Finite-Density Onsager-Type Theory for the Isotropic-Nematic Transition of Hard Ellipsoids

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We propose a simple density-functional theory for the isotropic-nematic transition of a system of hard ellipsoids which yields results in fair agreement with the computer simulation studies and which reduces exactly to Onsager's theory in the limit of infinitely dilute systems of infinitely long ellipsoids. When the free energy is expanded with respect to the Maier-Saupe quadrupole order parameter an explicit Landau theory is produced which yields good results for small nonsphericities. The theory also predicts a Lindemann rule for orientational freezing.

A system of nonspherical molecules can exhibit a large variety of liquid-crystal phases or mesophases with a symmetry in between that of the liquid and that of the crystal.[1] The simplest possible theoretical model for a nonspherical molecule is certainly a hard ellipsoid of revolution. A system of hard ellipsoids (HE) can therefore be expected to be as good a reference system for the theoretical study of the liquid-crystal phases as the system of hard spheres (HS) is for the study of the condensed phases of spherical molecules.[2] Recent computer simulations[3] have shown, moreover, that the phase diagram of HE already has a very rich structure, not unlike that of the real molecular systems. While previous theoretical investigations[4,5] have indicated how the classic liquid-crystal theories of Maier and Saupe[6] and of McMillan[7] can be incorporated into the general density-functional theory of phase coexistence,[8] relatively less attention has been paid to the relation between the latter theory and Onsager's theory[9] of the isotropic-nematic transition of infinitely dilute systems of infinitely long rods. It is the purpose of the present investigation to present a fairly simple extension of Onsager's theory to systems of HE of finite elongation and finite density. Only the isotropic-nematic transition of the HE system will be considered here, while the results will be compared to the most recent theoretical[10,11] and computer simulation[3] studies.

The form of the density-functional theory which will be used here is a straightforward extension to the HE systems of the theory used previously for the study of phase equilibria in HS systems.[12] Our starting point is the following exact expression[8,12] for the (Helmholtz) free energy of the ordered (nematic) phase, $F[\rho]$, viewed as a functional of its local number density $\rho(\mathbf{x})$, in terms of the corresponding free energy of the disordered (isotropic) phase, $F[\rho_0]$, of uniform and isotropic density ρ_0:

$$\beta F[\rho] = \beta F[\rho_0] + \int d^3x\, \rho(\mathbf{x})\ln[\rho(\mathbf{x})/\rho_0] - \int d^3x \int d^3x' \int_0^1 d\lambda (1-\lambda) c_2(\mathbf{x},\mathbf{x}';[\rho_\lambda])\Delta\rho(\mathbf{x})\Delta\rho(\mathbf{x}'), \tag{1}$$

where we have neglected the contribution from external fields and introduced the two-body direct correlation function, $c_2(\mathbf{x},\mathbf{x}';[\rho_\lambda])$, of a system of density $\rho_\lambda(\mathbf{x})$ $=\rho_0+\lambda\Delta\rho(\mathbf{x})$ with $\Delta\rho(\mathbf{x})=\rho(\mathbf{x})-\rho_0$. The constant inverse temperature is $\beta=1/k_B T$, while $\mathbf{x}=\{\mathbf{r},\mathbf{u}\}$ with $\mathbf{r}$ locating the center of the HE and $\mathbf{u}$ its orientation, viz., $\mathbf{u}$ is a unit vector along the axes of revolution of the HE. The λ integral in (1) results from a functional integration in density space[12] between the disordered ($\lambda=0$) and the ordered ($\lambda=1$) phase at constant average density, viz., $\rho=\rho_0$. The average density ρ is defined here as the spatial average of $\rho(\mathbf{x})\equiv\rho(\mathbf{r},\mathbf{u})$ over the volume with respect to $\mathbf{r}$ and over a unit sphere with respect to $\mathbf{u}$.

In order to locate the possible ordered phases we minimize the free energy (1) with respect to a suitably parametrized local density $\rho(\mathbf{x})$ which in the case of a nematic phase can be written, $\rho(\mathbf{x})=\rho f(\mathbf{u})$, with $f(\mathbf{u})$ the normalized angular distribution of the HE. In the following we will restrict ourselves to nematics with a uniaxial cylindrical symmetry around a director $\mathbf{n}$ and with a plane of symmetry perpendicular to $\mathbf{n}$. In this case $f(\mathbf{u})$ depends only on the angle θ between $\mathbf{u}$ and $\mathbf{n}$, viz., $f(\mathbf{u})=f(m)\equiv f(-m)$ with $\mathbf{u}\cdot\mathbf{n}=\cos\theta=m$. The simplest one-order-parameter possibility is to use the Maier and Saupe form,[1,6]

$$f(m) = \exp(\gamma m^2)\left[\int_0^1 dm \exp(\gamma m^2)\right]^{-1}, \tag{2}$$

so that for $-\frac{1}{2}\pi \le \theta \le \frac{1}{2}\pi$, $f(\cos\theta)$ is singly peaked around $\theta=0$ with an inverse width determined by γ and $\gamma\neq0$ corresponding to an anisotropic phase. Equation (2) is physically acceptable and mathematically more convenient than the Onsager trial function.[9] More general distributions can be considered but are found to give only little improvement.

Before the free energy of (1) can be minimized with respect to γ of (2) we also need an explicit expression for the direct correlation function of the different phases of the HE system. Since the theoretical information on the

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direct correlation function of nonspherical convex bodies is very scarce[13] we will assume a simple factorization of the translational ($\mathbf{r}$) and the orientational ($\mathbf{u}$) direct correlations:

$$c_2(\mathbf{r},\mathbf{u};\mathbf{r}',\mathbf{u}';[\rho]) = \Sigma(\mathbf{u}\cdot\mathbf{u}')c_{PY}\left[\frac{|\mathbf{r}-\mathbf{r}'|}{\sigma_0};\bar{\eta}(\eta)\right], \quad (3)$$

where the translational correlations of the HE system have been further approximated by those of HS of the same volume (or packing fraction $\eta = \frac{1}{6}\pi\sigma_0^3\rho$ with $\sigma_0^3 = \sigma_\parallel\sigma_\perp^2$ for ellipsoids of revolution with diameter $\sigma_\parallel$ along the axis of revolution and $\sigma_\perp$ perpendicular to this axis) described here within the Percus-Yevick (PY) approximation.[2] The angular direct correlations are taken care of by (3) through the factor $\Sigma(\mathbf{u}\cdot\mathbf{u}')$ which describes the volume excluded to two HE of respective orientations $\mathbf{u}$ and $\mathbf{u}'$ when averaged over the center to center orientations and divided by the molecular volume $v_{mol} = \frac{1}{6}\pi\sigma_\parallel\sigma_\perp^2$. Approximating the distance of closest approach of two HE by the Gaussian overlap model proposed by Berne and Pechukas,[14] one finds

$$\Sigma_{BP}(\mathbf{u}\cdot\mathbf{u}') = [1-\chi^2(\mathbf{u}\cdot\mathbf{u}')^2]^{1/2}(1-\chi^2)^{-1/2}, \quad (4)$$

with $\chi = (k^2-1)/(k^2+1)$ and $k = \sigma_\parallel/\sigma_\perp$ the aspect ratio, viz., $0 < k < 1$ for oblate and $1 < k < \infty$ for prolate HE. Notice that approximation (3) is akin to a perturbational treatment of the HE system around a HS reference system. For the isotropic phase of the HE system, the reference HS system is taken at the same density ($\bar{\eta}$) as the original HE system (η), viz., $\bar{\eta} = \eta$ in (3), whereas for the nematic phase the effective density, $\bar{\eta}$, of the reference HS system has to be taken smaller ($\bar{\eta} < \eta$) than the average density of the nematic (η) so as to take into account the reduction of the interactions in the ordered phase as compared to the disordered isotropic phase used as reference for the nematic. The explicit relation between $\bar{\eta}$ and η, $\bar{\eta} = \bar{\eta}(\eta)$, to be used in (3) will be determined from a structural scaling condition between the HE and the reference HS which takes into account the geometric constraints of the nematic phase. We will assume therefore that, at contact, the direct correlation functions of the HS system evaluated at the real and at the effective density are related by

$$c_{PY}\left[\frac{|\mathbf{r}|}{\sigma_0} = 1;\eta\right] = c_{PY}\left[\frac{|\mathbf{r}|}{\sigma_0} = x(\chi);\bar{\eta}\right], \quad (5)$$

where σ_0 is the average contact distance of the HE in the isotropic phase (so that the HE can be replaced by HS of diameter σ_0), whereas σ_0 times x (<1) is the average contact distance of the HE in the nematic phase. Since k is the natural length scale of the problem we put $x = k$ when $k < 1$ and $x = 1/k$ when $k > 1$, or in terms of χ, $x(\chi) = (1-|\chi|)^{1/2}/(1+|\chi|)^{1/2}$. It is clear that the difference between $\bar{\eta}$ and η as obtained from (5), or the expansion of $\bar{\eta}(\eta)$ around η in (3), can represent only a

rough estimate of the influence of the higher-order terms of (1) if the latter were to be expanded further with respect to $\Delta\rho(\mathbf{x})$. From the study of the liquid-solid transition[12] it is known, however, that these higher-order terms cannot be completely neglected because of the poor convergence properties of the $\Delta\rho(\mathbf{x})$ expansion. It is hoped therefore that (5) takes into account the essential physics of this effect in the same way as the structural scaling condition used elsewhere[12] did for the liquid-solid transition. Two important aspects of the above approximation scheme are that (1) it admits an exact symmetry between oblate and prolate HE of the same molecular volume, i.e., a $\chi \leftrightarrow -\chi$ invariance, and (2) it reduces exactly to the theory proposed by Onsager[9,15] for the nematic phase of a dilute system of long rods. The existence of an almost perfect oblate-prolate symmetry is indeed one of the major findings of the recent computer simulations,[3] while Onsager's theory[9] is an exact result in the limit as $k \to \infty$, $\eta \to 0$ with $k\eta = c$ constant.

For the *isotropic* phase we find from (3) that the excess thermodynamic properties of the HE are given by those of the HS of the same molecular volume, times the angular-averaged excluded volume (4), viz., for the compressibility equation of state,

$$\left[\frac{\beta p}{\rho}-1\right]_{HE} = H(\chi)\left[\frac{\beta p}{\rho}-1\right]_{HS}$$

$$= H(\chi)(4\eta-2\eta^2+a\eta^3)/(1-\eta)^3, \quad (6)$$

with

$$H(\chi) = \int d^3u \int d^3u' \Sigma_{BP}(\mathbf{u}\cdot\mathbf{u}')$$

$$= \frac{1}{2}\left[1+\frac{\arcsin\chi}{\chi(1-\chi^2)^{1/2}}\right],$$

where $a = 1$ when the PY approximation is used to describe the HS [as implied by (3)] and $a = 0$ when the more accurate Carnahan-Starling equation of state[2] is used. In Fig. 1 we compare the results of (6) with the computer simulations[3] and with some of the alternative theories[13] leading to explicit expressions [notice that (6) can also be obtained from the Pynn model[16] used by Singh and Singh[11]]. It is seen there that within the PY theory of HS the pressure of the HE is slightly overestimated by (6) but that with the Carnahan-Starling HS expression the agreement is very good. This, in view of the simplicity of (6), surprising result certainly points to the soundness of our basic approximation (3). For the *nematic* phase we find that the free energy has a second minimum (besides the one at $\gamma = 0$ corresponding to the isotropic phase) only above a threshold density, $\eta_0(k)$. Whereas $\eta_0(k)$ is a rapidly decreasing function of k (because of the oblate-prolate symmetry we only consider prolate HE, viz., $k > 1$), the order parameter at thresh-
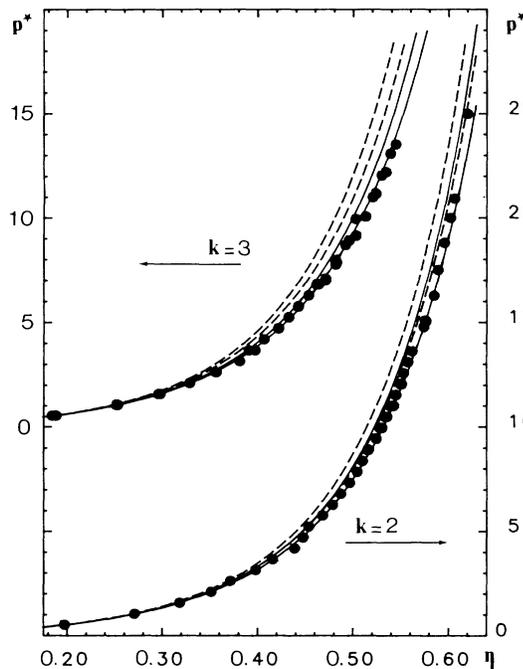
FIG. 1. Reduced pressure of the isotropic phase, $p^* = \beta p v_{mol}$, for $k = 2$ and 3 as given by Eq. (6) (solid line) and by scaled particle theory (dashed line) as extended to convex bodies by Gibbons and Boublik [see Eqs. (4.96) and (4.105) of Ref. 13]. In each case the upper curve corresponds to the version of the theory which in the limit of hard spheres ($k = 1$) reduces to the Percus-Yevick compressibility result while the lower curve corresponds to the version which reduces to the Carnahan-Starling result for $k = 1$. The dots correspond to the computer-simulation results of Frenkel and Mulder (Ref. 3) ($k = 3$ is the largest nonsphericity considered by the simulations).

FIG. 2. Coexisting densities (η) of the isotropic (lower curve) and nematic (upper curve) phases as a function of the aspect ratio k as obtained from various sources. We have from top to bottom (1) the computer simulations (Ref. 3) (dots), where the only available results correspond to $k = 2.75$ and 3, (2) the present theory (solid line), (3) the theory of Mulder and Frenkel (Ref. 10) (dot-dashed line), and (4) the theory of Singh and Singh (Ref. 11) (dashed line). When k decreases the coexisting densities increase and width of the transition decreases very rapidly. In the high-density region ($k < 2.5$) the isotropic-nematic transition will be preempted by a liquid-solid transition (Ref. 3). In the opposite low-density–large-k region we show in the inset how the present results (solid line) go slowly over into the Onsager limiting result $\eta = c/k$ (dashed line).

old, $\gamma_0 = \gamma(\eta_0(k),k)$, remains practically constant ($\gamma_0 \simeq 3$) pointing to the existence of a Lindemann rule[2] for orientational freezing. The nematic phase then stabilizes very quickly, first at constant density and then at constant pressure, while for still higher densities the free-energy extremum corresponding to the isotropic phase disappears as a minimum so that only the nematic phase survives. All these characteristics are very close to one another and decrease with k somewhat slower than assumed in the Onsager theory, viz., $k\eta(k)$ is a slightly increasing function of k for $k > 1$. The constant-pressure isotropic-nematic transitions have been located here by Maxwell's double-tangent construction which is much simpler but, because of the inherent thermodynamic inconsistency, not identical to the solution of the two-phase coexistence conditions used previously.[12] As seen from Fig. 2 the coexisting densities are slightly underestimated by the theory but smoothly join the simulation results ($k \simeq 3$) to the Onsager limit ($k = \infty$).

The theoretical and computer simulated phase diagrams are compared in Fig. 3.

Finally, we have also investigated the status of Landau's theory of weakly first-order transitions[1] by expanding the free energy in terms of the Maier-Saupe quadrupole order parameter, $q = \int_0^1 dm (\frac{3}{2} m^2 - \frac{1}{2})$ $\times f(m)$, which is a bounded order parameter ($0 < q < 1$) whereas γ is not, viz., $\beta F = \sum_n a_n q^n$, with truncation of this expansion after the q^4 term. We have compared the density-functional theory and its Landau approximation and found that for $k \leq 3$ the Landau theory performs surprisingly well, whereas for $k > 3$ it still predicts a transition at about the correct density but which is much too weak and narrow (as k tends to infinity q and $\Delta\eta/\eta_N$ tend, respectively, to 0.386 and 0.043 for the Landau theory, and 0.799 and 0.276 for the density-functional theory, whereas the exact[15] results are 0.792 and 0.274).
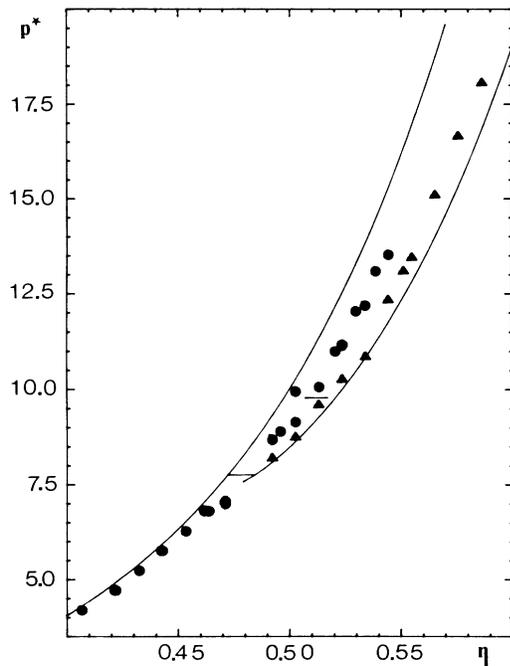
FIG. 3. Theoretical (solid line) and computer-simulation (Ref. 3) phase diagram in the pressure(p^*)-density(η) plane for $k = 3$. The tie line between the isotropic (dots) and nematic (triangles) branches of the simulations is indicated by a solid line segment. For $k = 3$ the coexisting densities are $\eta_I = 0.507$, $\eta_N = 0.517$ for the simulation results (Ref. 3), $\eta_I = 0.472$, $\eta_N = 0.484$ for the present theory, $\eta_I = 0.419$, $\eta_N - 0.437$ for the theory of Mulder and Frenkel (Ref. 10) and $\eta_I = 0.309$, $\eta_N = 0.330$ for the theory of Singh and Singh (Ref. 11).

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