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The isotropic and nematic liquid crystal phase of colloidal rods

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Abstract

The density-dependent distribution function of the orientation of the long axis of rod-like colloidal particles in the liquid crystalline nematic phase is numerically calculated as the solution of a nonlinear integral equation. From this solution, which is obtained by an iterative method that is explained in detail, the free energy, the pressure and the chemical potential can be computed, as well as the nematic order parameter. Moreover, the first-order phase transition from the disordered isotropic fluid phase to the nematic phase is analysed numerically. This study, presented at the level of advanced undergraduates or starting graduate students, not only illustrates the existence of liquid crystalline ordering for nonspherical particles, but also shows explicitly how thermodynamics, structure and symmetry are related.

1. Introduction

We are all familiar with the fluid and the crystalline state of matter, and know that these phases—when the molecules are approximately spherical—are distinguished by the degree of ordering of the *positions* of molecules. The study of the melting and freezing transition is, however, not a part of most physics curricula, even though this symmetry-breaking transition could serve as a daily-life example for this important concept in modern physics. The reason is perhaps that the translational and rotational symmetry of the liquid phase are both fully broken in the crystal phase, which makes this problem hard to crunch with methods available to most undergraduate students. In this paper a simpler yet realistic symmetry-breaking transition in a condensed-matter system is discussed: only rotational symmetry gets broken while up-down symmetry and translational invariance survive.

Cigar- or needle-shaped molecules exhibit additional forms of ordering except for fluid and crystalline phases: not only the positions but also the *orientations* of the molecules can be ordered. The most disordered phase is then the isotropic fluid phase, where all the particles translate and rotate freely (figure 1(a)), and the most ordered phase is the crystalline phase, where all the particles reside at regular lattice sites and point in the same direction

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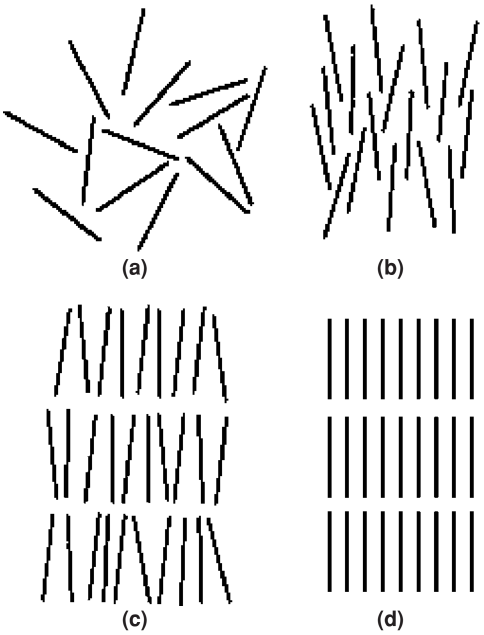

Figure 1. Schematic illustrations of typical configurations of rod-like particles in the (a) isotropic, (b) nematic, (c) smectic and (d) crystalline solid phase. The nematic and smectic phase are the examples of liquid crystalline phases with partial ordering; their properties are often in between those of completely disordered isotropic fluids and completely ordered crystals.

(figure 1(d)). In between there are mesophases, or liquid crystalline phases, characterized by ordering of the orientations of the particles, possibly with positional ordering. The simplest example is the nematic phase (figure 1(b)), for which the rod-like molecules translate randomly through space (as in a fluid), while pointing on average in a particular direction (this direction is called the nematic director). Another example of a liquid crystalline phase is the smectic phase (figure 1(c)), which consists of a sandwich-like structure of homogenous two-dimensional layers of oriented molecules, stacked on top of each other. Because of the periodicity in the direction of the director, the smectic phase can be seen as crystalline in one direction and liquid-like in the other two directions. The properties of these liquid crystalline phases are in between those of liquids and crystals (hence their names). For example, they can flow like a liquid but diffract light like a crystal. It is the combination of properties that causes liquid crystals to be so useful in applications, e.g. the liquid crystalline displays (LCDs). Liquid crystalline structures do not only occur in systems of rod-like molecules such as cholesterol, but also in solutions of macromolecules such as DNA, or in suspensions of rod-like colloidal particles such as tobacco mosaic virus [1, 2].

An important quantity for these systems is the concentration of rods, expressed as the number density $n = N/V$, with N the total number of rods in the system and V the volume of the solvent. Below a certain concentration of rods, $n < n_{\mathrm{I}}$, these systems are in the isotropic phase (I), which is the low-concentration regime where the rods hardly hinder each other, and hence their thermal motion causes them to translate and rotate freely without any preferred position or orientation. Above a certain concentration, $n > n_{\mathrm{N}}$, the rod–rod interactions are relevant and these systems are in the nematic phase (N): the rods keep translating freely through the solvent (by thermal motion), but with their orientations much more often in the vicinity of the north- and south pole of the unit sphere than on the equator. The transformation from the low-density isotropic phase to the high-density nematic phase turns out to be a first-order phase transition. This means that in the regime $n_{\mathrm{I}} < n < n_{\mathrm{N}}$, the isotropic and the nematic phases coexist with each other. The system spontaneously divides into two subsystems—a nematic phase and an isotropic phase—separated by a meniscus (a spontaneously formed interface).

In this project we will consider a simple but yet realistic model for a suspension of colloidal rods. In this model the rods are described as rigid cylinders of length L and diameter D, with $L \gg D$. The interactions between the rods are hard, like those between billiard balls: the rods cannot penetrate or deform each other, but they do not feel each other until they touch. This is clearly a simplification of reality, since real colloidal rods or DNA molecules are charged and somewhat flexible. Despite the simplifications, it has turned out that this model catches the essential physics of the isotropic–nematic transition. We will calculate the concentrations n_{I} and n_{N} of the coexisting isotropic and nematic phase, as well as the degree of orientational ordering in the nematic phase. These questions can be answered by considering the probability distribution $\psi(\mathbf{u})$ for a rod to have an orientation $\mathbf{u}$ on the unit sphere ($\mathbf{u}$ is a unit vector parallel to the long axis of the cylinder). This distribution is trivial in the isotropic phase (i.e. when $n < n_{\mathrm{I}}$), as any orientation on the unit sphere is equally probable and hence $\psi(\mathbf{u}) = 1/4\pi$. However, in the nematic phase ($n > n_{\mathrm{N}}$) the distribution $\psi(\mathbf{u})$ is nontrivial: it is the solution of a nonlinear integral equation that we will solve numerically. The method that we employ here is iterative: starting from an (educated) initial guess for $\psi(\mathbf{u})$ we keep improving it until self-consistency is obtained. Such a procedure is very common in the theory (and hence in the numerics) of interacting many-body systems.

2. The coordinate system

We first choose a convenient coordinate system in which the Cartesian z-axis is parallel to the nematic director. The three Cartesian components of a unit-vector can now be characterized by a polar angle $\theta \in [0, \pi]$ and by an azimuthal angle $\phi \in [0, 2\pi]$, i.e. we write $\mathbf{u} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$ where the third component refers to the z-axis. In this coordinate frame the unit surface element is given by $\mathrm{d}\mathbf{u} = \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$. The symmetry of the nematic phase is such that the orientation distribution is independent of ϕ, as the nematic director is (by definition) the symmetry axis for global rotations. As a consequence we can write $\psi(\mathbf{u}) = \psi(\theta)$. Moreover, the nematic phase has up-down symmetry: there is no difference between the northern and southern hemisphere (this symmetry distinguishes a nematic phase from a (ferro)magnetic phase where the up-down symmetry is broken). The up-down symmetry implies that $\psi(\theta) = \psi(\pi - \theta)$, and hence we only need to calculate $\psi(\theta)$ for $\theta \in [0, \pi/2]$. The normalization of $\psi(\theta)$ must be such that

$$\int \mathrm{d}\mathbf{u}\,\psi(\mathbf{u}) = 4\pi \int_0^{\pi/2} \mathrm{d}\theta\,\sin\theta\,\psi(\theta) = 1. \tag{1}$$

3. The nonlinear self-consistency problem

In this section, we present the nonlinear integral equation that describes the orientation distribution $\psi(\theta)$ for a given density n of rods, as first given by Onsager in the 1940s [1]. It is based on the minimum condition of the Helmholtz free energy with respect to $\psi(\theta)$. Onsager's derivation will be repeated in a simplified fashion in the appendix. Onsager introduced the dimensionless concentration of the rods

$$c = \frac{\pi}{4} L^2 D n,$$

and showed that the distribution function $\psi(\theta)$ is the solution of the nonlinear integral equation

$$\psi(\theta) = \frac{1}{Z} \exp\left[-\frac{16c}{\pi} \int_0^{\pi/2} \mathrm{d}\theta' \sin\theta' K(\theta, \theta') \psi(\theta') \right], \tag{2}$$

where the prefactor $1/Z$ is a constant such that the normalization of equation (1) is satisfied. In equation (2) we introduced the integral kernel

$$K(\theta, \theta') = \int_0^{2\pi} \mathrm{d}\phi \sqrt{1 - (\cos\theta \cos\theta' + \sin\theta \sin\theta' \cos\phi)^2}. \tag{3}$$

Finding the solution of the nonlinear equation (2) is a *self-consistency* problem, because the unknown distribution $\psi(\theta)$ is expressed in terms of itself.

In order to facilitate the numerical calculations below, we introduce also the auxiliary function

$$A(\theta) = \frac{16c}{\pi} \int_0^{\pi/2} \mathrm{d}\theta' \sin\theta' K(\theta, \theta') \psi(\theta'), \tag{4}$$

which describes the orienting field that all the other rods exhibit on a given rod with a polar angle θ. Expression (2) can be rewritten as a Boltzmann distribution

$$\psi(\theta) = \frac{1}{Z} \exp[-A(\theta)], \tag{5}$$

with $A(\theta)$ playing the role of a potential energy.

4. The discrete grid

We will determine the distribution $\psi(\theta)$ for a finite set of polar angles θ_k in the interval $[0, \pi/2]$, with $k = 1, 2, \ldots, N_\theta$ and N_θ the number of θ in the set. Although many possible choices exist we will here use the equidistant set

$$\theta_k = \frac{\pi}{2} \frac{k}{N_\theta + 1}, \qquad k = 1, 2, \ldots, N_\theta. \tag{6}$$

Since $\mathrm{d}\theta \sin\theta = -\mathrm{d}\cos\theta$, the trapezoidal integration scheme allows us to approximate

$$\int_0^{\pi/2} \mathrm{d}\theta \sin\theta g(\theta) \approx \sum_{k=1}^{N_\theta} \Delta_k g(\theta_k), \tag{7}$$

where $g(\theta)$ is an arbitrary function of θ, and where we define the positive measure of the integration interval associated with θ_k

$$\Delta_k = \begin{cases} 1 - (\cos\theta_k + \cos\theta_{k+1})/2, & k = 1 \\ (\cos\theta_{k-1} - \cos\theta_{k+1})/2, & k = 2, 3, \ldots, N_\theta - 1 \\ (\cos\theta_k + \cos\theta_{k-1})/2, & k = N_\theta. \end{cases} \tag{8}$$

This choice guarantees the correct normalization $\Sigma_k \Delta_k = 1$ for all $N_\theta \geqslant 2$. A reasonable choice is $N_\theta = 20$–40, and accurate results require $N_\theta = 100$–200.

The numerical scheme requires a particular choice for the number N_θ, e.g $N_\theta = 40$. Once this number is defined we can make declarations (in Fortran-, Mathematica-, or C-program, or any other programming language) of one-dimensional arrays of length N_θ containing the discrete set of angles θ_k (from equation (6)) and the measures Δ_k (from equation (8)), with $k = 1, 2, \ldots, N_\theta$. We also need a two-dimensional $N_\theta \times N_\theta$ array (a matrix) with elements $K_{kl} = K(\theta_k, \theta_l)$, with $k, l = 1, 2, \ldots, N_\theta$. These coefficients can be computed by the standard trapezoidal rule on an equidistant grid of, say, $N_\phi = 200$ azimuthal angles $\phi_j = 2\pi j/(N_\phi + 1)$ with $j = 1, 2, \ldots, N_\phi$,

$$K_{kl} = \frac{2\pi}{N_\phi + 1}\left(\frac{3}{2}g_{kl}(\phi_1) + \sum_{j=2}^{N_\phi - 1} g_{kl}(\phi_j) + \frac{3}{2}g_{kl}\left(\phi_{N_\phi}\right)\right), \tag{9}$$

where $g_{kl}(\phi) = \sqrt{1 - (\cos\theta_k \cos\theta_l + \sin\theta_k \sin\theta_l \cos\phi)^2}$. Since these coefficients do not depend on the value of c, it is advisable to store the elements of K_{kl} once they have been computed, such that they can be read from a file instead of recomputed when another calculation (on the same θ-grid) is desired.

5. The iterative scheme

In addition to the arrays θ_k, Δ_k and K_{kl}, we define three one-dimensional arrays of length N_θ as $A_k \equiv A(\theta_k)$, which is the auxiliary function defined in (4),$\tau_k \equiv \tau(\theta_k)$, which is the initial guess (or trial) solution, and $\psi_k \equiv \psi(\theta_k)$, the desired solution. For the initial guess, it is convenient to choose the Gaussian distribution $\tau_k = (c/\pi)^2 \exp[-2c^2\theta^2/\pi]$ for $\theta \in [0, \pi/2]$, as it turns out to be very similar, but of course not identical, to the final solution $\psi(\theta)$. A simpler, though less efficient choice, is the isotropic distribution ($\tau_k = 1/4\pi$ for all k), which is suitable as soon as $c > 4$ [3]. With τ_k as the initial guess, a loop can be set up. For this, we define an iteration counter i (initially $i = 0$), and the maximum number m of iterations that we are willing to perform, typically $m = 100$. Finally, we also need a measure for the accuracy with which we are satisfied. We define a tolerance t, which sets the magnitude for the largest acceptable deviation between the distributions of two consecutive iterations, for instance $t = 10^{-5}$. For a given density c, the loop is as follows:

(i) Increase the counter by one: $i = i + 1$. If $i > m$ print out: 'not converged', and exit the loop.

(ii) Use the trial solution τ_k to calculate the auxiliary function

$$A_k = \frac{16c}{\pi}\sum_{l=1}^{N_\theta} \Delta_l K_{kl} \tau_l \qquad \text{for all } \; k = 1, 2, \ldots, N_\theta \tag{10}$$

This represents, on the grid, the function $A(\theta)$ as defined in equation (4).

(iii) Calculate the normalization constant:

$$Z = 4\pi \sum_{k=1}^{N_\theta} \Delta_k \exp[-A_k] \tag{11}$$

which represents normalization of expression (5) on the grid.

(iv) Calculate the improved (new) estimate of the distribution function:

$$\psi_k = \frac{1}{Z}\exp[-A_k] \qquad \text{for all } \; k = 1, 2, \ldots, N_\theta. \tag{12}$$

This is the grid version of equation (5).

(v) Calculate the maximum δ of the difference between two consecutve solutions:

$$\delta = \max_k |\psi_k - \tau_k|. \tag{13}$$

(vi) If $\delta < t$ then ψ_k and τ_k are so close that self-consistency is obtained within the tolerance; store the solution $\psi(\theta_k) = \psi_k$, and exit the loop. If $\delta > t$, self-consistency has not been obtained; proceed by setting the new trial distribution to the newly obtained guess ($\tau_k = \psi_k$), and restart the loop at (i).

The outcome of this scheme should be the desired distribution function $\psi(\theta_k)$, unless convergence has not been obtained within m iterations. True convergence is found when the solution ψ_k does not depend significantly on numbers defining the numerical procedure (e.g.: m, N_θ). Including this procedure in a loop where a number of concentrations $c \in [c_{\rm min}, c_{\rm max}]$ are considered, should be no problem.

6. Thermodynamic and structural properties

Now that we are capable of determining $\psi(\theta)$ for a given density c, we are ready to study the thermodynamics and the structure of isotropic and nematic liquid crystal phases of rods. It is of interest to consider the c-dependence of the orientation distribution $\psi(\theta)$, e.g. by plotting this function for $c = 4.5, 5.0, 6.0, 7.0, 10$. One should observe that the distribution becomes more and more peaked about $\theta = 0$ for increasing c. Note that it is crucial that at least a few polar angles θ_k of the set are small enough to support the very peaked high-density distributions. One represents the degree of nematic ordering with the so-called nematic order parameter $= \langle(3\cos^2\theta - 1)/2\rangle$, which we rewrite as

$$S = 4\pi \int_0^{\pi/2} \mathrm{d}\theta \, \sin\theta \, \psi(\theta) \frac{3\cos^2\theta - 1}{2} \simeq 4\pi \sum_{k=1}^{N_\theta} \Delta_k \psi_k \frac{3\cos^2\theta_k - 1}{2}. \tag{14}$$

In the isotropic phase $S = 0$, in the coexisting nematic phase $S \simeq 0.79$ (see below), and S approaches unity upon increasing c further [3–7]. We note that this parameter can be measured experimentally (often the full distribution $\psi(\theta)$ requires more information than is experimentally available).

The distribution $\psi(\theta)$ for a given c is also the key to determining thermodynamic quantities. This can be understood if one realizes that the nonlinear integral equation (2) stems from the condition that $\psi(\theta)$ minimizes Onsager's free energy $f_O[\psi]$ of equation (A.3). This means that the free energy $f(c)$ (per particle per k_BT) at density c can be calculated by evaluating $f_O[\psi]$ with $\psi(\theta)$ the (numerically determined) distribution. Setting the arbitrary volume b equal to $(\pi/4)L^2D$ for convenience, we obtain for the free energy

$$\begin{aligned} f(c) &= \ln c - 1 + 4\pi \int_0^{\pi/2} \mathrm{d}\theta \, \sin\theta \, \psi(\theta) \ln\psi(\theta) \\ &\quad + 32c \int_0^{\pi/2} \mathrm{d}\theta \, \sin\theta \int_0^{\pi/2} \mathrm{d}\theta' \, \sin\theta' K(\theta,\theta')\psi(\theta)\psi(\theta') \\ &\simeq \ln c - 1 + 4\pi \sum_k \Delta_k \psi_k \ln\psi_k + 32c \sum_{k,l} \Delta_k \Delta_l K_{kl} \psi_k \psi_l \end{aligned} \tag{15}$$

where the solution $\psi(\theta_k)$ was used. Once the free energy is known the (dimensionless) pressure follows as $p(c) = c^2 \mathrm{d}f(c)/\mathrm{d}c$, which yields

$$\begin{aligned} p(c) &= c + 32c^2 \int_0^{\pi/2} \mathrm{d}\theta \, \sin\theta \int_0^{\pi/2} \mathrm{d}\theta' \, \sin\theta' K(\theta,\theta')\psi(\theta)\psi(\theta') \\ &\simeq c + 32c \sum_{k,l} \Delta_k \Delta_l K_{kl} \psi_k \psi_l. \end{aligned} \tag{16}$$

This dimensionless pressure is related to the osmotic pressure Π by $\Pi = k_BTp/b$, which is the excess pressure of the suspension with colloidal rods at a dimensionless concentration c over that of a pure solvent (for which $c = 0$). The dimensionless chemical potential $\mu(c) = f(c) + p(c)/c$ follows from equations (15) and (16). Some numerical results are given in table 1.

Table 1. Density dependence of the pressure p and the order parameter S, on the basis of a grid of $N_\theta = 320$ equidistant θ and a tolerance $t = 10^{-5}$.

c	p	S
4.5	14.76	0.834
5.0	15.98	0.878
5.5	17.31	0.904
6.0	18.69	0.923
6.5	20.10	0.936
7.0	21.54	0.946
7.5	22.98	0.953
8.0	24.44	0.959
8.5	25.91	0.964
9.0	27.38	0.968
9.5	28.85	0.972

Table 2. Grid dependence of the isotropic–nematic coexistence data.

N_θ	c_{I}	c_{N}	S_{N}	p_{IN}	μ_{IN}
10	3.210	4.079	0.7895	13.52	5.056
20	3.261	4.181	0.7989	13.89	5.172
40	3.282	4.191	0.7947	14.05	5.221
80	3.288	4.191	0.7929	14.10	5.236
160	3.290	4.191	0.7924	14.11	5.240
320	3.290	4.191	0.7922	14.12	5.241

Before turning our attention to the calculation of phase coexistence, we remark that analytical expressions for $f(c)$, $p(c)$ and $\mu(c)$ are available in the isotropic phase (where $\psi(\theta) = 1/4\pi$). These results are based on the fact that $\int_0^{\pi/2} \mathrm{d}\theta \sin\theta \int_0^{\pi/2} \mathrm{d}\theta' \sin\theta' K(\theta, \theta') = \pi^2/2$, from which one finds that

$$f_{\mathrm{iso}}(c) = \ln(c/4\pi) - 1 + c \qquad p_{\mathrm{iso}}(c) = c + c^2 \qquad \mu_{\mathrm{iso}}(c) = \ln(c/4\pi) + 2c.$$

The availability of these analytical results not only saves us the effort of determining these functions numerically, they are also a blessing for checking the code against bugs and for estimating the accuracy of the numerical procedure on the grid. The reason is that nothing prevents us from performing the test of calculating $\psi(\theta)$ with our iterative scheme for a density as low as e.g. $c = 1$. The result should be a numerical estimate of $\psi(\theta) = 1/4\pi$ and of the corresponding thermodynamic quantities f, p, μ, S.

Coexistence of an isotropic phase (with density $c = c_{\mathrm{I}}$) and nematic phase (with density $c = c_{\mathrm{N}}$ and order parameter S_{N}) requires mechanical and diffusive equilibrium between these two phases. These conditions are met if and only if the pressure and the chemical potential in the isotropic and nematic phase are the same, i.e.

$$p_{\mathrm{iso}}(c_{\mathrm{I}}) = p(c_{\mathrm{N}}) \qquad \mu_{\mathrm{iso}}(c_{\mathrm{I}}) = \mu(c_{\mathrm{N}}). \tag{17}$$

These conditions can be seen as two equations $p_{\mathrm{iso}}(c_{\mathrm{I}}) - p(c_{\mathrm{N}}) = 0$ and $\mu_{\mathrm{iso}}(c_{\mathrm{I}}) - \mu(c_{\mathrm{N}}) = 0$ for the two unknown densities c_{I} and c_{N}. It is straightforward to find the roots c_{I} and c_{N} numerically using numerical root-finding methods such as Newton–Raphson, or build-in routines in e.g. Mathematica. The dependence of the isotropic–nematic coexistence data on N_θ is illustrated in table 2. One observes that pretty accurate coexistence data can be obtained from N_θ as small as 10, whereas convergence to about four decimals requires $N_\theta = 320$.

There is another physically instructive way to check and interpret the obtained numerical values for the coexisting densities $c_{\rm I}$ and $c_{\rm N}$. It is based on a plot of the Helmholtz free energy per unit volume F/V as a function of density n, or in our dimensionless units $\phi(c) \equiv cf(c)$ as a function of c. Plotting the isotropic branch $\phi_{\rm iso}(c) = c\ln[c/4\pi] - c + c^2$ for $c \in (2.5, 5.0)$ and the numerically determined nematic branch $\phi_{\rm nem}(c)$ for $c \in (3.5, 5.0)$ should reveal that $\phi_{\rm iso}(c^\star) = \phi_{\rm nem}(c^\star)$ for the density $c^\star \simeq 3.539$. For $c > c^\star$ the nematic branch of the free energy is lower than the isotropic one, and vice versa for $c < c^\star$. Naively one could argue that the phase transition should take place at $c = c^\star$, since there, the free energy minimum crosses from one phase to the other. This reasoning is incorrect, however. The reason is that the system at a given density $c \in (c_{\rm I}, c_{\rm N})$ can lower its total free energy even further by splitting up into two subvolumes that coexist with each other: one with an isotropic phase at density $c_{\rm I}$ and the other with a nematic phase at density $c_{\rm N}$. If we denote the fraction of the volume that is occupied by the isotropic and the nematic phase by x and $1 - x$, respectively, then particle conservation dictates that $c = xc_{\rm I} + (1 - x)c_{\rm N}$, or equivalently $x = (c_{\rm N} - c)/(c_{\rm N} - c_{\rm I})$. The resulting total free energy per unit volume of the phase separated system is then the linear combination $\phi_{\rm sep} = x\phi_{\rm iso}(c_{\rm I}) + (1 - x)\phi_{\rm nem}(c_{\rm N})$, which can be written as

$$\phi_{\rm sep}(c) = \phi_{\rm iso}(c_{\rm I}) + \frac{c - c_{\rm I}}{c_{\rm N} - c_{\rm I}}\,(\phi_{\rm nem}(c_{\rm N}) - \phi_{\rm iso}(c_{\rm I}))\,.$$

Plotting this linear function $\phi_{\rm sep}(c)$ together with $\phi_{\rm iso}(c)$ and $\phi_{\rm nem}(c)$ should reveal that the phase-separated system has indeed a lower free energy than the homogenous isotropic or nematic phase, but only for $c \in (c_{\rm I}, c_{\rm N})$. In fact $\phi_{\rm sep}(c)$ represents the common tangent construction (or Maxwell construction); it is the optimal way to lower the free energy by a phase separation into two phases. One checks that the common tangent construction is equivalent to the condition of mechanical and diffusive equilibrium given in equation (17). One may, however, find it difficult to assess this common tangent construction from the scale of the plot, which is dominated by an essentially linear behaviour with c. A convenient trick to improve the visibility is to subtract $c\mu_{\rm IN}$ from all the three curves $\phi_{\rm sep}(c)$, $\phi_{\rm iso}(c)$, and $\phi_{\rm nem}(c)$, which eliminates the linear term. This combination reveals two clear minima at $c_{\rm I}$ and $c_{\rm N}$, of the same depth given by $-p_{\rm IN}$. This is, of course, no coincidence, as the combination $\phi(c) - \mu c$ is the grand potential per unit volume, which at fixed μ (here $\mu = \mu_{\rm IN}$) is minimal at the equilibrium density, the minimal value being the negative of the pressure.

7. Outlook

We have studied the orientational ordering and the thermodynamic properties of a system of rod-like colloidal particles in the isotropic and the liquid crystalline nematic phase. The key quantity is the orientation distribution function $\psi(\theta)$, which is numerically determined by solving a nonlinear integral equation iteratively. The liquid crystalline structure is independent of temperature because we restricted attention to hard-core interactions only. In this athermal limit the phase transition is driven by entropic effects only: at low densities the orientation entropy is maximized at the expense of free volume (a measure for translational entropy), and at high densities the free volume is maximized at the expense of orientation entropy. A similar iteration scheme as presented here can also be applied to study extensions of the present model to for instance binary mixtures of rods of different lengths [8, 9] or different diameters [10], self-assembling rods with a length that can shrink or grow [11], mixtures of flexible and stiff rods [12], mixtures of rod- and disc-like particles [13], polydisperse mixtures of rods (with a continuous distribution of sizes) [14, 15]. These extensions involve a separate distribution function $\psi^{(s)}(\theta)$ for every chemical species s in the system (or for every element

s of the contour of a chain in the case of flexible rods), and a kernel $K^{(ss')}(\theta,\theta')$ to describe the interactions between species s and s'. This is obviously a bit more involved than in the present project, but the rewards include a richer phenomenology such as demixing transitions with critical and triple points in the phase diagrams. Another possible extension of the present calculations involves the description of spatial inhomogeneities, such as in the smectic phase of figure 1(c) [16], the adsorption and film formation of rods in contact with a planar external wall [17], or the isotropic–nematic interface [18]. In these cases the distribution function is not only dependent on θ, but also on the Cartesian coordinate z and sometimes even (weakly) on ϕ; the corresponding kernel is of the type $K(z-z',\theta,\theta',\phi-\phi')$. However, the iteration scheme is not fundamentally different from that of the present study.

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Appendix. The free energy according to Onsager

It is well known that a system with a fixed number of particles (N) in a fixed volume V at a given temperature T will arrange itself such that its Helmholtz free energy $F = U - TS$ is minimized. Here U is the internal energy and S the entropy of the system. In the 1940s Onsager formulated an expression for the free energy of a system of N rods in terms of the (yet unknown) orientation distribution function $\psi(\theta)$. Here we briefly discuss a simplified version of Onsager's argument. In order to understand Onsager's argument one needs to recall from elementary statistical mechanics that the Helmholtz free energy of a classical ideal-gas mixture of $Nx_{\rm i}$ particles of species $i = 1, 2, \ldots, s$ in a volume V can be written as $Nk_BT\sum_{i=1}^{s} x_{\rm i}(\ln(Nx_{\rm i}b/V) - 1)$. Here $x_{\rm i}$ is the fraction of species i, such that $\sum_{i=1}^{s} x_{\rm i} = 1$. The parameter b is an irrelevant constant of dimension volume to make the argument of the logarithm dimensionless. Onsager viewed the suspension of N identical rods as a multicomponent mixture, where he distinguished the rods by their orientation. The fraction of rods with an orientation $\mathbf{u}$ is therefore $\psi(\mathbf{u})$, and this fraction plays the role of the composition variable $x_{\rm i}$ above. Assuming first that the rods do not interact with each other, then the free energy of this system is that of an ideal gas with a very large number of components, and one writes

$$\mathcal{F}_{id}[\psi] = Nk_BT\int \mathrm{d}\mathbf{u}\,\psi(\mathbf{u})\left(\ln\frac{Nb\psi(\mathbf{u})}{V} - 1\right), \tag{A.1}$$

where the integration is over the unit-sphere, and where b is an arbitrary constant of dimension volume for which we will make a convenient choice later. Of course we now have the normalization $\int \mathrm{d}\mathbf{u}\,\psi(\mathbf{u}) = 1$.

However, the rods of interest here do interact since they cannot penetrate each other. In other words, the rods exclude some volume to each other, and hence the volume that is available to a rod with orientation $\mathbf{u}$ is not the total volume V but a smaller volume that we call the free volume $V_f(\mathbf{u})$. The idea is now to calculate $V_f(\mathbf{u})$, which then replaces V in equation (A.1). We denote the volume that a rod with orientation $\mathbf{u}'$ excludes to another rod with orientation $\mathbf{u}$ by the so-called excluded volume $E(\mathbf{u},\mathbf{u}')$, to be calculated below for the long cylindrical rods of interest here. In order to find the free volume for a given rod with orientation $\mathbf{u}$ one needs to subtract the excluded volume due to all the other $N-1$ rods from the total volume. Since we are interested in $N \gg 1$ (e.g. $N = 10^{20}$) we set $N - 1 \approx N$ and write

$$V_f(\mathbf{u}) = V - \frac{N}{2}\int \mathrm{d}\mathbf{u}'\, E(\mathbf{u},\mathbf{u}')\psi(\mathbf{u}'), \tag{A.2}$$

where the factor $1/2$ corrects for double counting. Replacing the volume V in equation (A.1) by the free volume of equation (A.2), and using the low-density Taylor expansion $\ln V_f(\mathbf{u}) \simeq \ln V - (n/2)\int \mathrm{d}\mathbf{u}' E(\mathbf{u},\mathbf{u}')\psi(\mathbf{u}')$, yields the Onsager expression for the free energy (per particle, per $k_B T$) given by

$$f_O[\psi] = \int \mathrm{d}\mathbf{u}\, \psi(\mathbf{u})\,(\ln(nb\psi(\mathbf{u})) - 1) + \frac{n}{2}\int \mathrm{d}\mathbf{u}\int \mathrm{d}\mathbf{u}'\, E(\mathbf{u},\mathbf{u}')\psi(\mathbf{u})\psi(\mathbf{u}'). \tag{A.3}$$

Although this derivation may suggest that severe approximations have been made in order to arrive at equation (A.3), it turns out to be the exact low-n expansion, i.e. the next order term of the right-hand side is $\mathcal{O}(n^2)$. Moreover, it was shown by Onsager that equation (A.3) is even *exact* for rods in the needle limit $L/D \to \infty$, i.e. in that case the corrections can be ignored for densities in the regime of isotropic and nematic phases. In fact Onsager's expression (A.3) for the free energy of a system of infinitely long hard rods is one of the very few exactly known free-energy expressions for off-lattice systems of interacting particles.

The next problem to tackle is the calculation of the excluded volume. Using simple geometric arguments it is easy to see that $E(\mathbf{u},\mathbf{u}')$ only depends on the angle γ between the two rods, defined such that $\mathbf{u}\cdot\mathbf{u}' = \cos\gamma$. It is also easy to convince oneself that the excluded volume of two perpendicular rods ($\gamma = \pi/2$) is an $\mathcal{O}(L^2 D)$ volume, whereas it is only $\mathcal{O}(LD^2)$ for two parallel rods ($\gamma = 0$). It is a more complicated geometric problem to find the general γ-dependence

$$E(\mathbf{u},\mathbf{u}') = 2L^2 D|\sin\gamma| + \mathcal{O}(LD^2) = 2L^2 D\sqrt{1 - (\mathbf{u}\cdot\mathbf{u}')^2}, \tag{A.4}$$

where the $\mathcal{O}(LD^2)$ contributions can be ignored in the long-rod limit $L \gg D$. We work in this limit here. Derivations of this result can be found in a remarkable appendix of Onsager's original paper [1]. We have now calculated expressions (A.3) and (A.4) that give the free energy of a suspension of rod-like particles with density n at a given orientation distribution $\psi(\mathbf{u})$. However, the orientation distribution of such a suspension is not a quantity that can be imposed externally (in contrast with the composition of a mixture of gases, which can be controlled and fixed externally). Rather the suspension determines, at a given n, its own distribution $\psi(\mathbf{u})$ in such a way as to minimize the free energy $f_O[\psi]$. We have to consider the constraint that the normalization $\int \mathrm{d}\mathbf{u}\, \psi(\mathbf{u}) = 1$ must be retained. Mathematically this minimum condition can be written as a vanishing (functional) derivative of $f_O[\psi] - \lambda\int \mathrm{d}\mathbf{u}\psi(\mathbf{u})$ with respect to ψ, where λ is a Lagrange multiplier. This implies that the equilibrium distribution satisfies

$$\ln\psi(\mathbf{u}) + n\int \mathrm{d}\mathbf{u}'\, E(\mathbf{u},\mathbf{u}')\psi(\mathbf{u}') = \lambda - \ln(nb) \equiv \exp(-Z). \tag{A.5}$$

The prefactor Z is fixed by the condition that $\int \mathrm{d}\mathbf{u}\, \psi(\mathbf{u}) = 1$. If we now insert the excluded volume expression (A.4) into (A.5), together with the representation $\mathbf{u}\cdot\mathbf{u}' = \cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\phi - \phi')$ in the present coordinate system, one arrives directly at the nonlinear integral equation (2) with the kernel $K(\theta,\theta')$ as defined in (2) and the prefactor Z given in equation (5).

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