} \cosh \left(\alpha [2(1 + \cos \gamma)]^{\frac{1}{2}} \right) \sin^3 \gamma \cos \gamma d\gamma \quad \propto \langle \sin^4 \gamma \rangle_{\bar{\omega}_1, \bar{\omega}_2}. \quad (60)$$

\mathfrak{S}_1 corresponds to the integral of the leading term of the excluded volume of a cylinder or a spherocylinder (in the latter case it is the only angular-dependent term), and is the example considered by Onsager [37]. As will be seen in section III, \mathfrak{S}_2 and \mathfrak{S}_4 will be useful in obtaining an analytical expression for the order parameters S_2 and S_4 . The usefulness of \mathfrak{S}_3 is less obvious, however it turns out that this form of integral occurs when nematogens with attractive interactions are considered [167]. Integrals \mathfrak{S}_1 , \mathfrak{S}_2 and \mathfrak{S}_4 can also be used to provide analytical solutions for molecules interacting through an anisotropic potential resembling that proposed by Maier and Saupe [167]. The integrals developed in the functional fall into two classes: those with an odd-number index, in which the power of $\sin \gamma$ in the integrand is even (including zero), *e.g.*, Equations (57) and (59), which can conveniently be written in the form of Equation (55) (as will be shown later); those with an even-number index, in which the power of $\sin \gamma$ is odd, *e.g.*, Equation (58) and Equation (60), are conveniently written in the form of Equation (54).

The former class, with odd-number index, give rise to linear combinations of modified Bessel functions. The general form of this class of integral is \mathfrak{S}_{2n+1} for some

integer n (including zero):

$$\begin{aligned} \mathfrak{S}_{2n+1} &= \frac{(2n+1)C_{2n+1}}{2 \sinh^2 \alpha} \\ &\times \int_{\gamma=0}^{\pi} \cosh \left(2\alpha \cos \left(\frac{\gamma}{2} \right) \right) \sin^{2n} \gamma \cos \gamma d\gamma \\ &= \frac{(2n+1)C_{2n+1}}{2 \sinh^2 \alpha} \\ &\times \int_{\gamma=0}^{\pi} \cosh \left(2\alpha \cos \left(\frac{\gamma}{2} \right) \right) (1 - \cos^2 \gamma)^n \cos \gamma d\gamma. \end{aligned} \quad (61)$$

Expanding the product $(1 - \cos^2 \gamma)^n$, this integral decomposes into a series of integrals of the form $\mathfrak{S}_{2n+1} = \sum_i a_i \mathcal{I}_i$, where

$$\mathcal{I}_i = \int_{\gamma=0}^{\pi} \cosh \left(2\alpha \cos \left(\frac{\gamma}{2} \right) \right) \cos^{2i+1} \gamma d\gamma, \quad (62)$$

and a_i are prefactors to be determined and are functions of the index i ; the actual forms of these prefactors are not important for this discussion. In each integral \mathcal{I}_i , $\cos \gamma$ appears in the integrand raised to an odd integer

power, $2i + 1$. An integer power of $\cos \gamma$ can be expressed as some combination of cosines of integer multiples of γ [e.g., $\cos^3 \gamma = (\cos 3\gamma + 3 \cos \gamma)/4$]. The integral \mathfrak{S}_{2n+1} can be further rationalised as some combination $\sum_j a_j \mathcal{I}_j$ of integrals of the form

$$\mathcal{I}_j = \int_{\gamma=0}^{\pi} \cosh \left(2\alpha \cos \left(\frac{\gamma}{2} \right) \right) \cos j\gamma \, d\gamma, \quad (63)$$

where j represents an integer index, and the a_j are new prefactors to be determined. Substituting $u = \gamma/2$ this integral becomes

$$\begin{aligned} \mathcal{I}_j &= 2 \int_{u=0}^{\pi/2} \cosh(2\alpha \cos u) \cos 2ju \, du \\ &= \int_{u=0}^{\pi/2} \exp(2\alpha \cos u) \cos(2ju) \, du \\ &\quad + \int_{u=0}^{\pi/2} \exp(-2\alpha \cos u) \cos(2ju) \, du. \end{aligned} \quad (64)$$

This may be simplified by recognising that

$$\begin{aligned} \int_{u=0}^{\pi/2} \exp(-2\alpha \cos u) \cos(2ju) \, du \\ = \int_{u=\pi/2}^{\pi} \exp(2\alpha \cos u) \cos(2ju) \, du, \end{aligned} \quad (65)$$

which can be seen by considering the series representations of the exponentials, differing only in the sign of the odd powers of the cosines, and noting the correspondence between cosines in the interval $[0, \pi/2]$ and the negatives of cosines in the interval $[\pi/2, \pi]$. Thus \mathcal{I}_j can be written in the form of the standard integral representation [168] of a modified Bessel function,

$$\mathcal{I}_j = \int_{u=0}^{\pi} \exp(2\alpha \cos u) \cos(2ju) \, du = \pi I_{2j}(2\alpha), \quad (66)$$

giving a general form for the odd-number-indexed integral in terms of modified Bessel functions:

$$\mathfrak{S}_{2n+1} = \frac{\pi(2n+1)C_{2n+1}}{2 \sinh^2 \alpha} \sum_j a_j I_{2j}(2\alpha). \quad (67)$$

There are several options for dealing with modified Bessel functions [169]. Derivatives may be conveniently obtained using the relation

$$2I'_\nu(x) = I_{\nu-1}(x) + I_{\nu+1}(x) \quad (68)$$

wherein the recurrence relation, $I_{\nu-1}(x) - I_{\nu+1}(x) = (2\nu/x)I_\nu(x)$, gives in particular

$$\begin{aligned} \frac{\partial I_{2j}(2\alpha)}{\partial \alpha} &= 2 \left(I_{2j-1}(2\alpha) - \frac{j I_{2j}(2\alpha)}{\alpha} \right) \\ &= 2 \left(I_{2j+1}(2\alpha) + \frac{j I_{2j}(2\alpha)}{\alpha} \right). \end{aligned} \quad (69)$$

For ($x \leq 12$ or $x \leq \nu$), $I_\nu(x)$ is most conveniently calculated using the power series:

$$I_\nu(x) = \sum_{i=0}^{\infty} \frac{1}{i!(i+\nu)!} \left(\frac{x}{2} \right)^{2i+\nu}. \quad (70)$$

The following asymptotic expansion is preferred when ($x > 12$ and $x > \nu$) [169]:

$$\begin{aligned} I_\nu(x) &= \frac{e^x}{\sqrt{2\pi x}} \\ &\times \left\{ 1 + \sum_{i=1}^{\infty} (-1)^i \left(\frac{\prod_{j=1}^i 4\nu^2 - (2j-1)^2}{i!(8x)^i} \right) \right\}. \end{aligned} \quad (71)$$

In practise at the transition between the isotropic and nematic phase a value $\alpha \sim 10$ or higher is found, so in this case the asymptotic-expansion formula would be the more convenient choice; for the contribution of the leading term $I_2(2\alpha)$, this yields

$$\begin{aligned} I_2(2\alpha) &= \frac{\exp(2\alpha)}{2\sqrt{\pi\alpha}} \left\{ 1 - \frac{15}{16\alpha} + \frac{105}{512\alpha^2} \right. \\ &\quad \left. + \frac{315}{8192\alpha^3} + \frac{10395}{524288\alpha^4} + \dots \right\}. \end{aligned} \quad (72)$$

We illustrate this class of solution by considering the first and third integrals, \mathfrak{S}_1 and \mathfrak{S}_3 , as given in Equations (57) and (59). The first is solved immediately by inspection from Equation (66):

$$\begin{aligned} \mathfrak{S}_1 &= \frac{C_1}{2 \sinh^2 \alpha} \int_{\gamma=0}^{\pi} \cosh \left(2\alpha \cos \left(\frac{\gamma}{2} \right) \right) \cos \gamma \, d\gamma \\ &= \frac{C_1}{2 \sinh^2 \alpha} \pi I_2(2\alpha). \end{aligned} \quad (73)$$

This key result was obtained by Onsager [37]. The third integral is almost as simple:

$$\begin{aligned} \mathfrak{S}_3 &= \frac{3C_3}{2 \sinh^2 \alpha} \int_{\gamma=0}^{\pi} \cosh \left(2\alpha \cos \left(\frac{\gamma}{2} \right) \right) \sin^2 \gamma \cos \gamma \, d\gamma \\ &= \frac{3C_3}{2 \sinh^2 \alpha} \\ &\times \int_{\gamma=0}^{\pi} \cosh \left(2\alpha \cos \left(\frac{\gamma}{2} \right) \right) (\cos \gamma - \cos^3 \gamma) \, d\gamma. \end{aligned} \quad (74)$$

After substitution of $\cos^3 \gamma = \frac{1}{4} (\cos 3\gamma + 3 \cos \gamma)$,

$$\begin{aligned} \mathfrak{S}_3 &= \frac{3C_3}{2 \sinh^2 \alpha} \\ &\times \left\{ \frac{1}{4} \left[\int_{\gamma=0}^{\pi} \cosh \left(2\alpha \cos \left(\frac{\gamma}{2} \right) \right) \cos \gamma \, d\gamma \right. \right. \\ &\left. \left. - \int_{\gamma=0}^{\pi} \cosh \left(2\alpha \cos \left(\frac{\gamma}{2} \right) \right) \cos 3\gamma \, d\gamma \right] \right\}, \quad (75) \end{aligned}$$

for which Equation (66) gives the solution by inspection:

$$\mathfrak{S}_3 = \frac{3C_3}{2 \sinh^2 \alpha} \left\{ \frac{\pi}{4} (I_2(2\alpha) - I_6(2\alpha)) \right\}. \quad (76)$$

This is a key result for systems with attractions; it concludes our discussion of the first class of integral, of odd-numbered index, \mathfrak{S}_{2n+1} .

The second class of integral, with even-numbered index, \mathfrak{S}_{2n} , appears as

$$\begin{aligned} \mathfrak{S}_{2n} &= \frac{2nC_{2n}}{2 \sinh^2 \alpha} \\ &\times \int_{\gamma=0}^{\pi} \cosh \left(\alpha [2(1 + \cos \gamma)]^{\frac{1}{2}} \right) \sin^{2n-1} \gamma \cos \gamma \, d\gamma. \quad (77) \end{aligned}$$

This type of integral can always be solved analytically in a straightforward manner. The substitution

$$u = (1 + \cos \gamma)^{\frac{1}{2}}, \quad d\gamma = \frac{-2udu}{\sin \gamma}, \quad \cos \gamma = u^2 - 1, \quad (78)$$

is made so that the integral becomes

$$\begin{aligned} \mathfrak{S}_{2n} &= \frac{2nC_{2n}}{\sinh^2 \alpha} \\ &\times \int_{u=0}^{\sqrt{2}} \cosh \left(\alpha \sqrt{2}u \right) (u^2 - 1) u(2u^2 - u^4)^{n-1} du; \quad (79) \end{aligned}$$

the limits of integration the power $2(n-1)$ of $\sin \gamma$ is necessarily even, allowing the replacement of the sine term, via $(1 - \cos^2 \gamma)^{n-1}$, by $(2u^2 - u^4)^{n-1}$. The terms in u multiplying the cosh term will combine to form a simple polynomial, so that the integral decomposes into a combination of integrals $\mathfrak{S}_{2n} = \sum_k a_k \mathcal{I}_k$, where

$$\mathcal{I}_k = \int_{u=0}^{\sqrt{2}} \cosh \left(\alpha \sqrt{2}u \right) u^k du, \quad (80)$$

and the a_k are prefactors to be determined. Each integral \mathcal{I}_k can be routinely evaluated by successive integrations

by parts and will clearly give rise to a sum of terms involving $\sinh(2\alpha)$ and $\cosh(2\alpha)$. The integral \mathfrak{S}_2 , given as Equation (58), is evaluated in this way as

$$\begin{aligned} \mathfrak{S}_2 &= \frac{C_2}{\sinh^2 \alpha} \int_{\gamma=0}^{\pi} \cosh \left(2\alpha \cos \left(\frac{\gamma}{2} \right) \right) \sin \gamma \cos \gamma \, d\gamma \\ &= \frac{C_2}{\sinh^2 \alpha} \\ &\times \left\{ \sinh(2\alpha) \left[\frac{2}{\alpha} + \frac{6}{\alpha^3} \right] \right. \\ &\left. - \cosh(2\alpha) \left[\frac{5}{\alpha^2} + \frac{3}{\alpha^4} \right] - \frac{1}{\alpha^2} + \frac{3}{\alpha^4} \right\}. \quad (81) \end{aligned}$$

This is a key result for rod-like molecules. Similarly, \mathfrak{S}_4 , given as Equation (60), is evaluated as

$$\begin{aligned} \mathfrak{S}_4 &= \frac{4C_4}{\sinh^2 \alpha} \left\{ \cosh(2\alpha) \left[\frac{315}{\alpha^8} + \frac{585}{\alpha^6} + \frac{123}{\alpha^4} + \frac{4}{\alpha^2} \right] \right. \\ &\left. - \sinh(2\alpha) \left[\frac{630}{\alpha^7} + \frac{330}{\alpha^5} + \frac{30}{\alpha^3} \right] - \frac{315}{\alpha^8} + \frac{45}{\alpha^6} - \frac{3}{\alpha^4} \right\}. \quad (82) \end{aligned}$$

We note that this class of integral may also be evaluated from the order parameters using the addition theorem for spherical harmonics: \mathfrak{S}_2 may be evaluated from S_2 ; \mathfrak{S}_4 from S_4 and S_2 as will be shown in Section III.

G. General free energy with the Onsager trial function

By assuming that the orientational distribution function can be represented by the Onsager trial function, we are able to express the free energy of the nematogenic fluid explicitly as a function of α . Up to this point we have assumed an excluded-volume interaction expressed as a sum of terms proportional to increasing powers of $\sin \gamma$. Here we take this sum only as high as the fourth power, *i.e.*, $V_{\text{exc}} = \sum_{i=1}^4 C_i \sin^i \gamma$, requiring the integrals \mathfrak{S}_1 to \mathfrak{S}_4 that we calculated explicitly in Section II F. This is sufficiently general to accurately describe the excluded volume interaction of most commonly encountered cylindrically symmetrical model mesogens. The term in C_1 corresponds to the case studied by Onsager describing the free energy of a system of long rods. For hard spherocylinders the terms in C_0 and C_1 suffice to represent the free energy of the system; terms up to C_4 may be needed in order to capture the effects of more complicated forms of excluded volume.

We may write Equations (17) for the simple Onsager free energy or (25) for the Onsager free energy with the Parsons-Lee correction in the general form

$$\frac{A_{\text{OTF}}}{NkT} = \frac{A_{\text{iso}}^{\text{id}}}{NkT} + \mathcal{F}_{\text{orient}} [f_{\text{OTF}}] + G(\rho) \mathcal{F}_{\text{conf}} [f_{\text{OTF}}] \quad (83)$$

where the density dependence is introduced through the function $G(\rho)$ which takes the simple linear form for the original Onsager free energy or the equivalent hard-sphere form in the case of the Parsons-Lee correction. By using the Onsager trial function, the expressions for $\mathcal{F}_{\text{orient}} [f_{\text{OTF}}]$ and $\mathcal{F}_{\text{conf}} [f_{\text{OTF}}]$ are written as a function of

α as (see Sections II E and II F):

$$\mathcal{F}_{\text{orient}} [f_{\text{OTF}}] = \ln(\alpha \coth \alpha) - 1 + \frac{\arctan(\sinh \alpha)}{\sinh \alpha}, \quad (84)$$

and

$$\begin{aligned} \mathcal{F}_{\text{conf}} [f_{\text{OTF}}] = & C_0^* + C_1^* \frac{\pi I_2(2\alpha)}{2 \sinh^2 \alpha} \\ & + C_2^* \frac{1}{\sinh^2 \alpha} \left\{ \sinh(2\alpha) \left[\frac{2}{\alpha} + \frac{6}{\alpha^3} \right] - \cosh(2\alpha) \left[\frac{5}{\alpha^2} + \frac{3}{\alpha^4} \right] - \frac{1}{\alpha^2} + \frac{3}{\alpha^4} \right\} \\ & + C_3^* \frac{3\pi (I_2(2\alpha) - I_6(2\alpha))}{8 \sinh^2 \alpha} \\ & + C_4^* \frac{4}{\sinh^2 \alpha} \left\{ \cosh(2\alpha) \left[\frac{315}{\alpha^8} + \frac{585}{\alpha^6} + \frac{123}{\alpha^4} + \frac{4}{\alpha^2} \right] - \sinh(2\alpha) \left[\frac{630}{\alpha^7} + \frac{330}{\alpha^5} + \frac{30}{\alpha^3} \right] - \frac{315}{\alpha^8} + \frac{45}{\alpha^6} - \frac{3}{\alpha^4} \right\}. \end{aligned} \quad (85)$$

To determine the value of α that minimises the free energy, the free energy is differentiated with respect to α :

$$\begin{aligned} \left(\frac{\partial A_{\text{OTF}}/NkT}{\partial \alpha} \right)_{NVT} &= 0 \\ &= \left(\frac{\partial \mathcal{F}_{\text{orient}} [f_{\text{OTF}}]}{\partial \alpha} \right)_{NVT} \\ &+ G(\rho) \left(\frac{\partial \mathcal{F}_{\text{conf}} [f_{\text{OTF}}]}{\partial \alpha} \right)_{NVT}. \end{aligned} \quad (86) \quad \text{and}$$

The terms incorporating Bessel functions are easily differentiated making use of the rule given in Equation (69). The derivatives of the Onsager orientational and configurational functionals in terms of α are written as:

$$\frac{\partial \mathcal{F}_{\text{orient}} [f_{\text{OTF}}]}{\partial \alpha} = \frac{1}{\alpha} - \frac{\arctan(\sinh \alpha) \cosh \alpha}{\sinh^2 \alpha}, \quad (87)$$

$$\begin{aligned} \frac{\partial \mathcal{F}_{\text{conf}} [f_{\text{OTF}}]}{\partial \alpha} = & C_1^* \frac{\pi}{\sinh^2 \alpha} \left\{ \frac{\alpha I_4(2\alpha)}{3} + I_2(2\alpha) \left[\frac{\alpha^2 + 3}{3\alpha} - \coth \alpha \right] \right\} \\ & + C_2^* \frac{2}{\sinh^2 \alpha} \left\{ \cosh(2\alpha) \left[\frac{2}{\alpha} + \frac{11}{\alpha^3} + \frac{6}{\alpha^5} \right] - \sinh(2\alpha) \left[\frac{6}{\alpha^2} + \frac{12}{\alpha^4} \right] + \frac{1}{\alpha^3} - \frac{6}{\alpha^5} \right\} \\ & + C_3^* \frac{3\pi}{4 \sinh^2 \alpha} \left\{ I_4(2\alpha) \left[\frac{2}{\alpha} - \frac{(2\alpha^2 + 60) \coth \alpha}{3\alpha^2} - \frac{60}{\alpha^3} \right] - I_2(2\alpha) \left[\frac{4}{\alpha} + \frac{8 \coth \alpha}{3} \right] \right\} \\ & + C_4^* \frac{8}{\sinh^2 \alpha} \left\{ \frac{2520}{\alpha^9} - \frac{2430}{\alpha^7} + \frac{12}{\alpha^5} + \sinh(2\alpha) \left[\frac{2520}{\alpha^8} + \frac{1410}{\alpha^6} + \frac{168}{\alpha^4} + \frac{4}{\alpha^2} \right] \right. \\ & - \cosh(2\alpha) \left[\frac{1260}{\alpha^9} + \frac{2385}{\alpha^7} + \frac{576}{\alpha^5} + \frac{34}{\alpha^3} \right] + \coth \alpha \left(\frac{315}{\alpha^8} - \frac{45}{\alpha^6} + \frac{3}{\alpha^4} + \sinh(2\alpha) \left[\frac{630}{\alpha^7} + \frac{330}{\alpha^5} + \frac{30}{\alpha^3} \right] \right. \\ & \left. \left. - \cosh(2\alpha) \left[\frac{315}{\alpha^8} + \frac{585}{\alpha^6} + \frac{123}{\alpha^4} + \frac{4}{\alpha^2} \right] \right) \right\}. \end{aligned} \quad (88)$$

Judicious use of the recurrence relation, $I_{\nu-1}(2\alpha) + I_{\nu+1}(2\alpha) = \nu\alpha^{-1} I_{\nu}(2\alpha)$, enables one to express the derivative in terms of only two modified Bessel functions; here we choose to write the expression in terms

of I_2 and I_4 . These analytical expressions can be solved numerically for the equilibrium value of ordering parameter $\alpha = \alpha_{\text{eq}}$ corresponding to the minimum in the free energy.

The phase equilibria between an isotropic and anisotropic (nematic) fluid states is established by invoking the conditions of mechanical and chemical equilibrium. This involves equating the pressure and chemical potential for the isotropic and nematic phases using the usual thermodynamic relations $\mu = (\partial A/\partial N)_{V,T}$ and $p = -(\partial A/\partial V)_{N,T}$, where in the case of the nematic state the derivatives correspond to the state with the minimum Helmholtz free energy.

III. CALCULATING ORDER PARAMETERS, S_n

Orientational order parameters, S_n , are commonly used to characterise the degree of order of the phase. If the orientational distribution function of a fluid (nematogen) is $f(\theta)$ then S_n can be defined by

$$S_n = \int P_n(\cos(\theta))f(\theta)d\vec{\omega}, \quad (89)$$

where $P_n(\cos(\theta))$ is the n th Legendre polynomial. For example, $n = 2$ yields the nematic order parameter, which quantifies the degree of nematic order in the fluid ($S_2 = 0$ for an isotropic fluid, and $S_2 = 1$ for a perfectly ordered nematic). When the Onsager trial function is used to represent the orientational distribution, the order parameter becomes a function of α_{eq} that is representative of the equilibrium fluid. After substitution of the Onsager trial function, the calculation of the order parameter is facilitated by the further substitution $u = \alpha_{\text{eq}} \cos \theta$. For example, the nematic order parameter is simply obtained performing the integration by parts

$$S_2 = \frac{1}{4 \sinh \alpha_{\text{eq}}} \times \left\{ \frac{3}{(\alpha_{\text{eq}})^2} \int_{u=-\alpha_{\text{eq}}}^{\alpha_{\text{eq}}} u^2 \cosh u \, du - \int_{u=-\alpha_{\text{eq}}}^{\alpha_{\text{eq}}} \cosh u \, du \right\} = 1 - \frac{3 \coth \alpha_{\text{eq}}}{\alpha_{\text{eq}}} + \frac{3}{(\alpha_{\text{eq}})^2}. \quad (90)$$

This simple but useful relation has been noted in references [108, 161]. In similar fashion, S_4 is evaluated from $P_4(\cos \theta) = (35 \cos^4 \theta - 30 \cos^2 \theta + 3)/8$ as

$$S_4 = 1 + \frac{45}{(\alpha_{\text{eq}})^2} + \frac{105}{(\alpha_{\text{eq}})^4} - \coth \alpha_{\text{eq}} \left(\frac{10}{\alpha_{\text{eq}}} + \frac{105}{(\alpha_{\text{eq}})^3} \right). \quad (92)$$

The parameter S_4 can be used to quantify the degree of cubatic order in a system [170].

We can use S_{2n} as an alternative route to calculate the integrals \mathfrak{S}_{2n} , which were introduced in Section II F, using the addition theorem for spherical harmonics:

$$P_n(\cos \gamma) = P_n(\cos \theta_1)P_n(\cos \theta_2) + 2 \sum_{m=1}^n \frac{(n-m)!}{(n+m)!} \cos(m(\phi_1 - \phi_2)) \times P_n^m(\cos \theta_1)P_n^m(\cos \theta_2). \quad (93)$$

We illustrate here the case for \mathfrak{S}_2 . Taking the angle average (denoted by angular brackets) of P_2 yields

$$\begin{aligned} \langle P_2(\cos \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} &= S_2^2 \\ &= \iint P_2(\cos \theta_1)P_2(\cos \theta_2)f(\vec{\omega}_1)f(\vec{\omega}_2)d\vec{\omega}_1d\vec{\omega}_2 \\ &= \int P_2(\cos \theta_1)f(\theta_1)d\vec{\omega}_1 \int P_2(\cos \theta_2)f(\theta_2)d\vec{\omega}_2. \end{aligned} \quad (94)$$

The sum of terms in the azimuthal angles vanishes on integration since it leads to a sum of integrals from each of which the term $\int_{\phi=0}^{2\pi} \cos(m\phi)d\phi = 0$ can be factored.

If $P_2(\cos(\gamma))$ is written in terms of $\sin \gamma$ as $P_2(\cos(\gamma)) = 1 - (3/2)\sin^2 \gamma$, then

$$S_2^2 = \langle P_2(\cos \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} = 1 - \frac{3}{2} \langle \sin^2 \gamma \rangle_{\vec{\omega}_1, \vec{\omega}_2}. \quad (95)$$

A re-examination of integrals outlined in Section II F reveals that $\langle \sin^2 \gamma \rangle_{\vec{\omega}_1, \vec{\omega}_2} = \mathfrak{S}_2/C_2$, which means that we can express S_2 as a simple function of \mathfrak{S}_2 or, alternatively, that we can write the solution for \mathfrak{S}_2 [Equation (81)] directly from Equation (91) as

$$\mathfrak{S}_2 = \frac{2C_2}{3} \left\{ 1 - \left[1 - \frac{3 \coth \alpha_{\text{eq}}}{\alpha_{\text{eq}}} + \frac{3}{\alpha_{\text{eq}}^2} \right]^2 \right\}. \quad (96)$$

Equation (81) reduces to this expression if the double-angle formulae, $\cosh(2\alpha) = \cosh^2 \alpha + \sinh^2 \alpha$ and $\sinh(2\alpha) = 2 \sinh \alpha \cosh \alpha$, are invoked, together with the identity $\coth^2 \alpha = 1 + 1/(\sinh^2 \alpha)$.

In similar fashion, we can determine the order parameter S_4 . The fourth Legendre polynomial is defined as

$$\begin{aligned} P_4(\cos \gamma) &= \frac{1}{8} (35 \cos^4 \gamma - 30 \cos^2 \gamma + 3) \\ &= \frac{1}{8} (35 \sin^4 \gamma - 40 \sin^2 \gamma + 8). \end{aligned} \quad (97)$$

We can therefore express S_4 as the average

$$\begin{aligned} \langle P_4(\cos \gamma) \rangle_{\vec{\omega}_1, \vec{\omega}_2} &= S_4^2 = \frac{35}{8} \langle \sin^4 \gamma \rangle_{\vec{\omega}_1, \vec{\omega}_2} \\ &\quad - 5 \langle \sin^2 \gamma \rangle_{\vec{\omega}_1, \vec{\omega}_2} + 1; \end{aligned} \quad (98)$$

and since, by definition, $\langle \sin^4 \gamma \rangle_{\vec{\omega}_1, \vec{\omega}_2} = \mathfrak{S}_4/C_4$ while $\langle \sin^2 \gamma \rangle_{\vec{\omega}_1, \vec{\omega}_2} = \mathfrak{S}_2/C_2$ as noted earlier, this gives

$$\begin{aligned} \mathfrak{S}_4 &= \frac{8C_4}{35} \left\{ S_4^2 + \frac{10}{3} (1 - S_2^2) - 1 \right\} \\ &= 8C_4 \left\{ \frac{2}{(\alpha_{\text{eq}})^2} + \frac{63}{(\alpha_{\text{eq}})^4} + \frac{270}{(\alpha_{\text{eq}})^6} + \frac{315}{(\alpha_{\text{eq}})^8} \right. \\ &\quad \left. - 2 \coth \alpha_{\text{eq}} \left[\frac{15}{(\alpha_{\text{eq}})^3} + \frac{165}{(\alpha_{\text{eq}})^5} + \frac{315}{(\alpha_{\text{eq}})^7} \right] \right. \\ &\quad \left. + \coth^2 \alpha_{\text{eq}} \left[\frac{2}{(\alpha_{\text{eq}})^2} + \frac{60}{(\alpha_{\text{eq}})^4} + \frac{315}{(\alpha_{\text{eq}})^6} \right] \right\}. \end{aligned} \quad (99)$$

The higher integrals \mathfrak{S}_i for even i can be obtained in an analogous manner from the corresponding S_i .

IV. ALGEBRAIC EQUATION OF STATE FOR THE NEMATIC PHASE OF HARD SPHEROCYLINDERS

There are a number of reasons why the Onsager theory for isotropic-nematic phase equilibria is not commonly employed in engineering applications. Firstly, the Onsager treatment is not easy to follow, particularly if one is interested in generalising the approach to deal with more realistic systems and include attractive interactions. Even if the general expression for the Helmholtz free energy of the system is specified using the relatively simple Onsager trial function (Section II G), the expression involves Bessel integrals, and a numerical solution of a non-linear equation is required in order to establish the equilibrium orientational state of the system. Though the other thermodynamic properties, such as the pressure and chemical potential, can then easily be obtained from density derivatives of the free energy, a subsequent numerical solution for the conditions of equality of pressure and chemical potential is necessary in order to establish the isotropic-nematic equilibria. The numerical difficulties are particularly severe in the case of multicomponent mixtures. The common equations of state used in practice to describe fluid phase equilibria [171] are algebraic functions of the thermodynamic variables (e.g., temperature, density, and composition) and the molecular parameters, which makes the solution of the coexistence much easier; the van der Waals [172] equation is the seminal example of an algebraic (in this case cubic in density) equation of state of the fluid phase.

In order to make the Onsager approach more amenable within an engineering context it is highly desirable to cast the thermodynamic expressions in a closed algebraic form. We achieve this by expanding the general Onsager free energy developed in Section II G in terms of the parameter α to provide a tractable solution of the equilibrium state of the system. This is relatively straightforward once the orientational $\mathcal{F}_{\text{orient}}[f_{\text{OTF}}]$ and configurational $\mathcal{F}_{\text{conf}}[f_{\text{OTF}}]$ functionals have been expressed in terms of α . For a typical nematic state $\alpha \sim 10$ which corresponds to a nematic order parameter of $S_2 \sim 0.73$ [Equation (90)]; S_2 at the isotropic-nematic transition is usually greater than 50%. In the case of the orientational entropy [cf. Equation (84)], the last two terms are negligible when $\alpha \gg 1$:

$$\begin{aligned} \mathcal{F}_{\text{orient}}[f_{\text{OTF}}] &= \ln(\alpha) - 1 + \ln(\coth \alpha) \\ &+ \frac{\arctan(\sinh \alpha)}{\sinh \alpha} \\ &\approx \ln(\alpha) - 1, \end{aligned} \quad (100)$$

since $\ln(\coth \alpha) = \ln[(e^\alpha + e^{-\alpha})/(e^\alpha - e^{-\alpha})] \rightarrow 0$, and $\arctan(\sinh \alpha)/\sinh \alpha \rightarrow 0$. This is the approximation originally used by Onsager [37]. When a hard spherocylinder (cylinder of length L capped by hemispheres of diameter D) is used to describe the rod-like mesogen the excluded volume is exactly given by

$V_{\text{exc}}(\sin \gamma) = C_0 + C_1 \sin \gamma$, with $C_0 = \frac{4}{3}\pi D^3 + 2\pi D^2 L$ and $C_1 = 2L^2 D$ [37], and the molecular volume is simply $V_m = \pi D^3/6 + \pi L D^2/4$. The configurational functional [Equation (85)] for hard spherocylinders is thus given simply by

$$\mathcal{F}_{\text{conf}}[f_{\text{OTF}}] = C_0^* + C_1^* \frac{\pi I_2(2\alpha)}{2 \sinh^2 \alpha}, \quad (101)$$

where $C_0^* = C_0/V_m$ and $C_1^* = C_1/V_m$. This contribution can be rigorously evaluated by means of a numerical method to compute the modified Bessel function $I_2(2\alpha)$. In order to develop the desired compact algebraic form we choose to write the Bessel function as an asymptotic expansion in the orientational parameter α for which the general form is given by Equation (71):

$$\begin{aligned} I_2(2\alpha) &= \frac{\exp(2\alpha)}{2\sqrt{\pi\alpha}} \left\{ 1 - \frac{15}{16\alpha} + \frac{105}{512\alpha^2} + \frac{315}{8192\alpha^3} + \dots \right\} \\ &\approx \frac{\exp(2\alpha)}{2\sqrt{\pi\alpha}} \left\{ 1 - \frac{15}{16\alpha} + \mathcal{O}(\alpha^{-2}) \right\}. \end{aligned} \quad (102)$$

Clearly, only the first couple of terms in the series are required to describe a highly ordered nematic state where $\alpha \gg 1$. Substituting the truncated asymptotic expansion into Equation (101) yields

$$\mathcal{F}_{\text{conf}}[f_{\text{OTF}}] \approx C_0^* + C_1^* \sqrt{\frac{\pi}{\alpha}} \left\{ 1 - \frac{15}{16\alpha} \right\}, \quad (103)$$

When the orientational and configurational functionals are approximated by their forms for moderately ordered systems (Equations (100) and (103)), the Helmholtz free energy [Equation (83)] becomes a simple function of α and the usual thermodynamic variables (N , V , and T):

$$\begin{aligned} \frac{A}{NkT} &\approx \frac{A_{\text{iso}}^{\text{id}}}{NkT} + \ln(\alpha) - 1 \\ &+ G(\rho) \left[C_0^* + C_1^* \sqrt{\frac{\pi}{\alpha}} \left\{ 1 - \frac{15}{16\alpha} \right\} \right]. \end{aligned} \quad (104)$$

The ideal isotropic term is the simple function of density $A_{\text{iso}}^{\text{id}}/NkT = \ln(\mathcal{V}\rho) - 1$ as defined earlier. At this stage we have an analytical expression for the equation of state for the nematic phase of a system of hard spherocylinders, described in terms of the Onsager trial function. In order to describe the high density states of molecules with a moderate aspect ratio (L/D), the Parsons-Lee relation (see Section II B) is used where $G(\rho) = G(\eta) = (A_{\text{res}}^{\text{hs}}/NkT)/8 = (4\eta - 3\eta^2)/[8(1 - \eta)^2]$, in terms of the packing fraction $\eta = \rho V_m$.

The degree of orientational order of the system at equilibrium is quantified by the value of $\alpha = \alpha_{\text{eq}}$ which corresponds to a minimum in the nematic free energy. This is found in the usual way from an examination of the

derivative of Equation (104) with respect to α :

$$\begin{aligned} \frac{\partial}{\partial \alpha} \left(\frac{A}{NkT} \right)_{N,V,T} &= \frac{\partial \mathcal{F}_{\text{orient}} [f_{\text{OTF}}]}{\partial \alpha} + G(\rho) \frac{\partial \mathcal{F}_{\text{conf}} [f_{\text{OTF}}]}{\partial \alpha} \\ &\approx \frac{1}{\alpha} + G(\rho) C_1^* \sqrt{\pi} \left(\frac{45}{32 \alpha^{5/2}} - \frac{1}{2 \alpha^{3/2}} \right) \\ &= 0. \end{aligned} \quad (105)$$

For a fixed molecular aspect ratio this yields α as a function of the packing fraction, as intuitively expected. Defining the orientational variable $\Xi = \alpha^{1/2}$ and the coefficient $\zeta = -G(\rho) C_1^* \sqrt{\pi}/2$ we can rearrange Equation (105) as

$$\frac{1}{\Xi^5} \left\{ \Xi^3 + \zeta \Xi^2 - \frac{45\zeta}{16} \right\} = 0, \quad (106)$$

where the part of the expression enclosed in braces constitutes a cubic equation. This can be solved analytically to determine the equilibrium value of $\alpha = \alpha_{\text{eq}}$ as a function of the density of the fluid. Since our solution for α is in terms of a cubic polynomial, it is obvious that we will obtain three roots. The solution can be cast in the elegant geometric form of the general solution of a cubic which has been recently revised by Nickalls [173]:

$$\alpha_j = \frac{1}{9} \left\{ \zeta - 2\zeta \cos \left[\frac{2\pi}{3} j + \frac{1}{3} \arccos \left(\frac{1215}{32\zeta^2} - 1 \right) \right] \right\}^2, \quad (107)$$

where the value of $j = \{0, 1, 2\}$ denotes each root. As will become clear from an examination of the phase diagram shown in Section V, the root corresponding to the largest value of α , $\alpha_1 = \alpha_{\text{eq}}$ ($j = 1$), characterises the orientational order of the equilibrium nematic state with the lowest free energy. The roots representing the lowest and intermediate values of α would correspond to those for the ‘‘isotropic’’ (a small but finite α is obtained, when in reality $\alpha = 0$) and ‘‘metastable’’ states, though these should be viewed with considerable caution as the free-energy expression is obtained via truncation of the asymptotic expansion used to evaluate the modified Bessel function; this approximation is only valid for the larger values of α . At high densities there are always three positive solutions to Equation (107). As the density is lowered progressively below the isotropic-nematic transition one obtains a single positive real root (corresponding to a low ‘‘isotropic’’ value of α) and two imaginary roots; clearly the truncation that has been used for orientational and configurational terms does not provide a physically realistic representation of the system in this region. The equilibrium Helmholtz free energy of the nematic state $A(\alpha_{\text{eq}})$ is obtained from Equation (104) with the corresponding root for α_{eq} [cf. Equation (107) with $j = 1$]. One should mention that though Onsager [37] also examined a simple algebraic solution for α in terms of density by inverting the power series [cf. Equation (88) of his seminal paper], the adequacy of the approach is poor due to the simplifications made, see Figure (8).

As we will show, the use of a cubic solution does not compromise the accuracy of our approach in describing the nematic phase.

The corresponding expression for the chemical potential can also be expressed in closed algebraic form from the corresponding derivatives of the Helmholtz function:

$$\begin{aligned} \frac{\mu}{kT} &= \frac{\partial}{\partial N} \left(\frac{A}{kT} \right)_{VT} \\ &= \frac{\mu^0}{kT} + \ln(\eta) + \ln(\alpha_{\text{eq}}) - 1 \\ &\quad + G'(\rho) \left[C_0^* + C_1^* \sqrt{\frac{\pi}{\alpha_{\text{eq}}}} \left\{ 1 - \frac{15}{16\alpha_{\text{eq}}} \right\} \right], \end{aligned} \quad (108)$$

where the constant term is $\mu^0/kT = \ln[\mathcal{V}/(4\Omega V_m)]$, and the derivative of the Carnahan and Starling residual free energy is $G'(\rho) = G'(\eta) = \mu_{\text{hs}}^{\text{res}}/(8kT) = (3\eta^3 - 9\eta^2 + 8\eta)/[8(1 - \eta)^3]$. For the isotropic state the orientational term in Equation (108) is zero, $\ln(\alpha_{\text{eq}}) - 1 = 0$, and the terms between the square brackets are functions of the molecular parameters (D and L) and correspond simply to twice the average second virial coefficient, i.e., $2B_{2,\text{iso}}^* = C_0^* + \pi C_1^*/4$ [cf. Equation (35)].

The pressure p can also be obtained from the thermodynamic relationship $A = N\mu - pV$. The equation of state of the nematic phase of hard spherocylinders is thus expressed in the form of the compressibility factor as

$$\begin{aligned} Z &= \frac{pV}{NkT} = \frac{\mu}{kT} - \frac{A}{NkT} \\ &= 1 + \frac{Z_{\text{hs}}^{\text{res}}}{8} \left[C_0^* + C_1^* \sqrt{\frac{\pi}{\alpha_{\text{eq}}}} \left\{ 1 - \frac{15}{16\alpha_{\text{eq}}} \right\} \right], \end{aligned} \quad (109)$$

where the residual Carnahan and Starling [165] hard-sphere term is given in its usual form $Z_{\text{hs}}^{\text{res}} = \mu_{\text{res}}^{\text{hs}}/kT - A_{\text{res}}^{\text{hs}}/NkT = 2(2\eta - \eta^2)/(1 - \eta)^3$. It is important to reiterate that the expression is given in terms of the value of α_{eq} for the nematic phase with the minimum free energy. For the isotropic state the term in square brackets again corresponds to $2B_{2,\text{iso}}^*$. Interestingly, as the degree of orientational order characterised by α_{eq} is obtained from a cubic equation, the pressure of the nematic phase is essentially a cubic equation of state in the *orientational parameter* α . The well-known van der Waals equation of state for vapour-liquid equilibria [172] is a cubic equation of state in the *density* (molar volume) of the fluid; the widespread use of semi-empirical equations of state based on van der Waals’ approach in engineering applications stems from the fact that they can all be cast in a cubic form in the density. Though our analytical equation of state for the nematic phase cannot be expressed as a cubic function of density (it is based on the quartic Carnahan and Starling form), the fact that the degree of orientational order is obtained from a simple cubic equation in α will certainly make our approach much easier to apply in practice. An analogous approach can be developed to provide an algebraic equation of state for more

1 realistic models of mesogens which include attractive in-
 2 teractions (as we will show in a forthcoming publication);
 3 this allows one to examine vapour-liquid-nematic equilibria
 4 in thermotropic liquid crystalline systems.
 5

7 V. RESULTS AND DISCUSSION

10 We are now in a position to examine the adequacy of
 11 the use of an Onsager trial function to represent the ori-
 12 entational order in uniaxial molecules within an Onsager
 13 (or scaled Parsons-Lee) description of the nematic state.
 14 The original second-virial theory of Onsager [37] is ap-
 15 plicable only to molecules with large aspect ratios. The
 16 suitability of using a scaled Onsager free energy [81–83]
 17 in representing the isotropic-nematic phase transition in
 18 systems of hard ellipsoids [42, 83, 174, 175], hard spher-
 19 o-cylinders [11, 84], hard cylinders (oblate or prolate) [137–
 20 140], cut spheres [170], and hard-sphere chains [112, 176]
 21 has already been confirmed. Scaled Onsager theories
 22 which go beyond the original two-body theory of Onsager
 23 by including the higher-body terms in an approximate
 24 fashion provide an impressive description of the pressure
 25 and densities of the coexisting isotropic and nematic state
 26 (typically to an accuracy of better than 5% for molecules
 27 of moderate aspect ratio), and of the equation of state
 28 and degree of orientational order of the nematic phase.
 29 In the vast majority of these studies the orientational
 30 distribution function $f(\theta)$, which characterises the equi-
 31 librium ordered state, is obtained numerically by mini-
 32 mising the free energy, without constraining $f(\theta)$ to be
 33 of a particular functional form (e.g., by using the Gaus-
 34 sian or Onsager trial functions). In this case the integrals
 35 that define the orientational [Equation (6)] and configura-
 36 tional [Equation (16)] functionals are solved without
 37 need of approximations or assumptions. A full numeri-
 38 cal implementation of a scaled Onsager approach is not
 39 always the most advantageous in terms of ease of use,
 40 particularly if one is eventually interested in phase equi-
 41 libria of mixtures which require intensive computation.

42 The benefits of using a prescribed functional form for
 43 the orientational distribution function (such as that pro-
 44 posed by Onsager) arise from a reduction of the computa-
 45 tional demands of the problem from that of a variational
 46 problem [i.e., the evaluation of the convolution integral
 47 in Equation (27)] to the solution of the closed form equa-
 48 tion [such as Equation (86)]. In this section we show
 49 that the use of an Onsager trial function to describe the
 50 orientational distribution $f(\theta) \approx f_{\text{OTF}}(\theta)$ does not com-
 51 promise the adequacy of a scaled Onsager description of
 52 the isotropic-nematic transition. We also examine the
 53 accuracy of the truncated free energy where one can use
 54 a simple cubic solution for the orientational parameter α
 55 in terms of the density and molecular parameters, further
 56 simplifying the computations. Though the focus here is
 57 on a system of hard spherocylinders, the approach is ex-
 58 pected to be just as applicable to other simple models of
 59 mesogenic molecules.
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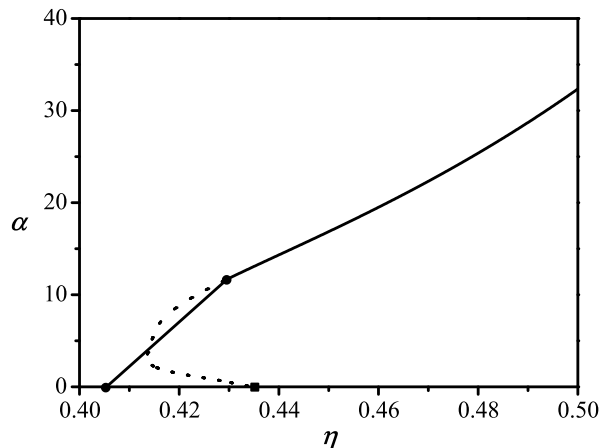


FIG. 3: The dependence of the variational parameter α on the packing fraction $\eta = \rho V_m$ for a system of hard spherocylinders of aspect ratio $L/D = 5$ determined from the scaled Onsager (Parsons-Lee) free energy [Equation (83)] described with the Onsager trial function $f_{\text{OTF}}(\theta)$. This represents the full numerical solution of the modified Bessel function for the state with the minimum free energy [Equation (85)]. The continuous curve corresponds to the stable nematic phase, and the dashed curve to the metastable/unstable states. The circles denote the isotropic-nematic phase transition ($\eta_I = 0.405$ and $\eta_N = 0.430$), and the square the bifurcation point ($\eta = 0.435$).

As we have already mentioned, the excluded volume for a pair of hard spherocylinders is given by $V_{\text{exc}}(\sin \gamma) = C_0 + C_1 \sin \gamma$, with $C_0 = \frac{4}{3}\pi D^3 + 2\pi D^2 L$ and $C_1 = 2L^2 D$. This simplifies the expression for the equilibrium value of the orientational parameter α (cf. Equation (88)) as the terms C_2 , C_3 and C_4 are all zero in this case. We have determined the equilibrium value α_{eq} for hard spherocylinders of aspect ratio $L/D = 5$ over a range of packing fractions η by solving Equation (85); standard quadrature is used to evaluate the Bessel function and a modified Newton-Raphson method [177] is used to solve for the roots in α . The density dependence of α_{eq} for the stable nematic phase of molecules with $L/D = 5$ is shown in Figure 3. As in the case of the truncated Onsager free energy developed in Section (IV), three positive roots for the values of α , corresponding to turning points in the free energy, are obtained at intermediate densities (see Figure 4 for a packing fraction of $\eta = 0.42$): the largest value is that of the nematic phase with the minimum free energy, the intermediate value is that of the metastable/unstable state, and the root $\alpha = 0$ is that of isotropic phase. For densities below the point of inflection seen in Figure 3 only the stable isotropic solution $\alpha = 0$ is found (see Figure 4 for $\eta = 0.4$). At densities above a bifurcation point (which for the $L/D = 5$ system is at $\eta \sim 0.435$) two roots are found corresponding to the stable nematic and isotropic states as can be seen

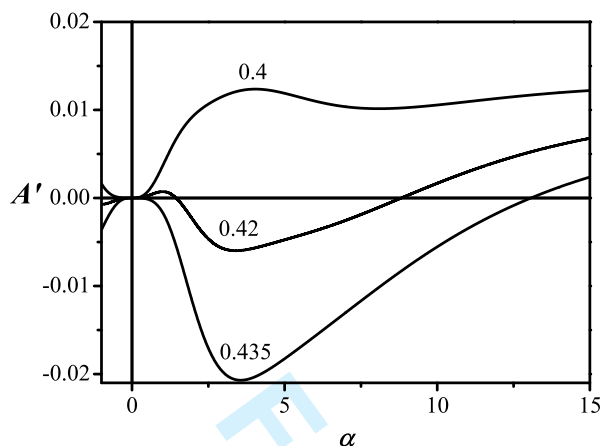


FIG. 4: The derivative $A' = \partial(A/NkT)/\partial\alpha$ of the scaled Onsager (Parsons-Lee) free energy [Equation (88)] as a function of the variational parameter α for a system of hard spherocylinders of aspect ratio $L/D = 5$. The stationary values in the free energy correspond to the points where the curves cross the x axis. In the case of the intermediate packing fraction of $\eta = \rho V_m = 0.42$ three roots can be seen: $\alpha = 0$, the isotropic state; $\alpha = 1.444$, the metastable/unstable nematic state; $\alpha = 8.823$, the stable nematic state. For the lower packing fraction of $\eta = 0.4$ only the isotropic solution $\alpha = 0$ is seen, while at (and beyond) the bifurcation density $\eta = 0.435$ only the isotropic $\alpha = 0$ and stable nematic solution $\alpha = 13.07$ are seen. The curves are symmetrical about the vertical axis, with equivalent negative roots in α (not shown).

in Figure 4, where the roots for $\partial(A/NkT)/\partial\alpha = 0$ for three different values of the packing fraction η are shown. The Onsager trial function is symmetrical about $\alpha = 0$ so equivalent negative roots are also found. The location of the isotropic-nematic transition is determined by numerically solving the conditions of mechanical and chemical equilibrium (see Section II G). The resulting coexistence values of the pressure, chemical potential and packing fractions of the isotropic and nematic states, and the corresponding values of α and nematic order parameter S_2 for hard spherocylinders ranging from $L/D = 3$ to 1000 are reported in Table I. The value of α at the isotropic-nematic transition for the $L/D = 5$ system (see Figure 3) is $\alpha_{\text{eq}} = 11.69$; in the case of the isotropic phase there is no orientational order which corresponds to $\alpha = 0$. The metastable root for α is also shown in Figure 3, and can be seen to extend from the transition point to lower values of α ; this branch does not correspond to a stable phase.

The orientational order of the phase is characterised by the nematic order parameter S_2 [cf. Equation (89)]. The simple parametric relation (91) in terms of α is obtained when the orientational distribution is described with the Onsager trial function $f_{\text{OTF}}(\theta)$. The density dependence of S_2 for $L/D = 5$ hard spherocylinders is depicted in

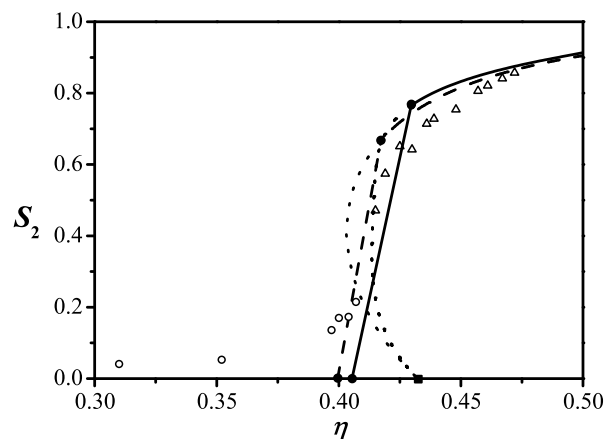


FIG. 5: The dependence of the nematic order parameter $S_2 = \langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \rangle$ on the packing fraction $\eta = \rho V_m$ for a system of hard spherocylinders of aspect ratio $L/D = 5$. The behaviour obtained from a scaled Onsager (Parsons-Lee) approach using the Onsager trial $f_{\text{OTF}}(\theta)$ is represented by the dashed curve, and that determined from the full numerical solution for $f(\theta)$ [178] is represented by the continuous curve; the dotted curves represent the metastable/unstable nematic branches. The filled circles denote the coexisting isotropic and nematic phases, and the filled square the bifurcation point ($\eta = 0.435$). The Monte Carlo simulation data [11] for the isotropic (open circles) and nematic (open triangles) are also shown for comparison.

Figure 5. The order parameter obtained from a scaled Onsager approach using $f_{\text{OTF}}(\theta)$ is compared with that determined from a full numerical solution of Equation (27) for $f(\theta)$ [178], and with Monte Carlo simulation data [11]. The degree of orientational order predicted from the scaled Onsager free energy (Equation 25) with the Onsager trial function is seen to be close to that obtained using the full numerical solution of $f(\theta)$, particularly at higher densities. A small difference can be seen at the isotropic-nematic transition, where a slight overestimate of S_2 is found when the Onsager trial function is used ($S_{2,\text{OTF}} = 0.765$ compared with the full numerical value of $S_2 = 0.668$). Kayser and Raveché [51] have also pointed out that the bifurcation point obtained with the Onsager trial function is the same as the one obtained in the case of the full numerical solution for $f(\theta)$, as can be seen in Figure 5; in this case, however, we are using the Parsons-Lee free energy (which is suitable for molecules with moderate aspect ratios) rather than the original Onsager form (which is accurate only in the long-molecule limit). The Parsons-Lee description clearly provides a good representation of the exact simulation data, even when $f(\theta)$ is approximated by $f_{\text{OTF}}(\theta)$. As has been noted by Williamson [166], the prediction of the order parameter from this type of scaled Onsager theory has the inherent problem that the free energy depends only on

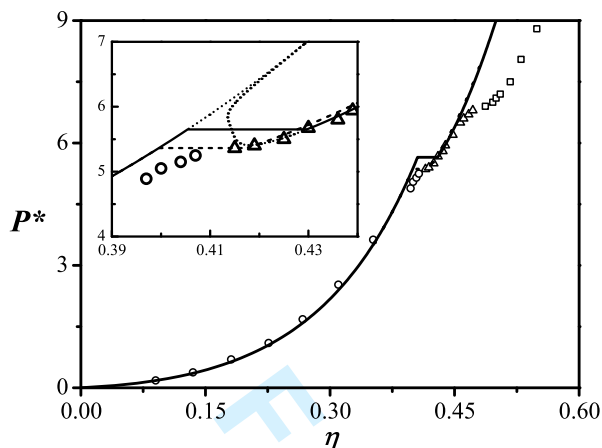


FIG. 6: The equation of state for a system of hard spherocylinders of aspect ratio $L/D = 5$, where $P^* = PV_m/kT$ is the reduced pressure and $\eta = \rho V_m$ is the packing fraction. The behaviour obtained from a scaled Onsager (Parsons-Lee) approach using the Onsager trial $f_{\text{OTF}}(\theta)$ is represented by the dashed curve, and that determined from the full numerical solution for $f(\theta)$ [178] is represented by the continuous curve; the two curves are virtually indistinguishable at the scale of the main figure but can be differentiated in the inset. The dotted curve shown in the inset represents the “van der Waals loop” found for the metastable/unstable nematic branches. The Monte Carlo simulation data [11] for the isotropic (circles), nematic (triangles), and smectic (squares) phases are also shown for comparison.

the angle between two particles, and the angular dependence of higher virial contributions is only approximate; further treatment of many-body correlations is needed to improve predictions of the degree of order in the system, particularly in the case of shorter molecules. Despite this the predictive capability of a scaled Onsager approach is impressive; the agreement with simulation improves progressively as the molecular aspect ratio increases, due to the fact that the order of the nematic phase at the transition increases with aspect ratio (see Table I).

The equation of state for $L/D = 5$ hard spherocylinders is shown on Figure 6 as a pressure-density isotherm. One can clearly distinguish the lower-density branch of the isotropic phase and the higher-density branch of the nematic. The description obtained using the scaled Onsager free energy with the Onsager trial function $f_{\text{OTF}}(\theta)$ and the full numerical solution of $f(\theta)$ [178], are compared with the Monte Carlo simulation data [11]. The scaled Onsager free energy clearly provides an excellent representation of both the isotropic and nematic branches. The solution obtained with $f_{\text{OTF}}(\theta)$ is virtually indistinguishable from the full numerical solution for most of the nematic branch, though differences are apparent at the isotropic-nematic transition: the use of the Onsager trial function leads to a small overestimate of

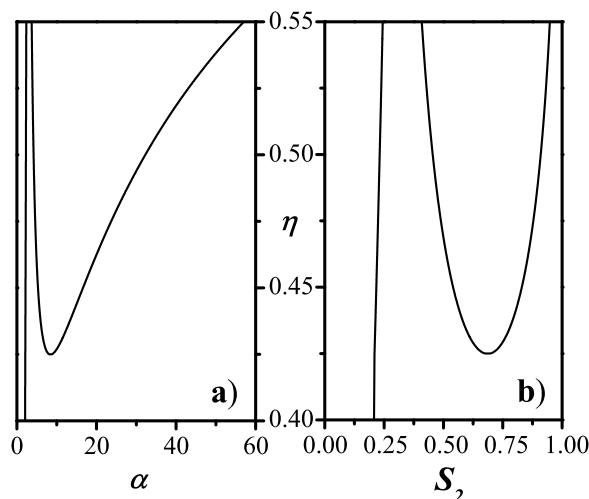


FIG. 7: The dependence of a) the variational parameter α and b) the nematic order parameter $S_2 = \langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \rangle$ on the packing fraction $\eta = \rho V_m$ for a system of hard spherocylinders of aspect ratio $L/D = 5$ determined from the cubic solution of [Equation (83)]. The closed-form expression is obtained from our truncated free energy [Equation (104)] using the Onsager trial function $f_{\text{OTF}}(\theta)$. The branches corresponding to the larger values of a) α and b) S_2 correspond to the stable nematic state; three roots can be clearly seen for packing functions above the minima in these curves.

the pressure and density of the nematic phase at coexistence (see the inset of Figure 6). The description obtained with the trial-function method thus suggests that the transition is predicted to be more first order than it really is. Considering the approximate nature of the approach the agreement with simulation is again found to be remarkably good over the full range of densities of the isotropic liquid and nematic phases. The metastable and unstable parts of the isotherm obtained with the scaled Onsager free energy described in terms of $f_{\text{OTF}}(\theta)$, which are also included in the inset of Figure 6, resemble a van der Waals loop though one should point out that the high-pressure point now represents a bifurcation point and not a maximum (see reference [51]). At a packing fraction of about $\eta = 0.48$ the system of $L/D = 5$ hard spherocylinders can be seen to exhibit a further transition from a nematic to a smectic A phase (layered structure) [11]. In the usual Onsager description, the free energy is a functional of the molecular orientational distribution but not on the position. As a consequence such an approach cannot be used to describe smectic layering, failing to capture the nematic-smectic transition (see Figure 6). Onsager-like free-energy functionals can be developed to provide an excellent description of the smectic phase (e.g., see reference [80]), but this is beyond the scope of this work.

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It is hoped that we have now convinced the reader that a good description of the isotropic and nematic phases of molecules with moderate to large aspect ratios can be achieved by using a scaled Onsager free energy when one approximates the orientational distribution function by the Onsager trial function (in terms of a single orientational parameter α). One may also have noticed that the orientational order at the isotropic nematic transition tends to be large ($\alpha > 10$). As was shown in Section IV the form of the Onsager (and scaled Onsager) free energy can be further simplified by retaining only the dominant terms for large values of α . By employing the Onsager trial function in the limit of large α one can obtain a simple closed-form cubic solution for the equilibrium value α_{eq} in terms of the density and the molecular parameters, which corresponds to the orientationally ordered state with the minimum free energy [see Equation (107)]. Here, we show that such a truncated free energy [Equation (104)] still provides an accurate description of the nematic branch beyond the isotropic-nematic transition, where the orientational parameter characterising the stable states is large. The cubic form obtained for the value of α corresponding to a turning point in the free energy indicates that up to three roots are possible. At high density three real positive roots are obtained, the largest value of which corresponds to α_{eq} for the nematic state with the minimum free energy (see Figure 7 a) in the case of $L/D = 5$ hard spherocylinders for packing fractions $\eta > 0.425$). In the case of lower density states only a single small positive root ($\alpha \sim 1$) is obtained which should be discarded (see Figure 7 a) in the case of $L/D = 5$ hard spherocylinders for packing fractions $\eta < 0.425$). This would correspond to an “isotropic” state with low orientational order; one would not expect to obtain the true solution for the isotropic phase of $\alpha = 0$ as the truncated free energy is only valid for large values of α . One may also have noticed that in the case of the solution obtained with the truncated free energy [Equation (104)], the system does not exhibit the bifurcation point which is seen with the full free energy (cf. Figure 3); this is again a consequence of approximations involved in the truncation. In Figure 7 b) we show the direct correspondence between the values of the nematic order parameter S_2 and the roots for α resulting from the simple relation (91). The density dependence of α and S_2 obtained for $L/D = 5$ hard spherocylinders with the Onsager trial function $f_{OTF}(\theta)$ from the scaled Onsager (Parsons-Lee) free energy [Equation (83)] (cf. Figures 3 and 5) is compared with the corresponding calculations with the truncated free energy [Equation (104)] in Figures 8 and 9. It is very gratifying to find that the results obtained with the truncated free energy are virtually indistinguishable from those of the full free energy at the isotropic-nematic transition and over the entire range of stability of the nematic phase. A clear difference is, however, observable for the metastable/unstable states: as we have already mentioned the truncated free energy does not reproduce the correct isotropic solution $\alpha = 0$

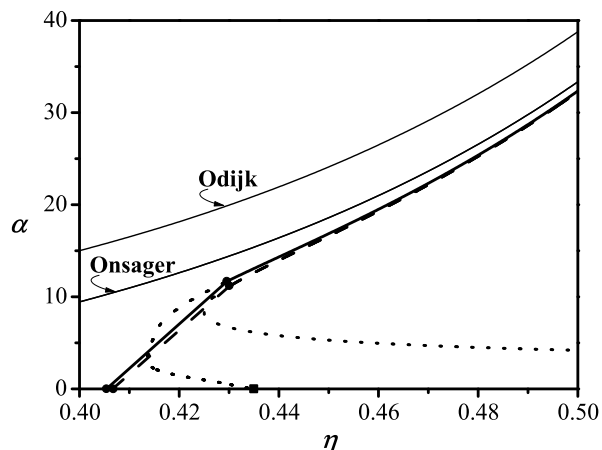


FIG. 8: The dependence of the variational parameter α on the packing fraction $\eta = \rho V_m$ for a system of hard spherocylinders of aspect ratio $L/D = 5$ determined with the Onsager trial function $f_{OTF}(\theta)$. The dashed curve is obtained from our truncated version of the scaled Onsager (Parsons-Lee) free energy [Equation (104)], while the continuous curve is obtained from the full numerical solution of the modified Bessel function [Equation (83)]; the dotted curves denote the metastable/unstable states. The circles denote the isotropic-nematic phase transition, and the square the bifurcation point ($\eta = 0.435$). The results obtained with approximate expression (110) proposed by Onsager [37], and with the similar relation suggested by Odijk [91] are also shown for comparison as thin continuous curves.

nor the bifurcation point. Since the proper isotropic free energy is used to construct the isotropic-nematic phase diagram the solutions in the metastable/unstable regions are of no further consequence.

The closed-form truncated free energy [Equation (104)] is clearly seen to provide a good representation of the nematic order when compared with the simulation data which are also included in Figure 9; a slight overestimate is seen close to the isotropic-nematic transition as mentioned earlier. The behaviour obtained with the simple algebraic relation for α proposed by Onsager for highly ordered states (Equation (88) of reference [37]) is also shown on Figure 8. Onsager essentially rearranges the asymptotic series for the modified Bessel function of the configurational functional as a power series in the inverse of α [cf. our Equation (102)], invokes the condition of a minimum in the free energy, retaining only terms up to α^{-1} , and inverts the series to obtain α as a function of the square of a reduced density. In order to apply this approach with the Parsons-Lee free energy for hard spherocylinders, one simply has to replace Onsager’s reduced density bc with $G(\rho) C_1^* \pi/4$:

$$\alpha \approx \frac{4}{\pi}(bc)^2 - \frac{45}{8} = \frac{\pi}{4} [G(\rho)C_1^*]^2 - \frac{45}{8} \quad (110)$$

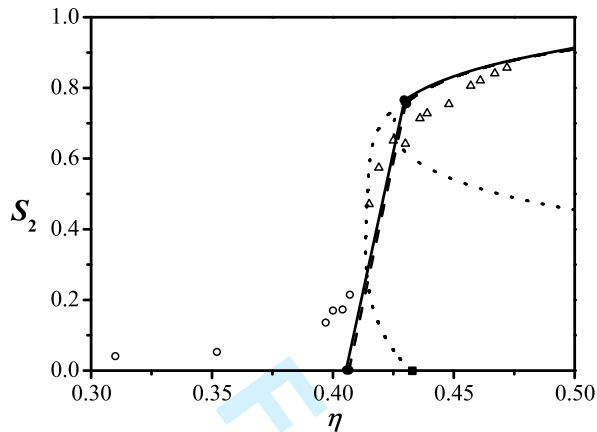


FIG. 9: The dependence of the nematic order parameter $S_2 = \langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \rangle$ on the packing fraction $\eta = \rho V_m$ for a system of hard spherocylinders of aspect ratio $L/D = 5$ with the Onsager trial function $f_{\text{OTF}}(\theta)$. The behaviour obtained from our truncated version of the scaled Onsager (Parsons-Lee) free energy [Equation (104)] is represented by the dashed curve, and that from the numerical solution of the modified Bessel function [Equation (83)] is represented by the continuous curve; the dotted curves represent the metastable/unstable nematic branches. The filled circles denote the coexisting isotropic and nematic phases, and the filled square the bifurcation point ($\eta = 0.435$). It is pleasing to see that the two approaches provide a virtually indistinguishable description for the isotropic-nematic transition and the stable nematic branch. The Monte Carlo simulation data [11] for the isotropic (open circles) and nematic (open triangles) are also shown for comparison.

A very similar expression (identical to that of Onsager but without the constant term $-45/8$) was also derived by Odijk [91] with a Gaussian trial function. As pointed out by Onsager, the description of the density dependence of α obtained in this way is rather poor (see Figure 8). The point of inflection is not reproduced with such an approach, but as one would expect Onsager's expression (110) approaches the correct limiting behaviour at high density where the orientational order is high; the Odijk expression does not provide the correct asymptotic limit. It is interesting to point out that though in common with Onsager (and Odijk) we discard terms beyond α^{-1} to truncate the free energy (see section IV), our resulting cubic solution describes the point of inflection and provides a very good description of the density dependence of α for the whole of the stable nematic branch. As a final demonstration of the adequacy of our truncated scaled Onsager free energy in describing the isotropic-nematic phase equilibrium we again examine the equation of state for $L/D = 5$ hard spherocylinders. In Figure 10 we show the density dependence of the reduced pressure determined from the Onsager trial-function ap-

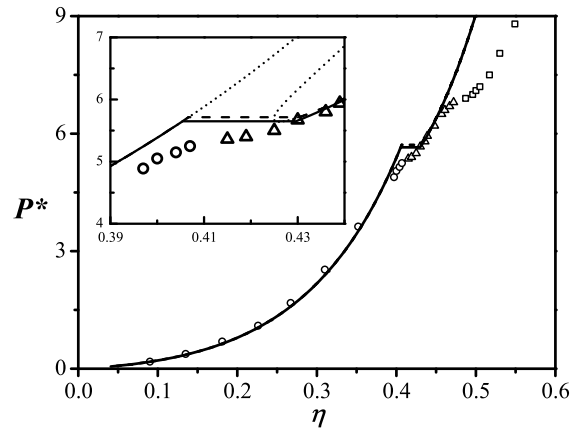


FIG. 10: The equation of state for a system of hard spherocylinders of aspect ratio $L/D = 5$, where $P^* = PV_m/kT$ is the reduced pressure and $\eta = \rho V_m$ is the packing fraction, described in terms of the Onsager trial function $f_{\text{OTF}}(\theta)$. The behaviour obtained from our truncated version of the scaled Onsager (Parsons-Lee) free energy [Equation (104)] is represented by the dashed curve, and that from the numerical solution of the modified Bessel function [Equation (83)] is represented by the continuous curve; the two approaches yield virtually indistinguishable results for this system. The dotted curve shown in the inset represents the “van der Waals loop” found for the metastable/unstable nematic branches. The Monte Carlo simulation data [11] for the isotropic (circles), nematic (triangles), and smectic (squares) phases are also shown for comparison.

proach with the full [Equation (83)] and truncated [Equation (104)] scaled Onsager (Parsons-Lee) free energies, together with the corresponding simulation data. As expected from the analysis of the nematic order, the isotherms obtained with the full and truncated free energies are almost indistinguishable. Both approaches are found to accurately describe the isotropic and nematic branches of the isotherm, with a slight overestimate of the pressure and density of the nematic phase at the transition. In summary one can say that the truncated free energy, which can be expressed in closed algebraic form, provides a simple yet accurate description of the ordering phase behaviour in such systems. The dependence of the isotropic-nematic transition on the aspect ratio of hard spherocylinders described with the Onsager trial function using our truncated free energy is compared to that obtained with a numerical solution of the Bessel function in Table I.

VI. CONCLUSIONS.

We have introduced and developed an approach which takes the form of a general Onsager type free-energy

functional that accounts for the repulsive interactions of cylindrically symmetrical mesogens [see Equation (25)]. An analytic form of the free energy is developed by use of the trial function originally suggested by Onsager [37]. A number of novel results are presented, indicating the true general nature of the Onsager approach. These new features will be invaluable in studies of real liquid crystalline materials, where attractive interactions have to be incorporated and a computationally straightforward determination of fluid phase equilibria is desired. We shall be providing further details of the development of an algebraic description of the thermodynamics of mesogens with both repulsive and attractive interactions in future work.

The Onsager trial-function method is first assessed by comparison with simulation data for hard spherocylinders. The results from the analytical form of the scaled Onsager equation of state for hard spherocylinders ($L/D = 5$) are in good agreement with those from the simulation, indicating that the Parsons-Lee correction to the Onsager's approach is suitable to describe ordering transitions for mesogens with realistic aspect ratios. It is worth pointing out that the free-energy expression here obtained extends the original scope of Onsager, since we show that the trial-function method can be generalised to describe different molecular geometries such as chains and discs, not just the leading excluded volume term for rod-like particles originally examined by Onsager [37]. The only requirement for this is that we express the excluded volume as a series of powers in $\sin \gamma$.

As mentioned at the beginning of the paper we seek to have an equation of state suitable for the intensive calculations routinely required in engineering applications. Though the analytical form of the free energy in terms of modified Bessel functions presented in the first part of the paper can be solved numerically, an alternative simple algebraic solution is developed. The Euler-Lagrange

extremum condition for the free-energy minimum is truncated to obtain a cubic equation in the orientational parameter α . The solution of the cubic expression provides a simple algebraic form for the equilibrium value α_{eq} in terms of the thermodynamic variables and molecular parameters, and as a consequence the equation of state becomes an algebraic function of thermodynamic state. This is equivalent to using a van der Waals-like equation of state.

Finally, we would like to emphasise that the Onsager approach for the configurational entropy functional has been recast in a general form that provides a way to analytically solve arbitrary orientational functionals expressed in terms of series of $\sin^i \gamma$. This should not be confused with the expansion of the excluded volume contribution (namely $\sin \gamma$) in spherical harmonics which is often employed to numerically determine the configurational contributions.

Acknowledgments

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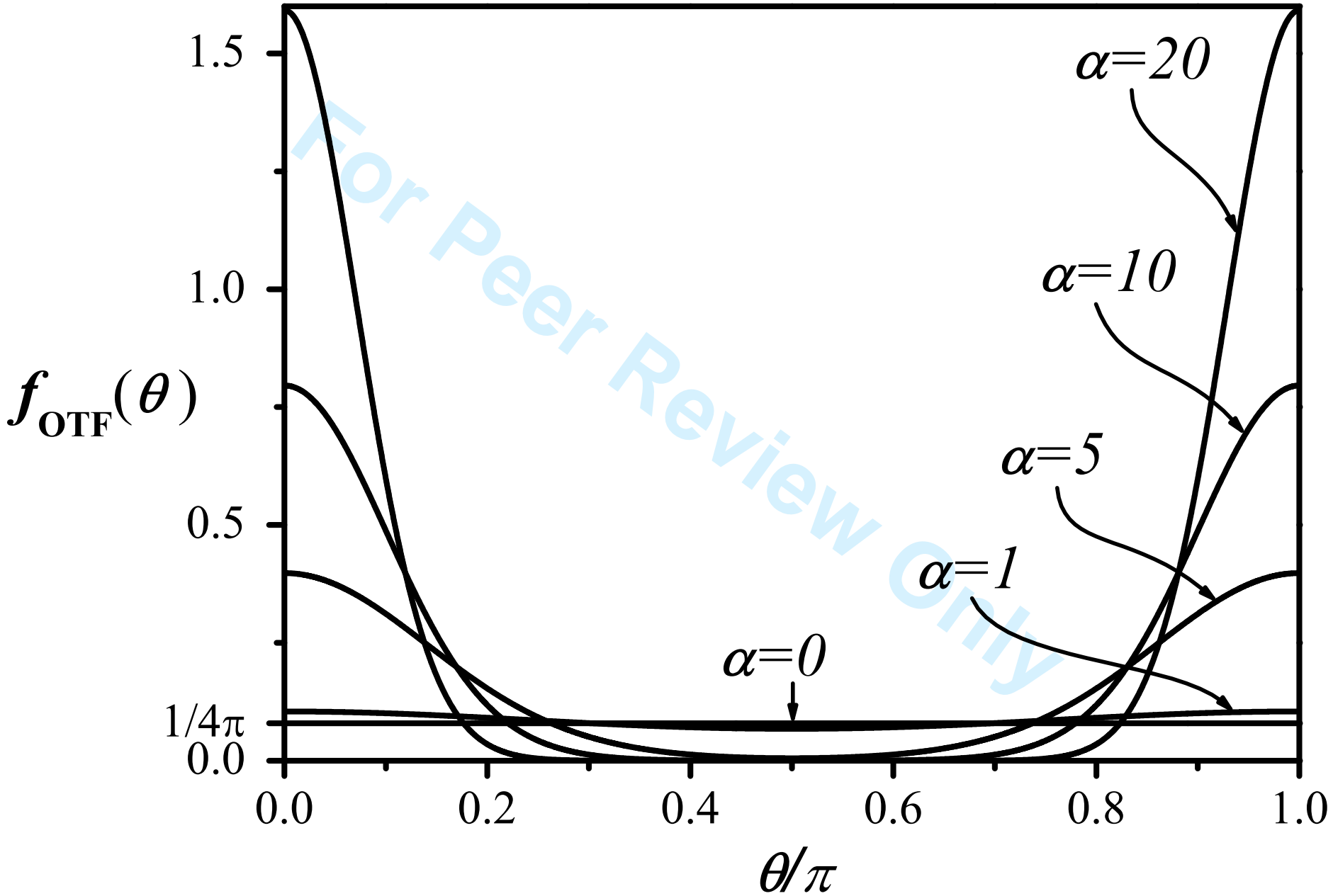
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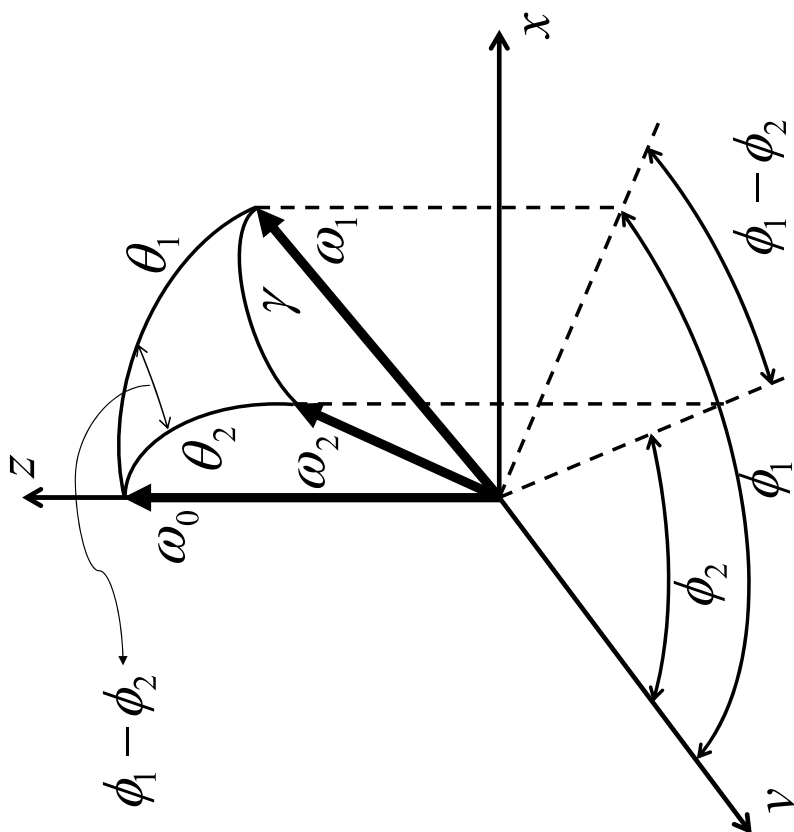
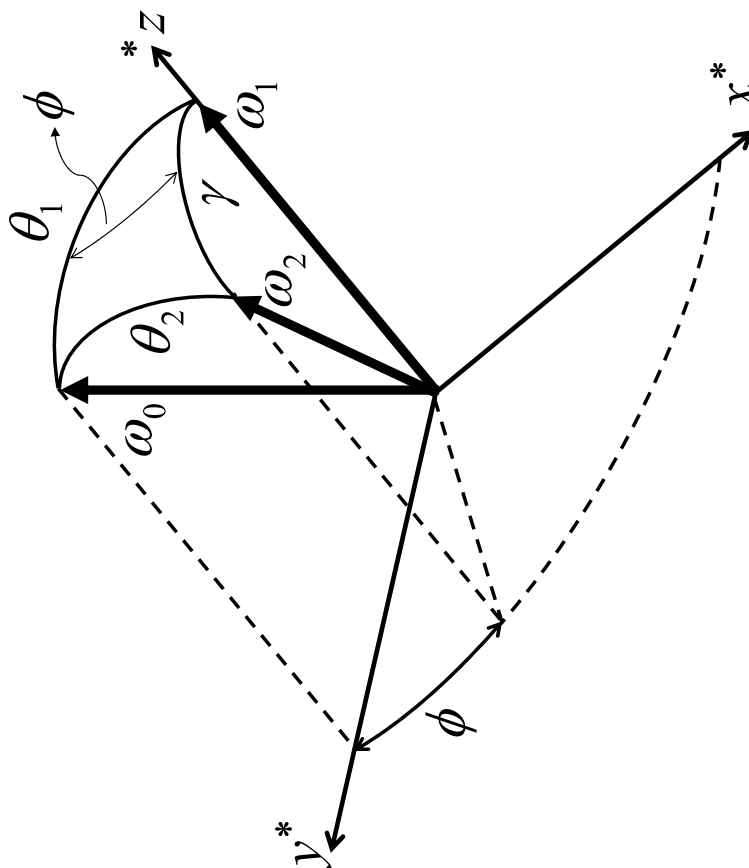
TABLE I: Isotropic-nematic transition obtained from the scaled Onsager (Parsons-Lee) free energy with the Onsager trial-function method for different values of aspect ratio L/D . The packing fractions ($\eta = \rho V_m$) of the coexisting states are given, together with the pressure p , chemical potential μ , and orientational parameter α . The $\mathcal{F}_{\text{conf}} [f_{\text{OTF}}]$ is computed via the full modified Bessel function [FMB, Equation (83)], and the truncated algebraic cubic solution [CUB, Equation (104)].

$\frac{L}{D}$		η_{iso}	η_{nem}	$\left[\frac{PV_m}{kT} \right]$	$\left[\frac{\mu}{kT} - \frac{\mu^0}{kT} \right]$	α	S_2
3	FMB	0.531349	0.546528	13.531971	33.227199	10.201939	0.734762
	CUB	-	-	-	-	-	-
4	FMB	0.460059	0.480404	8.150812	23.618309	11.023232	0.752536
	CUB	-	-	-	-	-	-
5	FMB	0.405413	0.429629	5.649302	18.744979	11.691228	0.765346
	CUB	0.405559	0.427231	5.656625	18.763038	10.121401	0.732883
6	FMB	0.362218	0.389209	4.255137	15.828508	12.249347	0.775083
	CUB	0.362287	0.387351	4.257820	15.835912	11.086108	0.753801
7	FMB	0.327240	0.356152	3.383766	13.892377	12.724235	0.782759
	CUB	0.327285	0.354535	3.385180	13.896699	11.731366	0.766074
8	FMB	0.298357	0.328541	2.794577	12.512759	13.133837	0.788974
	CUB	0.298390	0.327083	2.795447	12.515677	12.241277	0.774948
9	FMB	0.274115	0.305087	2.372773	11.478030	13.490992	0.794112
	CUB	0.274140	0.303747	2.373361	11.480177	12.665591	0.781839
10	FMB	0.253486	0.284886	2.057465	10.671381	13.805231	0.798432
	CUB	0.253506	0.283642	2.057889	10.673055	13.028232	0.787405
20	FMB	0.144371	0.172713	0.865377	7.165659	15.647120	0.820525
	CUB	0.144376	0.171952	0.865450	7.166166	15.045313	0.813855
40	FMB	0.077468	0.097296	0.395940	5.269297	16.943202	0.833388
	CUB	0.077470	0.096854	0.395961	5.269557	16.407917	0.828305
50	FMB	0.062887	0.079916	0.311165	4.821281	17.242794	0.836105
	CUB	0.062888	0.079550	0.311179	4.821506	16.719068	0.831297
100	FMB	0.032394	0.042247	0.150154	3.693994	17.887282	0.841659
	CUB	0.032394	0.042049	0.150159	3.694161	17.384548	0.837359
500	FMB	0.006639	0.008862	0.029194	1.752173	18.447704	0.846193
	CUB	0.006639	0.008820	0.029195	1.752303	17.959308	0.842257
1000	FMB	0.003330	0.004458	0.014546	1.018409	18.520547	0.846764
	CUB	0.003330	0.004437	0.014546	1.018535	18.033762	0.842870

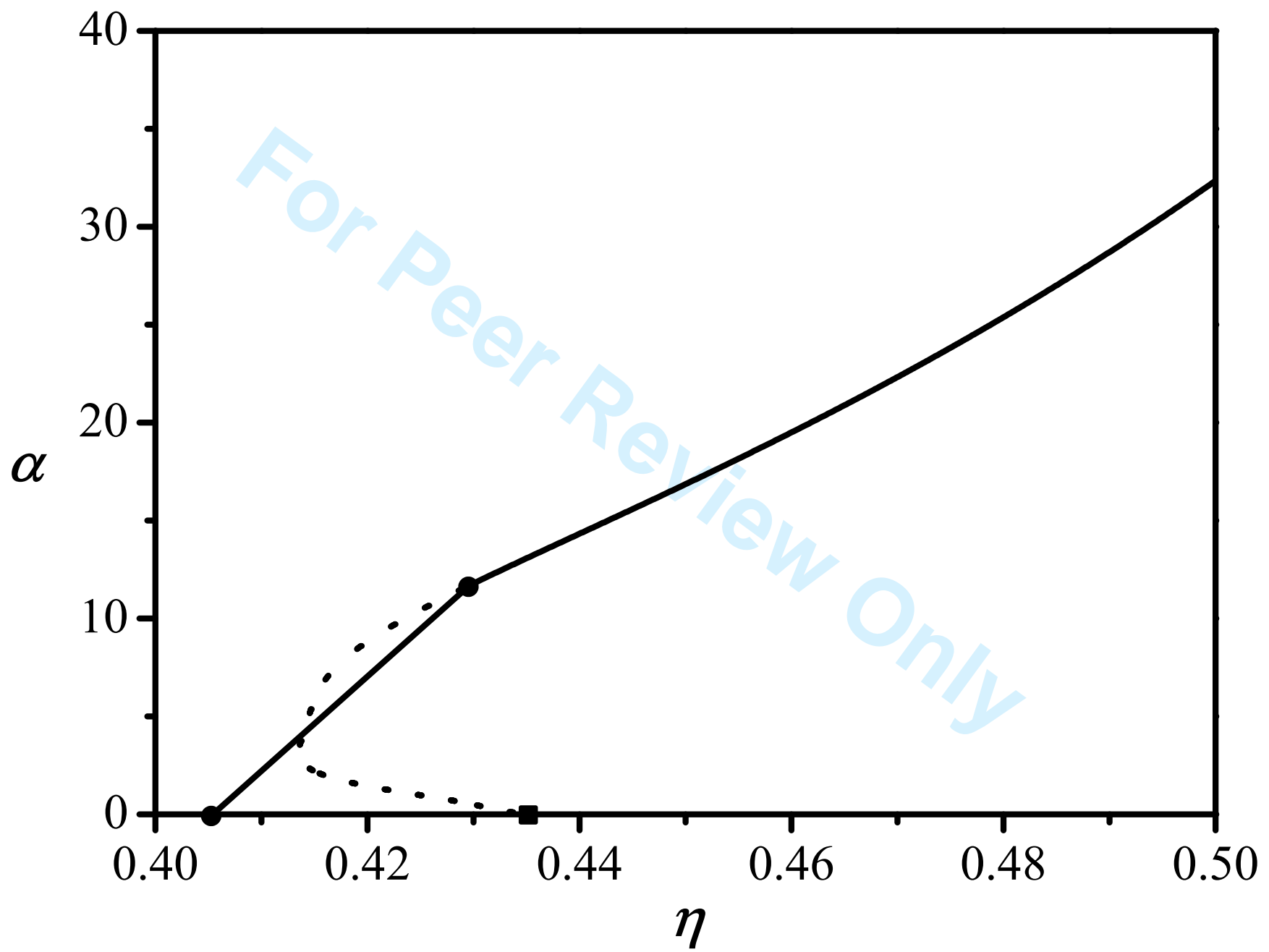
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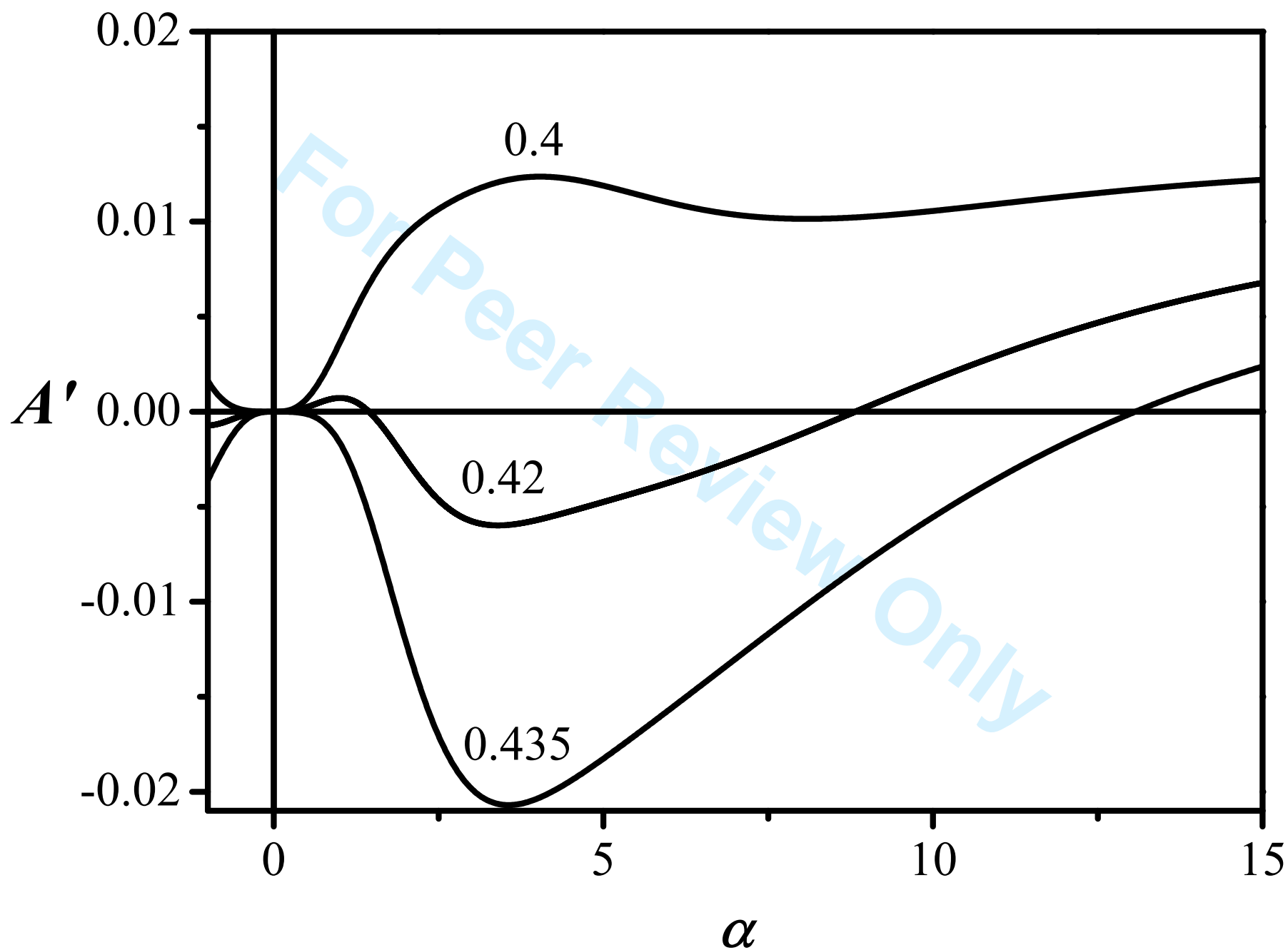


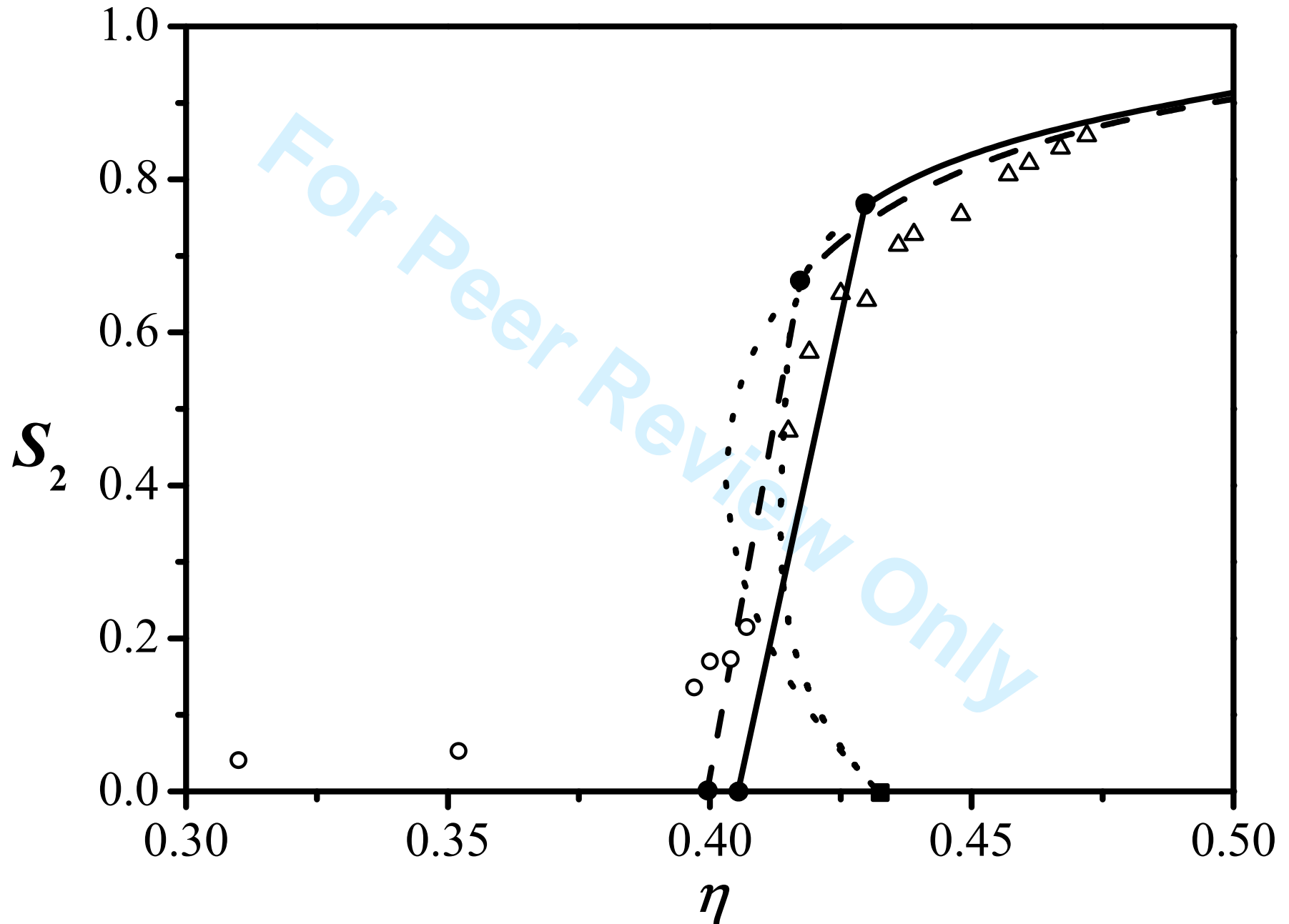
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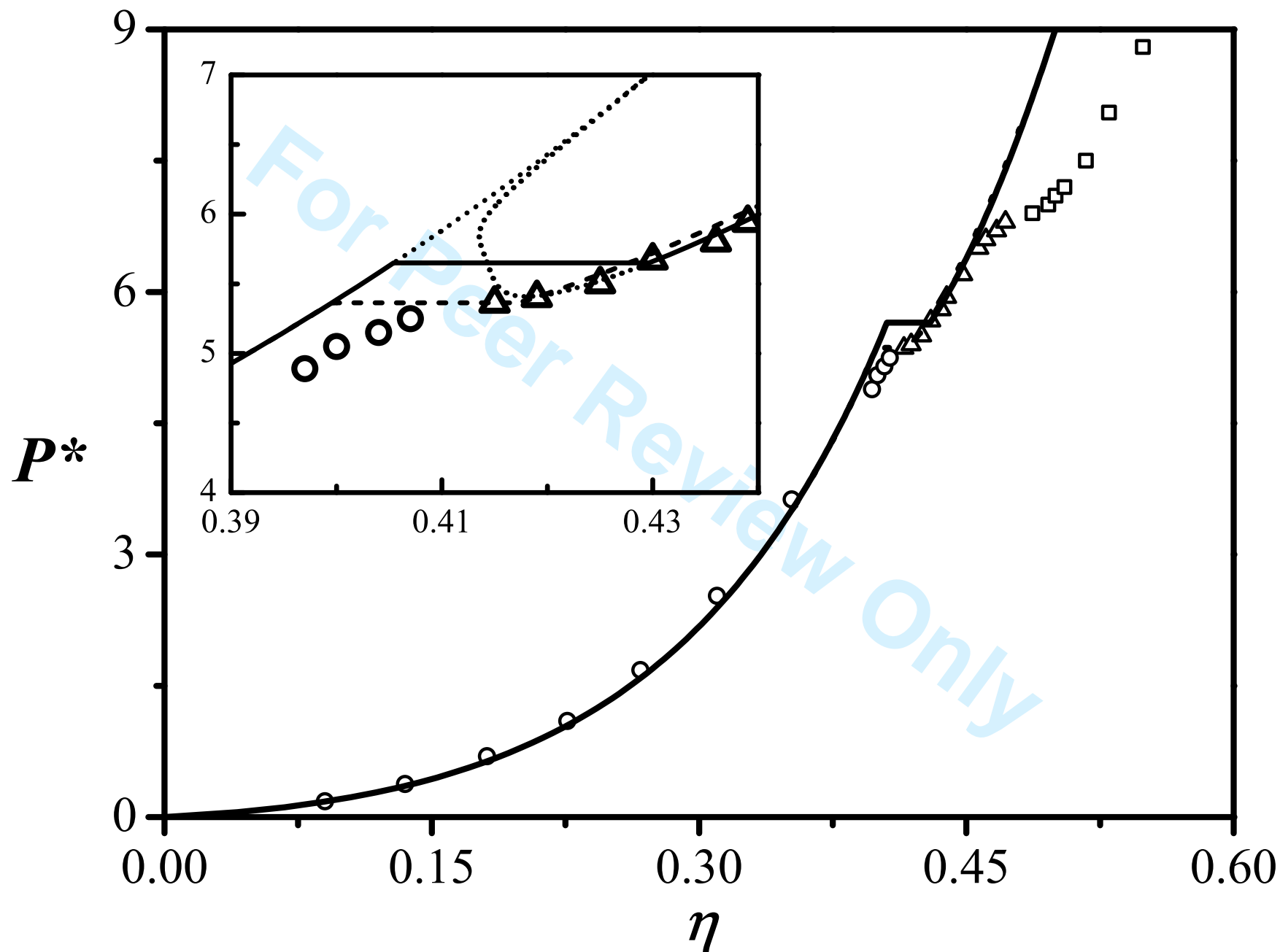


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