Density-functional, Landau, and Onsager theories of the isotropic-nematic transition of hard ellipsoids

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We propose a density-functional theory for the isotropic-nematic transition of hard ellipsoids which is in fair quantitative agreement with the recent computer simulations of this system and which improves considerably upon the earlier theoretical attempts. The theory has an explicit oblate-prolate symmetry and leads to simple analytic expressions, e.g., for the equation of state of the isotropic phase. When the free energy of the nematic phase is expanded with respect to the Maier-Saupe quadrupole order parameter, an explicit Landau theory is produced, which is shown to underscore considerably the strength and the width of the transition. A virial expansion of the free energy produces in turn an Onsager theory for finite elongations whose results are shown to tend only very slowly to their Onsager limiting value. We also propose a Lindemann rule for orientational freezing.

I. INTRODUCTION

The main reason to study systems of hard convex bodies is that they provide us with *simple* reference systems for the investigation of more realistic systems. For instance, it is well known that the study of systems of hard spheres (HS), both by theory[1] and computer simulations,[2] has played an important role in the elaboration of present day liquid-state theory[1] and in our understanding of the liquid-solid phase transition.[2] The HS system is also known to be a very good reference system for a perturbational study of realistic systems of spherical molecules.[1] In the case of non-spherical molecules the number of possible geometric shapes is much larger but within the context of convex bodies the simplest possible reference system appears to be a system of hard ellipsoids (HE). It is well known that such nonspherical molecules can form a very large variety of liquid-crystal phases or mesophases with a symmetry in between that of the liquid and of the crystal.[3] Recent computer simulations[4] have shown that systems of HE do exhibit some of these liquid-crystal phases and can thus indeed be used as simple reference systems for the study of nonspherical convex molecules. The very existence of a HS crystal[2] and a HE nematic phase[4] also shows that the attractive forces are not essential for the occurrence of, respectively, positional freezing and orientational freezing, and that both phase transitions are thus monitored by the *repulsive* forces leading to a competition between entropic and excluded volume effects. The simulations have, moreover, shown[4] that liquid crystal phases can be formed both by prolate (rodlike) and by oblate (dislike) HE. These various facts taken together indicate that the HE system can be expected to yield a good reference system for a perturbational treatment[5] of more realistic systems of nonspherical convex molecules.

It is the purpose of this investigation to present a simple, HS-based, theory for two of the simplest phases of the HE system together with their phase coexistence. The two phases which will be considered here are the fully disordered, uniform and isotropic, fluid phase, and the orientationally ordered, uniform and anisotropic, nematic phase, designated hereafter, respectively, as the (isotropic) I phase and the (nematic) N phase. The HE system considered here will, moreover, be composed of ellipsoids of revolution so that the corresponding N phase is always uniaxial.

The most convenient theoretical framework available at present for the study of several phases and their coexistence from a unified point of view appears to be the density-functional theory (DFT). This approach to equilibrium statistical mechanics bears its name from the fact that it views the thermodynamic potential of the system as a functional of the average one-body density. The version of the DFT which will be used here[6] is based on the Helmholtz free energy as thermodynamic potential. For convenience a brief summary is given in Sec. II. Its application to the approximate description of the I phase is then described in Sec. III. The N phase and the I-N coexistence are studied in Sec. IV. The relation to the classical theories of Landau[7] and Onsager[8] as well as to some recent theoretical[9–11] and computer simulation[4] studies is developed in Sec. V, whereas the final section (Sec. VI) contains our conclusions. A preliminary account of the present investigation has already been presented elsewhere,[12] whereas some related liquid-crystal studies[13] should also be mentioned here.

II. THE DFT IN THE HELMHOLTZ FREE-ENERGY LANGUAGE

In the traditional approach to equilibrium statistical mechanics one starts from a set of equations (usually the Born-Green-Yvon hierarchy[1,5]) for the structural functions (the n-body densities) which once solved are used to compute the thermodynamic data from which the phase coexistence can then eventually be inferred. In the more modern approach this rather lengthy procedure is

shortcut by considering directly the relevant thermodynamic data (free energy, pressure, chemical potential) as given functionals of the structural functions. This now widely used so called "density-functional theory" can be presented in various ways (see Ref. 6 for an extensive list of references). In the early presentations of the DFT the starting point was taken to be the grand-canonical thermodynamic potential or Landau free energy, $\Omega=\Omega(\mu,V,T)$, for which the chemical potential μ, the volume V, and the temperature T are the natural variables. This set of variables together with the Gibbs-Duhem relation $\Omega=-pV$, between Ω and the pressure p, make Ω a very convenient potential for the study of phase coexistence. This certainly is the case as far as the exact manipulations are concerned but becomes more questionable once approximations to Ω and hence to p are introduced because then the two-phase equilibrium conditions of constancy of p and constancy of μ are no longer treated on the same level of approximation since p is approximated while μ remains an independent variable. For this reason we have favored a presentation of the DFT based on the canonical thermodynamic potential or Helmholtz free energy, $F=F(\rho,V,T)$, for which the number of particles N or the (average number) density $\rho=N/V$ is the natural variable besides V and T. It is this approach, in which F is the quantity to be approximated and both p and μ are deduced from it, which will be used here. Details can be found elsewhere[6,14] but for convenience a summary is included here.

In the DFT the Helmholtz free energy F is viewed, moreover, as a functional of the *local* (average number) density $\rho(\mathbf{x})$, $F=F(\rho,V,T;[\rho])$, or omitting as usual the thermodynamic variables (ρ,V,T) and focusing our attention on this functional dependence, indicated by square brackets, we write briefly $F=F[\rho]$. The related Landau free energy $\Omega=\Omega[\rho]$ and Gibbs free energy $G=G[\rho]$ can then be obtained from $F[\rho]$ by a functional Legendre transformation as

$$G[\rho]=\int d\mathbf{x}\,\rho(\mathbf{x})\frac{\delta F[\rho]}{\delta\rho(\mathbf{x})}\ , \tag{2.1}$$

$$\Omega[\rho]=F[\rho]-G[\rho]\ , \tag{2.2}$$

where $\mathbf{x}$ stands for all (one-body) degrees of freedom with $d\mathbf{x}$ normalized over the volume, $\int d\mathbf{x}=V$, so that

$$\rho=\frac{1}{V}\int d\mathbf{x}\,\rho(\mathbf{x}) \tag{2.3}$$

represents the *average* density. The reduced thermodynamic potentials will be denoted $f[\rho]=F[\rho]/V$ for the Helmholtz free energy density, $p[\rho]=-\Omega[\rho]/V$ for the pressure, and $\mu[\rho]=G[\rho]/\rho V$ for the chemical potential (the latter two interpretations follow from the Gibbs-Duhem relations[7]). The above expressions still correspond to arbitrary (metastable) states $\rho(\mathbf{x})$. The equilibrium state can be selected by using the extremum principle of the given potential. For the Helmholtz free energy, used here as basic potential, this principle reads

$$\delta F\,|_{\rho,V,T}\equiv\int d\mathbf{x}\,\frac{\delta F[\rho]}{\delta\rho(\mathbf{x})}\bigg|_{\rho,V,T}\delta\rho(\mathbf{x})=0\ , \tag{2.4}$$

which implies

$$\frac{\delta F[\rho]}{\delta\rho(\mathbf{x})}\bigg|_{\rho,V,T}=\mu[\rho] \tag{2.5}$$

since at constant ρ we have

$$\int\frac{d\mathbf{x}}{V}\delta\rho(\mathbf{x})\equiv\delta\rho\equiv 0\ .$$

Indeed, using (2.5) in (2.4) leads to $\delta F\equiv\mu V\,\delta\rho=0$. From the chain rule

$$\frac{\partial f[\rho]}{\partial\rho}=\frac{1}{V}\int d\mathbf{x}\frac{\delta F[\rho]}{\delta\rho(\mathbf{x})}\frac{\partial\rho(\mathbf{x})}{\partial\rho} \tag{2.6}$$

and (2.5) we find that, *at equilibrium*, the chemical potential can be obtained from the free-energy density as

$$\mu[\rho]=\frac{\partial}{\partial\rho}f[\rho]\ , \tag{2.7}$$

whereas from (2.1) μ is also seen to be the Gibbs free-energy per particle $G/\rho V$ so that, *at equilibrium*, (2.2) yields also the pressure p in terms of f as

$$p[\rho]=\rho\frac{\partial f[\rho]}{\partial\rho}-f[\rho]\ , \tag{2.8}$$

and both p (2.8) and μ (2.7) can thus be expressed in terms of the same (approximate) free-energy density f.

Besides satisfying the extremum condition (2.5), the true equilibrium state $\rho(\mathbf{x})$ should also make $F[\rho]$ a minimum. In other words, at equilibrium, the following expression $(\beta=1/k_BT)$:

$$\beta\frac{\delta^2F[\rho]}{\delta\rho(\mathbf{x})\delta\rho(\mathbf{x}')}\equiv\frac{\delta(\mathbf{x}-\mathbf{x}')}{\rho(\mathbf{x})}-c(\mathbf{x},\mathbf{x}';[\rho])\ , \tag{2.9}$$

defining the (two-body) direct correlation function (DCF) $c(\mathbf{x},\mathbf{x}';[\rho])$ should be a positive definite functional. Both sides of (2.9) can then be integrated twice along a linear path in density space[14] at a constant average density and starting from a known reference state ρ_0 to yield[14]

$$\begin{aligned}\beta f[\rho]=\beta f[\rho_0]&+\frac{1}{V}\int d\mathbf{x}\,\rho(\mathbf{x})\ln[\rho(\mathbf{x})/\rho_0]\\&-\frac{1}{V}\int d\mathbf{x}\int d\mathbf{x}'\int_0^1 d\lambda(1-\lambda)\\&\times c(\mathbf{x},\mathbf{x}';[\rho_0+\lambda\Delta\rho])\\&\times\Delta\rho(\mathbf{x})\Delta\rho(\mathbf{x}')\ ,\end{aligned} \tag{2.10}$$

where $\Delta\rho(\mathbf{x})\equiv\rho(\mathbf{x})-\rho_0$, $\rho_0\equiv\rho$, and $f[\rho_0]$ is the free-energy density of the reference state. The property (2.10), which is the central relation of DFT, is exact [notice that for simplicity the contributions from external symmetry breaking potentials have not been written down explicitly since they are assumed to yield a negligible contribution to the bulk thermodynamics in the limit of a large system whereas, as usual, the reference state has been considered to be a fully disordered state, $\rho_0(\mathbf{x})\equiv\rho_0$]. The way in which (2.10) will be used by us is then as follows: (1) For each phase an approximate expression of the functional $c(\mathbf{x},\mathbf{x}';[\rho])$ is sought for in terms of the disordered reference system DCF (for which the functional dependence on ρ degenerates into an ordinary function

$c(\mathbf{x},\mathbf{x}';[\rho_0])\equiv c(\mathbf{x},x';\rho_0)$); (2) for each phase, the local density $\rho(\mathbf{x})$ is suitably parametrized and these parameters are then determined by minimizing $f[\rho]$ as given by the previous approximation to the rhs of (2.10); (3) for each phase, the value of $\rho(\mathbf{x})$ and of $f[\rho]$ for the parameter values corresponding to the minimum are used to compute the thermodynamics of the given phase from (2.7) and (2.8); (4) the two-phase coexistence is then located by equating the chemical potentials and the pressures of a given pair of phases (the temperature T is considered as a constant parameter throughout). The underlying physics is thus completely contained in the first two steps whereas the last two steps are purely technical. We now work out the above program for the I-N transition of a system of HE (alternative approaches to the DFT are discussed in Ref. 6).

III. THE ISOTROPIC PHASE

For the I phase several simplifications occur because of its translational and rotational invariance. The local density $\rho(\mathbf{x})$ of a uniform and isotropic (fluid) phase is a constant, equal to the average density ρ, and all the functionals of $\rho(\mathbf{x})$ degenerate into ordinary functions of ρ. Hence we have for the I phase $\rho(\mathbf{x})\equiv\rho$ and $c(\mathbf{x},\mathbf{x}';[\rho])\equiv c(\mathbf{x},\mathbf{x}';\rho)$. If we locate the ellipsoid in space with the aid of the position of its center ($\mathbf{r}$) and a unit vector ($\mathbf{u}$) along the axes of revolution $\mathbf{x}=(\mathbf{r},\mathbf{u})$, we can write, moreover, $c(\mathbf{x},\mathbf{x}',\rho)\equiv c(\mathbf{r}-\mathbf{r}';\mathbf{u},\mathbf{u}';\rho)$ for the DCF of the I phase. The basic theories of HE, or of convex bodies in general,[5,15] are not at present sufficiently advanced to provide us with the necessary analytic expression of the DCF (see Ref. 15 for a review of this question). As a possible alternative, Pynn first suggested[16] to use a HS DCF with an orientation-dependent HS diameter. The consequences of this model were worked out by Lado and found[17] to yield good results for both the thermodynamics and the structure. The main drawback of Pynn's model appears to be that it predicts an isotropic DCF at the origin and at contact, which is unphysical.[17] The alternative we propose here is based on the idea of factorizing the translational ($\mathbf{r},\mathbf{r}'$) and the angular ($\mathbf{u},\mathbf{u}'$) variables:

$$c(\mathbf{r}-\mathbf{r}';\mathbf{u},\mathbf{u}';\rho)=\Sigma(\mathbf{u}\cdot\mathbf{u}')c_0(\,|\,\mathbf{r}-\mathbf{r}'\,|\,,\rho)+\cdots \tag{3.1}$$

or, in other words, of expressing the DCF of the HE in terms of those of a reference HS system. For the latter we take HS of the same volume as the HE and describe the DCF of these HS within the Percus-Yevick (PY) approximation:[1]

$$c_0(\,|\,\mathbf{r}\,|\,,\rho)=c_{\mathrm{PY}}\left[\frac{|\,\mathbf{r}\,|}{\sigma_0},\eta\right], \tag{3.2}$$

where σ_0 is the HS diameter and $\eta=(\pi/6)\sigma_0^3\rho$ the corresponding packing fraction of either the HS or the HE since both have the same molecular volume $v_{\mathrm{mol}}=(\pi/6)\sigma_0^3=(\pi/6)\sigma_\parallel\sigma_\perp^2$ for ellipsoids of revolution with diameter $\sigma_\parallel$ along the axis of revolution and diameter $\sigma_\perp$ perpendicular to this axis. While (3.2) takes care of the translational correlations of the HE, which on the average cannot be very different from those of HS of the same volume with σ_0 playing the role of a rotationally averaged HE diameter, it still remains to determine the angular correlations described here by $\Sigma(\mathbf{u}\cdot\mathbf{u}')$ of (3.1) and which result from the intrinsically anisotropic HE interactions, as opposed to the isotropic HS interactions. Assuming that the density effects are sufficiently well taken care of by the translational term $c_0[(\,|\,\mathbf{r}-\mathbf{r}'\,|\,),\rho]$, we now evaluate the angular term $\Sigma(\mathbf{u}\cdot\mathbf{u}')$ to lowest order in density. In this case $\Sigma(\mathbf{u}\cdot\mathbf{u}')$ represents the volume excluded to two HE of given orientations $\mathbf{u}$ and $\mathbf{u}'$, averaged over the orientations of their center-to-center position $\mathbf{r}-\mathbf{r}'$, and divided by the HE volume:

$$\Sigma(\mathbf{u}\cdot\mathbf{u}')=\int\frac{d\hat{\mathbf{w}}}{4\pi}\left[\frac{\pi}{6}\sigma^3(\hat{\mathbf{w}};\mathbf{u},\mathbf{u}')\Big/\frac{\pi}{6}\sigma_\parallel\sigma_\perp^2\right], \tag{3.3}$$

where $\hat{\mathbf{w}}=(\mathbf{r}-\mathbf{r}')/|\,\mathbf{r}-\mathbf{r}'\,|$ is a unit vector along the line joining the centers and $\sigma(\hat{\mathbf{w}};\mathbf{u},\mathbf{u}')$ is the contact distance of two HE of orientations $\mathbf{u}$ and $\mathbf{u}'$. The precise determination of the contact distance of two HE, $\sigma(\hat{\mathbf{w}};\mathbf{u},\mathbf{u}')$, is a complicated geometrical problem.[15] An interesting, approximate but analytic, expression for it can however be obtained from the Gaussian overlap method[18] of Berne and Pechukas. In this method each ellipsoid is replaced by a Gaussian distribution

$$g(\mathbf{r},\mathbf{A})=e^{-\mathbf{r}\cdot\mathbf{A}^{-1}\cdot\mathbf{r}}/(\pi^3\,|\,\mathbf{A}\,|\,)^{1/2} \tag{3.4}$$

with the center at $\mathbf{r}=\mathbf{0}$ and anisotropic width matrix given by

$$\mathbf{A}=\sigma_\parallel^2\mathbf{uu}+\sigma_\perp^2(\mathbf{1}-\mathbf{uu}) \tag{3.5}$$

so that the distribution $g(\mathbf{r};\mathbf{A})$ is essentially concentrated inside an ellipsoid of revolution with $\mathbf{u}$ as unit vector along the symmetry axis and with a diameter $\sigma_\parallel$ along $\mathbf{u}$ and a diameter $\sigma_\perp$ in any direction perpendicular to $\mathbf{u}$. Convoluting two such ellipsoidal Gaussian distributions and using the result

$$\int d\mathbf{r}'\,g(\mathbf{r}',\mathbf{A})g(\mathbf{w}+\mathbf{r}',\mathbf{A}')=g(\mathbf{w},\mathbf{A}+\mathbf{A}')\,, \tag{3.6}$$

one can finally estimate the contact distance $\sigma(\hat{\mathbf{w}};\mathbf{u},\mathbf{u}')$ from the relation

$$\mathbf{w}\cdot(\,\mathbf{A}+\mathbf{A}')^{-1}\cdot\mathbf{w}=\mathbf{w}^2/2\sigma^2(\hat{\mathbf{w}};\mathbf{u},\mathbf{u}')\,, \tag{3.7}$$

yielding, after some algebra,

$$\frac{\sigma_\perp^2}{\sigma^2(\hat{\mathbf{w}};\mathbf{u},\mathbf{u}')}=1-\chi\frac{[(\hat{\mathbf{w}}\cdot\mathbf{u})^2+(\hat{\mathbf{w}}\cdot\mathbf{u}')^2-2\chi(\hat{\mathbf{w}}\cdot\mathbf{u})(\hat{\mathbf{w}}\cdot\mathbf{u}')(\mathbf{u}\cdot\mathbf{u}')]}{[1-\chi^2(\mathbf{u}\cdot\mathbf{u}')^2]}\,, \tag{3.8}$$

where χ is the eccentricity parameter defined in terms of the aspect ratio of the ellipsoids $k=\sigma_\parallel/\sigma_\perp$ by

$$\chi=\frac{k^2-1}{k^2+1}=\frac{\sigma_\parallel^2-\sigma_\perp^2}{\sigma_\parallel^2+\sigma_\perp^2}\,,\quad k=\left[\frac{1+\chi}{1-\chi}\right]^{1/2}=\frac{\sigma_\parallel}{\sigma_\perp} \tag{3.9}$$

so that $k>1$ (or $0<\chi<1$) corresponds to prolate (rodlike) ellipsoids, $0<k<1$ (or $-1<\chi<0$) to oblate (disklike) ellipsoids, and $k=1$ (or $\chi=0$) to a sphere. Using,

finally, expression (3.8) into (3.3), one finds after some algebra for the Berne and Pechukas (BP) approximation to (3.3),

$$\Sigma(\mathbf{u}\cdot\mathbf{u}')=\left[\frac{1-\chi^2(\mathbf{u}\cdot\mathbf{u}')^2}{1-\chi^2}\right]^{1/2}\equiv\Sigma_{\mathrm{BP}}(\mathbf{u}\cdot\mathbf{u}')\ , \tag{3.10}$$

which is the desired analytic expression of the excluded volume to two identical ellipsoids of aspect ratio k and orientations $\mathbf{u}$ and $\mathbf{u}'$. Notice that (3.10) is an even function of χ, and hence invariant for the interchange of $\sigma_{\parallel}$ and $\sigma_{\perp}$, so that oblate and prolate ellipsoids of the same molecular volume will have identical excluded volumes (this property will be referred to below as the oblate-prolate symmetry of Σ). Combining the results (3.10) and (3.2) we arrive at the following approximate expression:

$$c(\mathbf{r}-\mathbf{r};\mathbf{u},\mathbf{u}';\rho)=\Sigma_{\mathrm{BP}}(\mathbf{u}\cdot\mathbf{u}')c_{\mathrm{PY}}\left[\frac{|\mathbf{r}-\mathbf{r}'|}{\sigma_0},\eta\right] \tag{3.11}$$

for the DCF of the I phase of the HE system. To test expression (3.11) we compute the thermodynamics of the I phase from (2.10) or directly from the equivalent compressibility equation for the pressure p,

$$\beta\frac{\partial p}{\partial\rho}=1-\rho\int d\mathbf{r}\int d\mathbf{u}\int d\mathbf{u}'\,c(\mathbf{r};\mathbf{u},\mathbf{u}';\rho)\ , \tag{3.12}$$

which, with the use of approximation (3.11), yields

$$\beta\frac{\partial p}{\partial\rho}=1-H(\chi)\eta I(\eta)\ , \tag{3.13}$$

or integrating (3.13) with respect to the density,

$$\frac{\beta p}{\rho}\equiv Z(\eta,\chi)=1+H(\chi)[Z_0(\eta)-1]\ , \tag{3.14}$$

where $H(\chi)$

$$H(\chi)\equiv\int d\mathbf{u}\int d\mathbf{u}'\,\Sigma_{\mathrm{BP}}(\mathbf{u}\cdot\mathbf{u}')=\frac{1}{2}\left[1+\frac{\arcsin\chi}{\chi(1-\chi^2)^{1/2}}\right] \tag{3.15}$$

is the orientationally averaged excluded volume (see Fig. 1) and $Z(\eta,\chi)$ the compressibility factor of the HE, whereas $I(\eta)$,

$$\eta I(\eta)=\rho\int d\mathbf{r}\,c_0\left[\frac{|\mathbf{r}|}{\sigma_0},\eta\right]\ , \tag{3.16}$$

and $Z_0(\eta)$,

$$Z_0(\eta)=1-\frac{1}{\eta}\int_0^{\eta}d\eta'\,\eta' I(\eta')\ , \tag{3.17}$$

are related, respectively, to the inverse isothermal compressibility and the compressibility factor of the reference HS system. As a result of the factorization approximation (3.11) it is sufficient to know the HS compressibility factor $Z_0(\eta)$ in order to obtain from (3.14) and (3.15) the equation of state of the HE fluid for arbitrary eccentricities χ. For the HS equation of state we can use

$$I(\eta)=-[8-2\eta+4(1-a)\eta^2-(1-a)\eta^3]/(1-\eta)^4\ , \tag{3.18a}$$

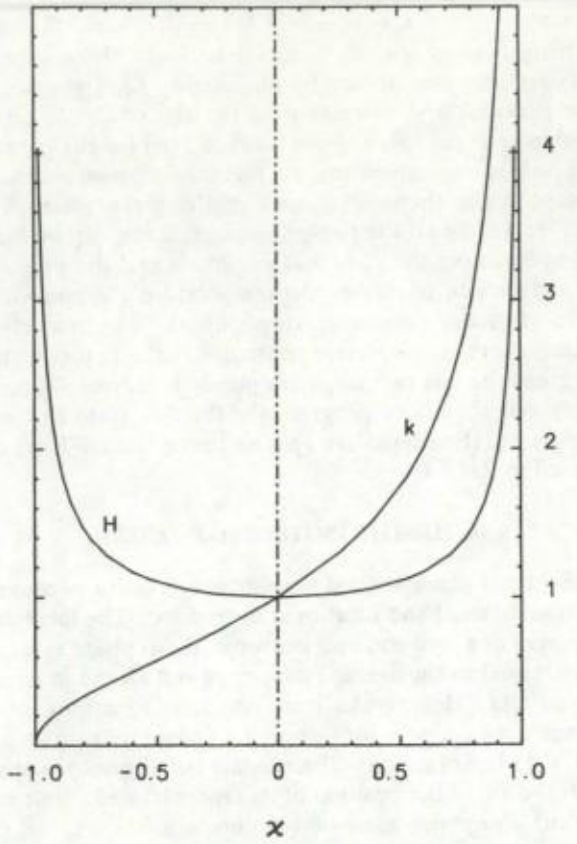

FIG. 1. Average excluded volume $H(\chi)$ of (3.15) and the aspect ratio k as a function of the eccentricity parameter χ of (3.9). Notice the rapid increase of H for $k>3$.

$$Z_0(\eta)=(1+\eta+\eta^2-a\eta^3)/(1-\eta)^3\ , \tag{3.18b}$$

which for $a=0$ corresponds to the PY result (3.2) and for $a=1$ to the more accurate Carnahan-Starling (CS) expression.[1] In Fig. 2 we compare the predictions of (3.14) to the available computer simulation results of Frenkel and Mulder.[4] The oblate-prolate symmetry is not perfect but the overall agreement is quite remarkable especially in view of the analytic simplicity of (3.14). The only alternative analytic equations of state for HE fluids known to us are those corresponding to the extensions[15] of scaled particle theory to convex bodies but these equations are more complicated and less accurate than (3.14) (see Fig. 1 of Ref. 12).

IV. THE NEMATIC PHASE

In the uniform N phase the local density of HE, $\rho(\mathbf{x})\equiv\rho(\mathbf{r},\mathbf{u})$, is no longer a constant but a function of the orientation variable $\mathbf{u}$ which can be written $\rho(\mathbf{x})=\rho h(\mathbf{u})$, with ρ the average density and $h(\mathbf{u})$ the normalized ($\int d\mathbf{u}\,h(\mathbf{u})=1$) angular distribution. For HE of revolution we expect the N phase to be uniaxial with a cylindrical symmetry around some director $\mathbf{n}$ ($\mathbf{n}^2=1$) and a plane of symmetry perpendicular to $\pm\mathbf{n}$. In this case $h(\mathbf{u})$ can depend only on the angle θ between $\mathbf{n}$ and $\mathbf{u}$ or equivalently on $\mathbf{u}\cdot\mathbf{n}=\cos\theta=m$. Let us write therefore $h(\mathbf{u})=h(\mathbf{u}\cdot\mathbf{n})=h(m)=h(-m)$ with the normalization

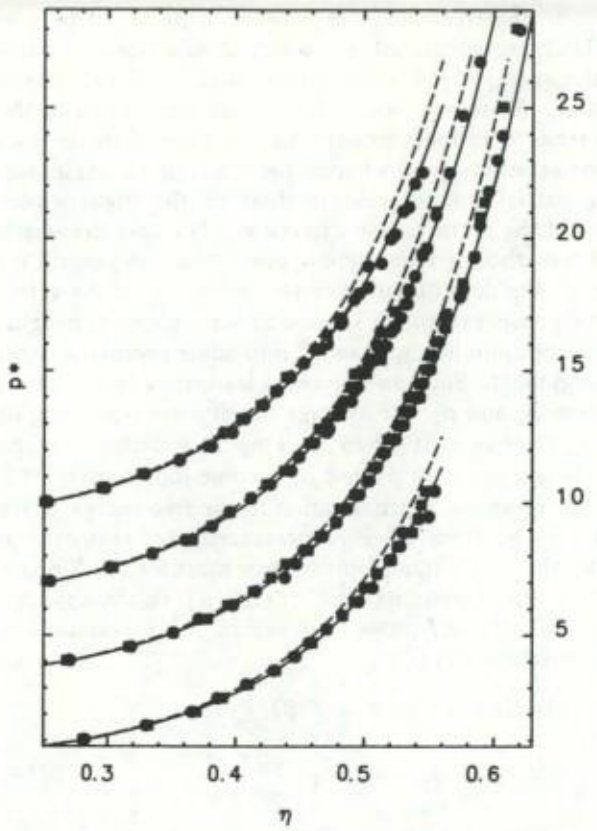

FIG. 2. Reduced pressure $p^*=\beta p v_{\rm mol}$ vs the packing fraction $\eta=\rho v_{\rm mol}$ for the *isotropic* phase of hard ellipsoids of various aspect ratios k as obtained from (3.14) with $a=0$ (dashed lines, PY) and $a=1$ (solid lines, CS) and compared to all the available computer simulation results of Frenkel and Mulder (Ref. 4) for k (>1) (circles, prolate HE) and $k'=1/k$ (squares, oblate HE) with, from bottom to top, $k=1.25$, 2, 2.75, and 3. (To separate the curves the p^* scales have been shifted by three units between each curve: The scale shown corresponds to the bottom curve $k=1.25$.) The oblate-prolate symmetry of the simulation results is clearly apparent.

condition $\int_0^1 dm\, h(m)=1$. A completely general parametrization of $h(m)=h(-m)$ is provided by $h(m)=\sum_l \alpha_{2l} P_{2l}(m)$ with $P_{2l}(m)=P_{2l}(-m)$ the even-order Legendre polynomials.[19] This expression has, however, the disadvantage that the positiveness of $h(m)$ cannot be guaranteed *a priori* once the series $h(m)=\sum_l \alpha_{2l} P_{2l}(m)$ is truncated. One can avoid this by writing $h(m)=\exp[\sum_l \gamma_{2l} P_{2l}(m)]$ and angular distributions of nematics have indeed been determined in this form in the literature.[20] To determine $h(m)$ accurately several terms (up to $l=7$ in Ref. 20) have to be retained in the series $\sum_l \gamma_{2l} P_{2l}(m)$. Here, our purpose however is not to determine $h(m)$ accurately but instead to use $h(m)$ in the expression (2.10) of the free energy where many of the detailed features of $h(m)$ are integrated out. For the present purpose it will therefore be sufficient to retain only one term ($l=1$) besides the normalization constant ($l=0$) and we will hence parametrize $h(m)$ as follows:

$$h(m)=\frac{e^{\gamma P_2(m)}}{Z(\gamma)}\ ,\quad Z(\gamma)=\int_0^1 dm\, e^{\gamma P_2(m)}\ , \tag{4.1}$$

with $P_2(m)=\frac{1}{2}(3m^2-1)$ the second Legendre polynomial. Notice that in Ref. 12, $h(m)$ was written as

$$h(m)=e^{\gamma' m^2}/\int_0^1 dm\, e^{\gamma' m^2}\ ,$$

which is equivalent to (4.1) with $\gamma'=\frac{3}{2}\gamma$. We have checked that adding more terms ($l>2$) generally changes the free-energy minimum by less than $\frac{1}{2}\%$ (see also Sec. V A). This shows once more[6] that it is much easier to determine the free-energy minimum variationally than to solve the corresponding Euler-Lagrange equation for $h(m)$ and substitute this result into the free-energy expression. The one order-parameter (γ) trial function (4.1) is thus both mathematically convenient and physically reasonable. For $\gamma=0$ it corresponds to an isotropic distribution [$h(m)\equiv 1$], whereas for $\gamma>0$ the angular distribution $h(m)$ is peaked around $m=\pm 1$ (or $\theta=0$ and π, see Fig. 3) and corresponds to an N phase. The form (4.1) was also used in the classic work of Maier and Saupe[21] as a mean-field distribution corresponding to a quadrupole attraction, and since then it has become customary to discuss the nematic phase in terms of the quadrupole order-parameter q:

$$q=\int_0^1 dm\, P_2(m) h(m)=q(\gamma)\ , \tag{4.2}$$

which has the advantage over γ ($0<\gamma<\infty$) of (4.1) to be a bounded order parameter ($0<q<1$). The relation be-

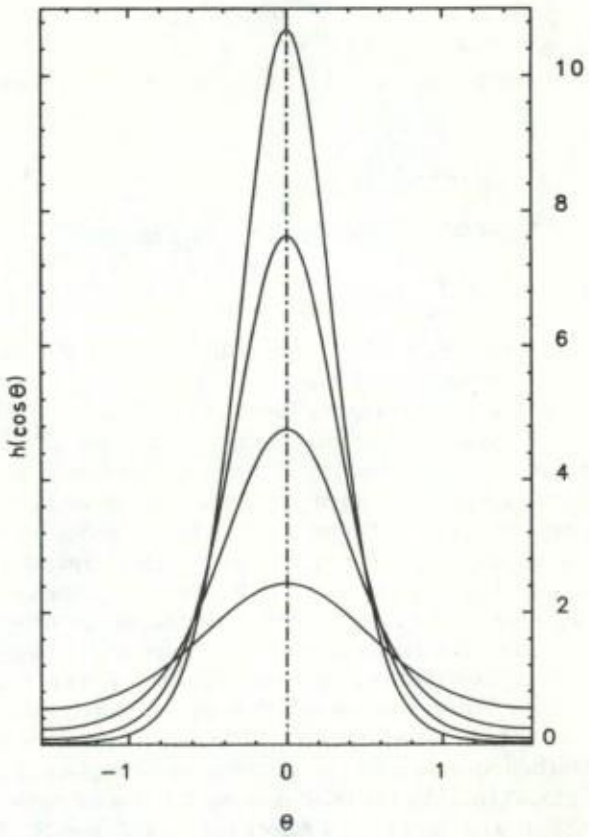

FIG. 3. Angular distributions $h(\cos\theta)$ of (4.1) as a function of θ for, from top to bottom, $\gamma=4$ ($q=0.712$), $\gamma=3$ ($q=0.605$), $\gamma=2$ ($q=0.439$), and $\gamma=1$ ($q=0.220$).

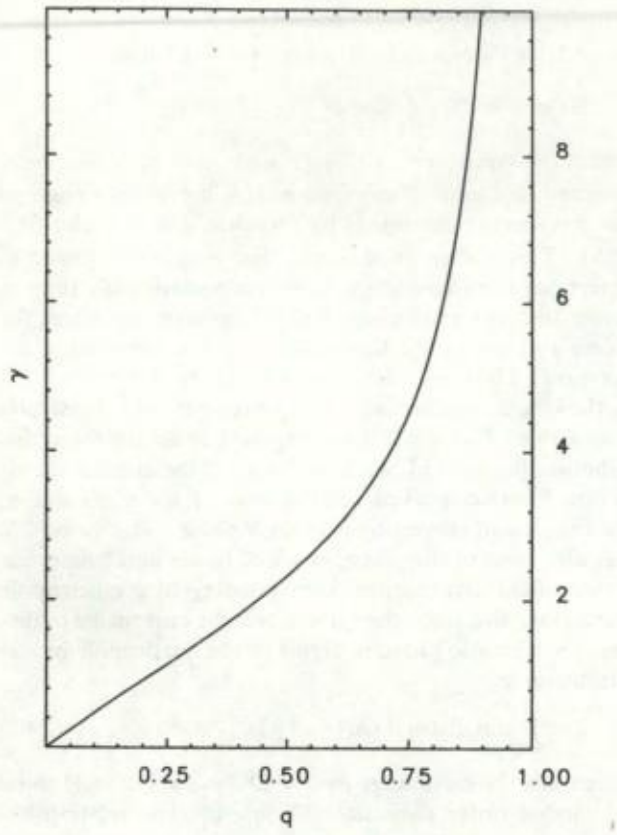

FIG. 4. Relation between the two order parameters γ of (4.1) and q of (4.2).

tween γ and $q=q(\gamma)$ (see Fig. 4) is easily obtained from (4.1) as

$$q(\gamma)=\frac{\partial}{\partial\gamma}[\ln Z(\gamma)] , \tag{4.3}$$

where $Z(\gamma)$ of (4.1) is related to Dawson's integral[19]

$$F(x)=e^{-x^2}\int_0^x dt\, e^{t^2} ,$$

and the properties of $Z(\gamma)$ can easily be deduced from the known properties[19] of $F(x)$.

To complete our program for the N phase we still have to find an approximation for the DCF $c(\mathbf{x},\mathbf{x}';[\rho_0+\lambda\Delta\rho])$, appearing in the exact free-energy expressions (2.10). In related contexts, several authors[6] have expanded this DCF in a perturbation series with respect to $\Delta\rho(\mathbf{x})$. The convergence of this expansion however is slow,[6] e.g., in lowest order no HS freezing can be predicted in this way,[14] whereas the higher-order terms involve the largely unknown triplet and higher-order direct correlation functions. This is *a fortiori* the case for the HE system for which even the pair correlations are not known accurately.[15] The alternative to such a perturbation expansion we propose[6] is to replace the DCF $c(\mathbf{x},\mathbf{x}';[\rho_\lambda])$ by the DCF of some reference I phase, $c(\mathbf{x},\mathbf{x}';\bar{\rho}_\lambda)$, with $\rho_\lambda(\mathbf{x})=\rho_0+\lambda\Delta\rho(\mathbf{x})$ the local density of the N phase and $\bar{\rho}_\lambda$ the corresponding (average) density of the reference I phase. The rationale behind this approximation is similar to the one used for the trial function (4.1): In the free-energy expression (2.10) the details of the DCF are integrated out, which should result in fairly similar averaged pair correlations for the N phase and the I phase. Moreover, when $\bar{\rho}_\lambda$ is expanded around ρ, the first term reproduces exactly the first term of the perturbation series in $\Delta\rho(\mathbf{x})$ whereas the remainder corresponds to a partial infinite resummation of the higher-order terms of the perturbation expansion. The only drawback of this method is that there appears to be no general recipe for the determination of the density $\bar{\rho}_\lambda$ of the reference I phase, except for the use of some physical insight, the latter cumulating usually[6] into some geometric scaling argument. Such an argument leads then to a relation between $\bar{\rho}_\lambda$ and ρ_λ, the average density corresponding to $\rho_\lambda(\mathbf{x})$. [Notice that when working at constant average density ($\rho=\rho_0$) both ρ_λ and $\bar{\rho}_\lambda$ become independent of λ and the resulting approximation to the free energy (2.10) acquires the form of a renormalized second-order, in $\Delta\rho(\mathbf{x})$, theory.] To implement these ideas for the N phase we first approximate its DCF $c(\mathbf{x},\mathbf{x}';[\rho])$ by the approximate DCF of the I phase proposed in (3.11), evaluated at a reference density $\bar{\rho}$,

$$c(\mathbf{x},\mathbf{x}';[\rho])\simeq c(\mathbf{r}-\mathbf{r}',\mathbf{u}\cdot\mathbf{u}',\bar{\rho}) \simeq \Sigma_{\mathrm{BP}}(\mathbf{u}\cdot\mathbf{u}')c_{\mathrm{PY}}\left[\frac{|\mathbf{r}-\mathbf{r}'|}{\sigma_0},\bar{\eta}\right] , \tag{4.4}$$

with $\bar{\eta}=(\pi/6)\sigma_0^3\bar{\rho}$ the packing fraction of the equivalent HS system (see Sec. III). To find the geometric constraint leading to a structural scaling relation we first observe that, if the DCF of the I phase at the reference density $\bar{\rho}$ is to describe, in some averaged sense, the pair structure of the N phase of average density ρ, then $\bar{\rho}$ will have to be *lower* than ρ so as to take into account the *lowering* of the interactions as a result of the *increased* ordering of the HE in the N phase compared to the disordered I phase. From the geometry of the molecular arrangements it is clear that in the I phase any HE can be freely rotated around any axes whereas in the N phase it can be freely rotated only around its symmetry axes. As a consequence the *average* contact distance between two neighboring ellipsoids will be smaller in the N phase than in the I phase. In the I phase this average contact distance is σ_0, the diameter of the equivalent HS system introduced in Sec. III to describe the translational correlations of the HE. In the N phase the average contact distance will thus be reduced to x times σ_0 with $x\leq 1$. Estimating x by comparing the volumes occupied by the freely rotating HE in either phase, one finds that for ellipsoids of revolution x scales like the aspect ratio k when $k<1$ or like $1/k$ when $k>1$, or in terms of the eccentricity parameter χ of (3.9),

$$x(\chi)=\left[\frac{1-|\chi|}{1+|\chi|}\right]^{1/2}=\begin{cases} k & \text{if } k<1 \\ 1/k & \text{if } k>1 . \end{cases} \tag{4.5}$$

This geometric constraint on the average contact distance is finally translated into a structural scaling relation by switching from the HE to the equivalent HS system used in Sec. III to describe the translational correlations of the HE system. Scaling accordingly the equivalent HS sys-

tem *at contact* we obtain

$$c_{\mathrm{PY}}\left[\frac{|\mathbf{r}|}{\sigma_0}=1,\eta\right]=c_{\mathrm{PY}}\left[\frac{|\mathbf{r}|}{\sigma_0}=x(\chi),\bar{\eta}\right], \tag{4.6}$$

which for each χ defines the packing fraction $\bar{\eta}$ of the I phase to be used in (4.4) to describe the correlations of the N-phase of packing fraction η. The relation $\bar{\eta}=\bar{\eta}(\eta,\chi)$ resulting from (4.6) is shown in Fig. 5. Combining now (2.10) with (4.1) and (4.4) we arrive finally at the following expression for the reduced free-energy density of the N phase relative to that of the I phase of the same density ($\rho=\rho_0$),

$$\frac{\beta}{\rho}\Delta f\equiv\frac{\beta}{\rho}(f[\rho]-f[\rho_0])\equiv\frac{\beta}{\rho}(f_N-f_I):$$

$$\frac{\beta}{\rho}\Delta f=\int d\mathbf{u}\,h(\mathbf{u})\ln h(\mathbf{u})-\frac{\rho}{2}\int d\mathbf{r}\,c_{\mathrm{PY}}\left[\frac{|\mathbf{r}|}{\sigma_0},\bar{\eta}(\eta,\chi)\right]\times\int d\mathbf{u}\int d\mathbf{u}'\,\Sigma_{\mathrm{BP}}(\mathbf{u}\cdot\mathbf{u}')[h(\mathbf{u})-1]\times[h(\mathbf{u}')-1] \tag{4.7}$$

or

$$\frac{\beta}{\rho}\Delta f=\int_0^1 dm\,h(m)\ln h(m)-\frac{\eta}{2}I(\bar{\eta}(\eta,\chi))[H(\gamma,\chi)-H(\chi)], \tag{4.8}$$

$$H(\gamma,\chi)=\int_0^1 dm\int_0^1 dm'\,h(m)h(m')\int_0^1 dx\sum_{\pm}\left[\frac{1-\chi^2[mm'\pm(1-m^2)^{1/2}(1-m'^2)^{1/2}\cos(\frac{1}{2}\pi x)]^2}{4(1-\chi^2)}\right]^{1/2}, \tag{4.9}$$

and $H(\chi)\equiv H(\gamma=0,\chi)$ is given by (3.15), whereas [see (3.16)–(3.18)]

$$\eta I(\bar{\eta})=\rho\int d\mathbf{r}\,c_{\mathrm{PY}}\left[\frac{|\mathbf{r}|}{\sigma_0},\bar{\eta}\right]=-\eta(8-2\bar{\eta}+4\bar{\eta}^2-\bar{\eta}^3)/(1-\bar{\eta})^4, \tag{4.10}$$

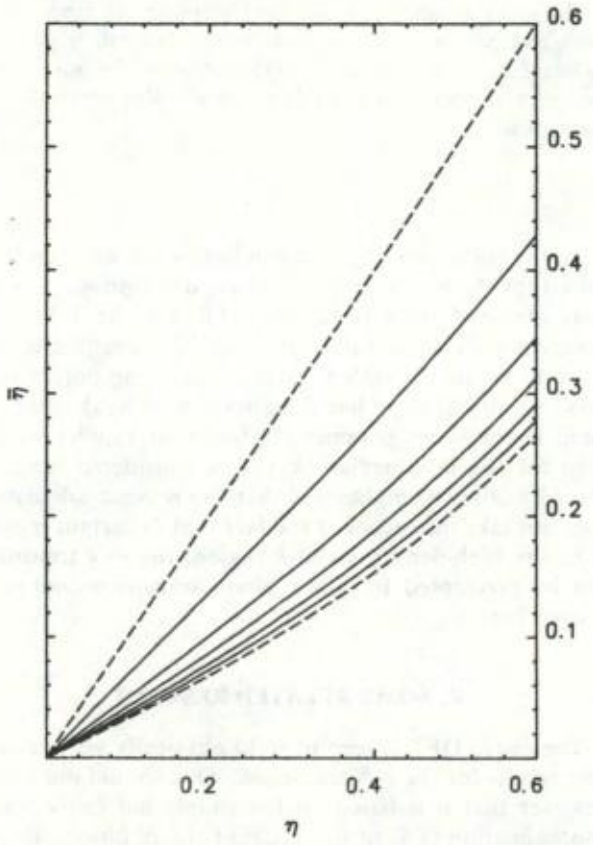

FIG. 5. Relation between $\bar{\eta}$ and η as obtained from (4.6) for various aspect ratios, with from top to bottom, $k=1.3,2,3,5,10$. Also shown (dashed curves) are the two extreme cases $k=1$ and $k=\infty$.

with $\bar{\eta}=\bar{\eta}(\eta,\chi)$ determined from (4.6). Notice also that from (4.1) and (4.12) the ideal term can be simply written in terms of $Z(\gamma)$ as

$$\int_0^1 dm\,h(m)\ln h(m)=\gamma q-\ln Z(\gamma)\equiv\left[\gamma\frac{\partial}{\partial\gamma}-1\right]\ln Z(\gamma), \tag{4.11}$$

whereas (4.9) has to be computed numerically. Physically, the first term in the rhs of (4.8) represents the difference in orientational entropy between the two phases and the second term, which is proportional to $H(\gamma,\chi)-H(\chi)$, the difference in average excluded volume. It is only when the average excluded volume in the N phase, $H(\gamma,\chi)$, is lower than the average excluded volume in the I phase, $H(\chi)$, that this excluded volume term can compete with the entropy term and stabilize the nematic.

Minimizing now (4.8) with respect to γ we obtain, for each η and χ, the free-energy density of the corresponding N phase. Because of the prolate-oblate symmetry of the present theory (all expressions are even functions of χ) it is sufficient to do this for $k>1$. At low density (small η) the only free-energy minimum corresponds to the I phase ($\gamma=0$). Above a threshold density η_0 a second minimum appears at a value of γ which we denote $\gamma_0(\neq 0)$. The corresponding N phase is thus marginally stable. Its physical characteristics η_0 and $q_0=q(\gamma_0)$ have a very different k dependence (see Table I). Whereas η_0 decreases rapidly with increasing k (>1), roughly as $1/k$, the order parameter at threshold, q_0, remains practically constant, $q_0\simeq\frac{1}{3}$. This corresponds to a Lindemann rule[1] for orientational freezing: For quadrupole moments q below $q\simeq\frac{1}{3}$ the nematic phase is always unstable. Once the N-phase is stabilized ($\eta>\eta_0$, $q\geq q_0$) a very small increase in density (i.e., a few percent increase in η) lowers rapidly the free energy of the nematic below that of the I phase of the same density. Some values (η_1,q_1) corresponding to this state of marginal thermodynamic stability ($\Delta f=0$) are given in Table II. A further slight in-

TABLE I. The reduced free-energy difference $(\beta/\rho)\Delta f$, the packing fraction η_0, and order parameter q_0 for the marginally stable nematic phase of hard ellipsoids of various aspect ratios k as obtained from the density-functional theory.

k	η_0	q_0	$\frac{\beta}{\rho}\Delta f$
1.3	0.7701	0.325	0.004 26
1.8	0.6499	0.331	0.004 49
2	0.6125	0.334	0.004 60
2.75	0.5031	0.344	0.005 03
3	0.4746	0.347	0.005 16
4	0.3867	0.357	0.005 64
5	0.3263	0.366	0.006 02
7	0.2491	0.376	0.006 55
10	0.1846	0.385	0.007 01
15	0.1295	0.392	0.007 37
20	0.1000	0.395	0.007 53

crease of the density quickly transforms the free-energy minimum corresponding to the I phase into a *maximum*, leaving the N phase as the only stable phase at higher densities. This rapid evolution is a manifestation of the weakly first-order character of the I-N transition which is seen to involve only a very small region of metastability of the low-density nematic phase and the high-density isotropic phase. An example of this scenario is shown in Fig. 6.

The I-N phase transition point can be obtained by solving the conditions of equality of the pressure and the chemical potential of the two phases. These conditions are equivalent to solving numerically Maxwell's double tangent construction for the free energies:

$$\frac{\partial f_I}{\partial \rho_I}=\frac{\partial f_N}{\partial \rho_N}=\frac{f_N-f_I}{\rho_N-\rho_I}\ , \tag{4.12}$$

where we have used (2.7) and (2.8). There are other ways[14] to express the two-phase coexistence conditions but in the present context these would involve additional numerical calculations and have therefore been discarded here. The advantage of the Maxwell construction is that (4.12) requires only the free energies as input. Needless to say, these different routes to the coexistence conditions are not strictly equivalent once the approximations have been introduced. This problem of the thermodynamic inconsistency of these different routes is unavoidable here

TABLE II. The packing fraction η_1 and the order parameter q_1 for various k values of the nematic phase at marginal thermodynamic stability ($\Delta f=0$) as obtained from the density-functional theory.

k	η_1	q_1
2	0.6144	0.45
2.75	0.5055	0.44
3	0.4771	0.45
5	0.3291	0.43
10	0.1869	0.44
20	0.1016	0.43

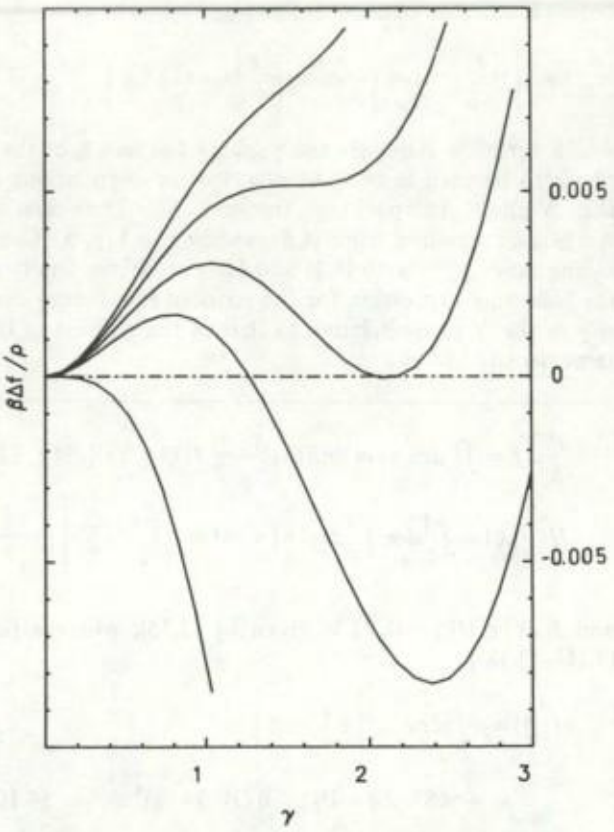

FIG. 6. Reduced free-energy difference $(\beta/\rho)\Delta f$ of Eq. (4.8) vs the order parameter γ for hard ellipsoids of aspect ratio $k=3$ and packing fraction, from top to bottom, $\eta=0.4725$, 0.4746, 0.4771, 0.4800, and 0.4950. Notice the very rapid changes with respect to η in this region and also the small free-energy scale.

since the corresponding problem has as yet not even been solved for the much simpler I-phase description. The results obtained from (4.12) and (4.8) for the I-N coexistence are shown in Table III. The I-N transition is seen there to be always rather narrow (involving only a very small density change) but not always very weak since the jump in the order parameter q increases rapidly with k even for the intermediate k values considered here. It should finally be emphasized that the present calculation does not take into account the fact that in certain regions (e.g., the high-density small-k region) the I-N transition can be preempted by other phase transitions not considered here.

V. SOME RELATED RESULTS

The above DFT is seen to yield physically very reasonable results for the I-N transition. One should not forget however that it is based on the simple but fairly rough approximation (4.4) to the DCF of the N phase. Before testing the results of the DFT against the computer simulations,[4] which is our final goal, it may thus be of interest to compare it also to a number of alternative theoretical attempts to describe the I-N transition of a system of HE.

TABLE III. The isotropic-nematic coexistence data for various k values as obtained from the density-functional theory ($p^*=\beta p v_{\rm mol}$, $\mu^*=\beta\mu$).

k	η_I	η_N	p^*	μ^*	q
2	0.6120	0.6175	24.3	50.2	0.50
2.75	0.5012	0.5117	9.62	25.7	0.55
3	0.4722	0.4843	7.76	22.3	0.56
5	0.3213	0.3423	2.78	12.2	0.64
10	0.1787	0.2037	1.03	7.77	0.72
20	0.0957	0.1157	0.47	5.99	0.77

A. The Onsager theory

As seen from Table III the above DFT predicts that the coexisting densities decrease rapidly with increasing aspect ratio k, roughly as $1/k$. This is consistent with the fundamental idea behind Onsager's theory[8,3] of the I-N transition which states that for very large aspect ratios this transition should occur already in a dilute system. It is rather exceptional that a phase transition can be studied with the aid of a virial expansion and it required Onsager's insight to observe that the virial expansion ($\eta\to 0$) *combined* with the large aspect ratio limit ($k\to\infty$) would not destroy the I-N transition. In this so-called Onsager limit ($\eta\to 0$, $k\to\infty$, $k\eta=$const) the Onsager theory becomes, moreover, exact and it is thus interesting to inquire whether the above DFT is consistent with this exact limiting case. Returning to (4.8) we see that the ideal term remains unchanged in this limit whereas the Onsager limit of the excess term can be taken in two steps. First we expand $\eta I(\bar{\eta})$ for small η. From (4.6) it follows that $\bar{\eta}\to 0$ as $\eta\to 0$, whereas (4.10) implies $I(0)=-8$ and hence $\eta I(\bar{\eta})\to -8\eta$. Next we compute the large-k limit, i.e., $\chi\to 1$, of (4.9) by returning to (3.10) and (3.9):

$$\lim_{k\to\infty}\frac{1}{k}\Sigma_{\rm BP}(\mathbf{u}\cdot\mathbf{u}')=\lim_{\chi\to 1}\frac{[1-\chi^2(\mathbf{u}\cdot\mathbf{u}')^2]^{1/2}}{1+\chi}$$
$$=\tfrac{1}{2}[1-(\mathbf{u}\cdot\mathbf{u}')^2]^{1/2}\,, \qquad (5.1)$$

and using $\mathbf{u}\cdot\mathbf{u}'=\cos\omega$, $[1-(\mathbf{u}\cdot\mathbf{u}')^2]^{1/2}=|\sin\omega|$, with ω the angle between $\mathbf{u}$ and $\mathbf{u}'$, we obtain finally the Onsager limit of (4.1) in the form

$$\frac{\beta}{\rho}\Delta f\bigg|_{\rm Ons}=\int d\mathbf{u}\,h(\mathbf{u})\ln h(\mathbf{u})$$
$$+c(\langle\,|\sin\omega|\,\rangle_N-\langle\,|\sin\omega|\,\rangle_I)\,, \qquad (5.2)$$

which is precisely Onsager's result.[8,3] In Eq. (5.2), $\langle\cdots\rangle_{N,I}$ denotes an average over the angular distribution $h_{N,I}(\mathbf{u})$,

$$\langle\,|\sin\omega|\,\rangle_{N,I}=\frac{4}{\pi}\int d\mathbf{u}\int d\mathbf{u}'\,h_{N,I}(\mathbf{u})h_{N,I}(\mathbf{u}')$$
$$\times[1-(\mathbf{u}\cdot\mathbf{u}')^2]^{1/2}\,, \qquad (5.3)$$

with $h_I(\mathbf{u})=1$ and hence $\langle\,|\sin\omega|\,\rangle_I=1$. We have also put $c=\frac{1}{2}\rho v_{\rm excl}$ in (5.2) with $v_{\rm excl}$, the average excluded volume which when measured in terms of the molecular volume $v_{\rm mol}$ yields $c=(\pi/2)k\eta$ for HE and hence differs by a factor $\pi/2$ from the hard cylinder expression originally considered by Onsager (this is only one of the subtle differences in geometric packing properties which exist between cylinders and ellipsoids, see also Ref. 4 on this point). The Onsager limit of the above DFT reproduces thus exactly Onsager's theory. This fact can now be used here to test the approximation involved in using the trial function (4.1). Although in his original paper[8] Onsager did use a one parameter trial function similar to (4.1), namely, $h(m)=\gamma(\cosh\gamma m)/(2\sinh\gamma)$, which is physically similar but mathematically less convenient than (4.1), his equation has subsequently been solved numerically[20,22,23] for an arbitrary angular distribution $h(m)$. These high-precision calculations, using either seven Legendre polynomials[20] or a grid of 250 points in m space,[23] have established that Onsager's theory predicts an I-N transition between an I-phase corresponding to $c_I=3.290$ and an N-phase corresponding to $c_N=4.189$. The transition is thus fairly wide, $\Delta c/c_N=\Delta\eta/\eta_N=0.215$, and also quite strong, $q=0.792$. Using our simple trial function (4.1) we find, instead, $c_I=3.315$, $\Delta c/c_N=0.216$, and $q=0.799$, whereas the original Onsager values are $c_I=3.340$, $\Delta c/c_N=0.256$, and $q=0.848$. The above DFT based on (4.1) reproduces thus the exact result to within $\frac{1}{2}\%$, which for the present purpose is largely enough. Having established that in the Onsager limit the results of the DFT do reproduce the results of Onsager's theory we can now in turn inquire how rapidly the Onsager limit will in fact be approached. In other words we can look for the k value below which both theories start to deviate appreciably. To this end we use the low density or virial expansion of the DFT, i.e., Eq. (4.8) with $I(\bar{\eta})$ replaced by $I(0)=-8$, and compare its results for large but finite k values to those of the full DFT. This is equivalent to using Onsager's theory for the study of dilute systems of HE of *finite* elongation. The results are compared in Fig. 7. It is seen there that the approach to the Onsager regime is in fact very slow. The coexisting densities reach their Onsager limit for $k>100$ while the order parameter q reaches its limiting value for $k>300$. The k values found here are large but nevertheless consistent with those often quoted in the experimental literature.[24]

B. The Landau theory

In the opposite limit where $k\to 1$ the above DFT predicts that the I-N transition is pushed towards the *high*-density region where Onsager's virial expansion argu-

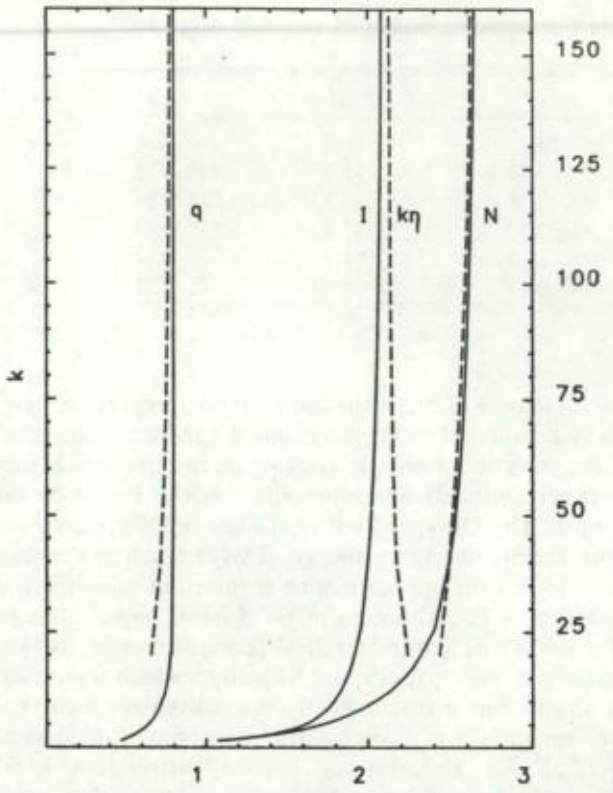

FIG. 7. Order parameter q and the Onsager variable $k\eta$ at the I-N coexistence in the large-k domain: DFT (solid lines) and the virial expansion of the DFT (dashed lines). Notice the very slow approach to the limiting situation described by Onsager's theory and also the breakdown of the virial expansion for the smaller k values.

ment is no longer applicable. Nevertheless, as $k \to 1$, the transition also becomes *weakly* first order ($\Delta\eta \to 0$) and one enters the realm of Landau's phenomenological theory[7,25] of phase transitions. The basic idea behind Landau's theory is to approximate the free energy by a truncated expansion of it with respect to some order parameter. Since our original order parameter γ of (4.1) is unbounded ($0 < \gamma < \infty$) there is little hope that expansions with respect to γ will lead to a convergent series. The physical order parameter which imposes itself in the present context is the Maier-Saupe quadrupole order parameter q of (4.2). This order parameter is bounded ($0 < q < 1$) and belongs to an irreducible representation of the rotational symmetry group.[25] In terms of q the Landau approximation to (4.8) can then be written

$$\frac{\beta}{\rho}\Delta f\bigg|_L = \sum_{n=0}^{4} a_n q^n + O(q^5) , \tag{5.4}$$

where the expansion has been truncated at the minimal order which guarantees the existence of a two-minima (or three-extrema) free energy (one at $q=0$ for the I phase and one at $q \neq 0$ corresponding to the N phase). The physical consequences of the Landau theory are easily worked out on the basis of (5.4) and are well known.[7,25] In the present context we have the advantage over the phenomenological theory that the coefficients a_n of (5.4) can be computed explicitly as functions of η and k whereas in the original Landau theory they have to be treated as phenomenological parameters. In other words, comparing the Landau approximation (5.4) with the original DFT expression (4.8) we are able here to test explicitly the assumptions behind Landau's theory. In order to obtain the expressions of the coefficients a_n of (5.4) we proceed as follows. We first expand (4.8) with respect to γ:

$$\frac{\beta}{\rho}\Delta f = \sum_{n=0}^{4} b_n \gamma^n + O(\gamma^5) , \tag{5.5}$$

and next expand similarly $q = q(\gamma)$ of (4.3),

$$q = \frac{\gamma}{5} + \frac{\gamma^2}{35} - \frac{\gamma^3}{175} - \frac{\gamma^4}{385} + O(\gamma^5) . \tag{5.6}$$

Inversion of the series (5.6) yields $\gamma = \gamma(q)$,

$$\gamma = 5q - \frac{25}{7}q^2 + \frac{425}{49}q^3 - \frac{51875}{3773}q^4 + O(q^5) , \tag{5.7}$$

and substituting (5.7) in (5.5) yields finally (5.4). The explicit evaluation of (5.5) involves some lengthy but elementary algebra which will be skipped here but which is most easily performed with the aid of some computer algebra method. The final result for the Landau free-energy density is expression (5.4) with

$$a_0 = a_1 = 0 , \tag{5.8a}$$

$$a_2 = \tfrac{5}{2} - (\eta/2) I(\bar{\eta}) [5H_1(\chi) - 15H_2(\chi)] , \tag{5.8b}$$

$$a_3 = -\tfrac{25}{21} , \tag{5.8c}$$

$$a_4 = \tfrac{425}{196} - (\eta/2) I(\bar{\eta}) [\tfrac{225}{49} H_1(\chi) - \tfrac{2250}{49} H_2(\chi) + \tfrac{1125}{7} H_3(\chi)] , \tag{5.8d}$$

where the $H_n(\chi)$ are given by

$$H_1(\chi) = \frac{1}{2\chi}\left[\chi + \frac{\arcsin\chi}{(1-\chi^2)^{1/2}}\right] \equiv H(\chi) , \tag{5.9a}$$

$$H_2(\chi) = \frac{1}{4\chi^3}\left[\frac{\chi^3}{2} + \frac{\chi}{4} + \frac{(\chi^2 - \frac{1}{4})}{(1-\chi^2)^{1/2}}\arcsin\chi\right] , \tag{5.9b}$$

$$H_3(\chi) = \frac{1}{16\chi^5}\left[\frac{\chi^5}{3} + \frac{5}{12}\chi^3 - \frac{\chi}{8} + \frac{\left[\chi^4 - \frac{\chi^2}{2} + \frac{1}{8}\right]}{(1-\chi^2)^{1/2}}\arcsin\chi\right] , \tag{5.9c}$$

$$H_n(\chi) = \frac{1}{\chi^{2n-1}(1-\chi^2)^{1/2}} \times \int_0^{\chi} dy_n\, y_n \times \int_0^{y_n} dy_{n-1}\, y_{n-1} \cdots \int_0^{y_2} dy_1 (1-y_1^2)^{1/2} , \tag{5.9d}$$

while $I(\bar{\eta})$ is still given by (4.10). Although one does not expect the Landau theory to be applicable in the strongly

first-order Onsager limit, for further reference it will be useful to quote here also the value of the expansion coefficient a_n of (5.8) in the Onsager limit [$\eta \to 0$, $k \to \infty$, $(\pi/2)k\eta = c$],

$$a_2^{\text{Ons}} = \tfrac{5}{8}(4-c) , \tag{5.10a}$$

$$a_4^{\text{Ons}} = \tfrac{425}{196} - \tfrac{225}{3136}c , \tag{5.10b}$$

whereas a_0, a_1, and a_3 remain unchanged. Having now at our disposal the explicit expression of $a_n = a_n(\eta, X)$, the Landau free energy (5.4) can be worked out analytically. The three extrema of (5.4) with respect to q correspond to

$$q_0 = 0 , \tag{5.11a}$$

$$q_\pm = \frac{-3a_3 \pm (9a_3^2 - 32a_2a_4)^{1/2}}{8a_4} , \tag{5.11b}$$

which are easily computed from (5.8) for each η and X. It can also be verified from (5.8) that $a_3 < 0$, whereas at *low* density one has $a_2 > 0$, $a_4 > 0$, and $9a_3^2 < 32a_2a_4$, so that at low density the only real extremum (5.11) corresponds to an I phase ($q_0 = 0$) and it is a minimum. At higher densities, when $9a_3^2 \geq 32a_2a_4$, there will be three real extrema, $q_0 < q_- \leq q_+$, with q_- corresponding to a maximum and q_0, q_+ to the two minima describing, respectively, the I phase (q_0) and the N phase (q_+). The density of marginal stability of the N phase as a function of the aspect ratio k or the eccentricity X, say $\eta_0 = \eta_0(X)$, is given by the solution of the equation $9a_3^2 = 32a_2a_4$. Increasing the density further one reaches a point, say, $\eta_1 = \eta_1(X)$, where the N phase reaches thermodynamical equilibrium with the I phase, $\Delta f(q_0) = 0 = \Delta f(q_+)$ or, explicitly,

$$a_3(9a_3^2 - 32a_2a_4)^{1/2} = 3a_3^2 - 16a_2a_4 .$$

At still higher densities, say, $\eta_2 = \eta_2(X)$, we reach a point where a_2 changes sign. Above this point the extremum at $q = q_0$ becomes a maximum and only the N phase corresponding to $q = q_+$ survives as a stable phase whereas the I phase is unstable. The Landau approximation reproduces thus qualitatively quite closely the scenario observed above for the DFT. From Tables IV–VII and Fig. 8 we see that the quantitative trends are also fairly well reproduced except for two features. First, the q values predicted by the Landau theory are too low (roughly by a factor of 2). The DFT predicts hence a transition which is much stronger than the one predicted by its Landau approximation. The density change at coexistence ($\Delta\eta$) and the overall density change from marginal stability of the N phase (η_0) to marginal stability of the I phase (η_2) is too small. Hence the Landau theory predicts a transition which is also too narrow compared to the full DFT. Notice however that since $a_3 \neq 0$ the transition predicted by the Landau theory remains everywhere of first order. If we add the Onsager limit to the Landau approximation, i.e., use (5.10) in (5.4), then these defects become dramatic. In this combined approximation the width of the I-N transition is $\Delta\eta/\eta_N = 0.042$ and its strength $q = 0.386$ whereas the corresponding DFT values are $\Delta\eta/\eta_N = 0.216$ and $q = 0.799$. Notice, however, that even in this extreme case the prediction for the midpoint of the transition, $(\eta_N + \eta_I)/2\eta_N = 0.979$ for the Landau theory and 0.892 for the DFT, remains reasonable. Since the only difference between the present DFT and its Landau approximation (5.4) stems from the use of a *truncated* expansion with respect to the order parameter, it is fair to conclude on this example that the Landau theory yields a fair description and a fair location of the I-N transition but very poor predictions for the width and the strength of the phase transition, and this remains true even in regions where the transition is weak as originally assumed in the derivation[25] of the Landau theory.

TABLE IV. The same as Table I but obtained from the Landau theory. Notice the good agreement for η_0 but not for q_0.

k	η_0	q_0	$\frac{\beta}{\rho}\Delta f$
2	0.6177	0.210	0.0014
2.75	0.5097	0.214	0.0015
3	0.4815	0.216	0.0015
5	0.3338	0.223	0.0016
10	0.1907	0.231	0.0018
20	0.1040	0.234	0.0019
100	0.0227	0.236	0.0019
200	0.0115	0.238	0.0019

C. Related density-functional theories

It is clearly not possible to discuss here the large number of theoretical attempts concerned with the I-N transition (some background information can however be obtained from Refs. 9–11,13,21–25). Some recent publications[9–11] will nevertheless be considered here since they are both based on the density-functional theory and explicitly concerned with HE, and hence closely related to the present work.

The theory of Mulder and Frenkel[9] starts from what is essentially a diagrammatic approach to the DFT described in Sec. II. They perform a virial expansion of the free-energy functional $F[\rho]$ and speed up its convergence properties by going over to a y expansion,[26] i.e., an expansion with respect to $\eta/(1-\eta)$, and truncate the latter at third order requiring as input the second and third virial coefficients of the N phase. The second virial coefficient is expressed in terms of the excluded volume of

TABLE V. The same as Table II but obtained from the Landau theory.

k	η_1	q_1
2	0.6191	0.280
2.75	0.5114	0.285
3	0.4832	0.287
5	0.3356	0.296
10	0.1921	0.306
20	0.1049	0.311
100	0.0229	0.313
200	0.0116	0.313

TABLE VI. The point of marginal stability of the I phase ($a_2=0$) as obtained from the Landau theory.

k	η_2
2.75	0.5245
3	0.4968
5	0.3499
10	0.2034
20	0.1121
100	0.0247
200	0.0125

two HE of fixed orientation, i.e., $\Sigma(\mathbf{u}\cdot\mathbf{u}')$ of (3.3), for which they use Isihara's exact but complicated threefold infinite series representation[27] instead of the simple approximation (3.10). The evaluation of the third virial coefficient presents, however, a formidable mathematical problem which is partly bypassed by performing numerical MC (Monte Carlo) estimates for it but even this can be done with reasonable computer time only for some orientationally averaged quantity.[9] The final results obtained for the equation of state of the I phase are in good agreement with those obtained in Sec. III from the much simpler expression (3.14). The results obtained for the I-N transition are again in qualitative agreement with those obtained here except that the transition is predicted to occur at much lower densities and with a larger width. It is our impression that the y expansion used by Mulder and Frenkel carried with it some of the defects of the original virial expansion on which it is based.

In the recent theory of Singh and Singh[10] one starts from the DFT expression for the free energy of the ordered (N) phase and expands it around the disordered (I) phase to third order in the local density change. The resulting equation involves the two- and three-particle DCF. The latter is neglected except for those contributions which can be expressed as a density derivative of the two-particle DCF. For the latter Pynn's approximation[16] is used. As observed by Lado[17] this approximation has the disadvantage to predict an isotropic DCF at the origin and also at contact. This local defect disappears in integrated quantities and indeed the equation of state obtained for the I phase by Singh and Singh[10] turns out to be identical[28] to the one presented in Sec. III. The equations for the N phase are finally solved by using a two-order-parameter approximation for the orientational distribution $h(m)$ of the form $h(m)=1+\alpha_2 P_2(m)+\alpha_4 P_4(m)$. The qualitative predictions of this theory are again in agreement with those found here. The I-N transition however is found to occur at much lower densities than predicted by the other attempts. It is not unreasonable to think that the very poor approximation used for $h(m)$, which does not guarantee positivity, could be responsible for this.

In a very recent publication[11] Marko proposes a DFT based on a second-order expansion in $\Delta\rho(\mathbf{x})$ of the free energy of the nematic phase around that of the coexisting isotropic phase. The DCF of the I phase is approximated by a variational modification of Pynn's model[16] and the angular distribution $h(m)$ is taken to be of the form $\propto\exp[\gamma_2 P_2(m)+\gamma_4 P_4(m)]$. The I-N transition densities are comparable to the present results but the width and the order parameter q of the transition are more than one order of magnitude smaller (see Table VIII).

D. Computer simulation results

Having checked the predictions of our DFT against the available theoretical results we now turn to the ultimate goal, namely, a direct comparison with the computer simulations of Frenkel and Mulder[4] which prompted the present investigation. These authors have performed constant-volume and constant-pressure Monte Carlo simulations of a system of $\sim 10^2$ HE. The aspect ratios considered are $k=1.25$, 2, 2.75, and 3 together with the corresponding oblate systems ($k'=1/k$). They have found a remarkable symmetry between the prolate (k) and oblate ($1/k$) systems of HE of the same molecular volume. This symmetry is not perfect but could presumably be reinforced by taking into account the finite-size effects. The occurrence of this symmetry is a clear manifestation of the dominance of geometric packing effects which is also witnessed here by the fact that the exact pair excluded volume of (3.10) possesses this oblate-prolate invariance property. The DFT proposed here, and hence also the Landau theory of Sec. V B, has this symmetry built in exactly [cf. Sec. III and the $\chi\rightarrow-\chi$ invariance of (4.8)], a property not shared by the theories discussed in Sec. V C. In Sec. III we have already compared all the available computer generated equations of state of the I phase to the present DFT. The agreement is not perfect but quite reasonable in view of the very simple analytic expression (3.14) proposed here. The overall agreement obtained here is also better than the one obtained from other theoretical attempts, e.g., the extensions of scaled particle theory to the I phase of convex bodies proposed by Gibbons[29,15] and Boublik[30,15] (see Fig. 1 of Ref. 12). The N-phase branch of the equation of state together with the I-N coexistence region is shown in

TABLE VII. The same as Table III but obtained from the Landau theory.

k	η_I	η_N	p^*	μ^*	q
2	0.6182	0.6201	25.9	52.8	0.30
2.75	0.5098	0.5132	10.4	27.3	0.32
3	0.4816	0.4853	8.45	23.7	0.32
5	0.3332	0.3389	3.11	13.2	0.35
10	0.1898	0.1955	1.19	8.62	0.37
20	0.1034	0.1072	0.55	6.80	0.38

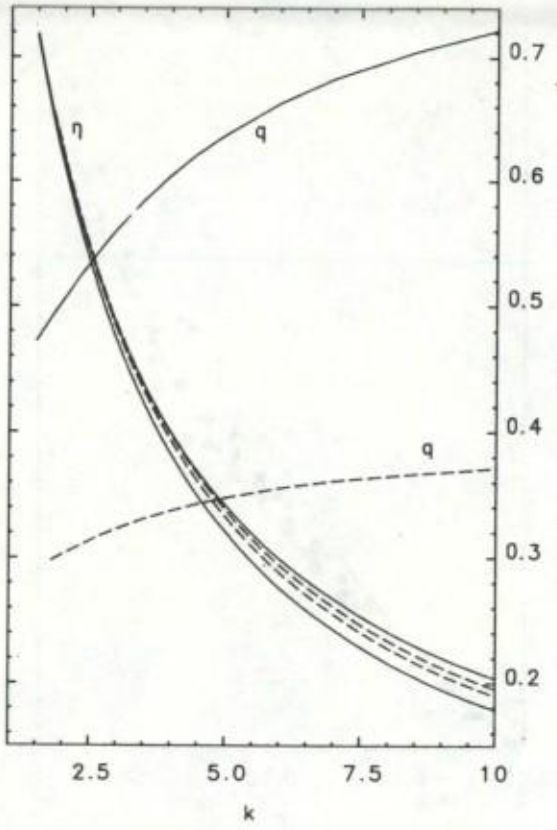

FIG. 8. Order parameter q and the coexisting densities (η; I phase is the lower curve, N phase is the upper curve) of the I-N coexistence in the small-k domain: DFT (solid lines) and Landau approximation (dashed lines).

Fig. 9 for $k=2.75=1/k'$ and in Fig. 10 for $k=3=1/k'$. The agreement is again fair and better than with the other theories. The I-N coexistence data are compared in Table VIII. For $k=2=1/k'$ and $k=1.25=1/k'$ the simulations have shown that the I-N transition is preempted by an isotropic-solid transition. This possibility has not been considered here but the fact that for these aspect ratios the DFT predicts the I-N transition to occur at a density above the HS isotropic-solid transition is consistent with these computer findings.

VI. CONCLUSIONS

The density-functional theory, in the Helmholtz free-energy language (see Sec. II), has been used to formulate an approximate theory of the orientational freezing transition of a system of hard ellipsoids as a first approximation to the isotropic-nematic transition of more realistic liquid crystals by focusing our attention solely on the anisotropic steric effects produced by the anisotropy of the molecular shape. Above a minimal quadrupole moment, providing an orientational Lindemann rule, the theory predicts a stable nematic phase, both for rodlike and disklike molecules, as a result of a competition between the orientational entropy and the anisotropic excluded volume effects. The latter have been described within an approximation which factorizes the translational and orientational direct correlations. The orientational correlations have been described in a manner first suggested by Onsager for infinitely elongated molecules[8] while Onsager's original virial expansion is corrected for finite density effects by assimilating the translational correlations of the hard ellipsoids to those of hard spheres of the same volume.

The mathematical implementation of the theory has been kept as simple as possible by resorting to a realistic one-order-parameter angular distribution of the Maier-Saupe form[21] in order to minimize the free energy for a wide range of densities and of length to breadth ratios. Further simplifications are provided by using an approximate but closed analytic form of the pair excluded volume due to Berne and Pechukas[18] together with the Percus-Yevick[1] hard-sphere direct correlation function.

The results of the theory reproduce all the qualitative features provided by the computer simulations of Frenkel and Mulder[4] with good quantitative agreement between theory and simulation for the isotropic phase and fair agreement for the nematic phase and the isotropic-

TABLE VIII. The isotropic-nematic coexistence data.

k	η_I	$\Delta\eta$	p^*	μ^*	q
2.75	0.561[a]	0.009	15.7	35.7	
	0.517[b]	0.001			0.010
	0.501[c]	0.011	9.62	25.7	0.548
	0.449[d]	0.015	6.55		0.553
	0.329[e]	0.018			0.532
3	0.507[a]	0.010	9.79	25.1	
	0.493[b]	0.001			0.017
	0.472[c]	0.012	7.76	22.3	0.561
	0.420[d]	0.018	5.31		0.568
	0.309[e]	0.021			0.547

[a]Frenkel and Mulder (MC) (Ref. 4).
[b]Marko (Ref. 11).
[c]Present calculation.
[d]Mulder and Frenkel (Ref. 9).
[e]Singh and Singh (Ref. 10).

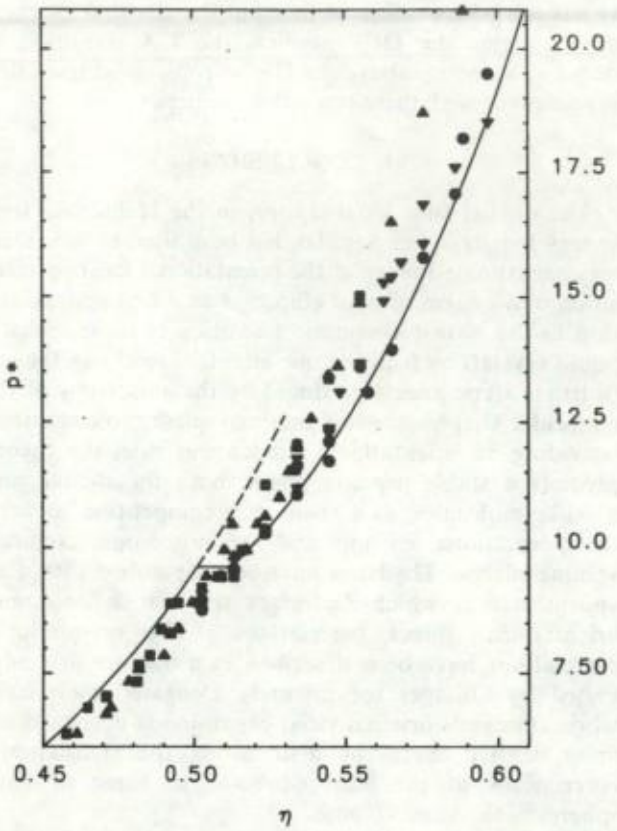

FIG. 9. Pressure ($p^* = \beta p v_{mol}$) density ($\eta = \rho v_{mol}$) phase diagram in the isotropic-nematic two-phase coexistence region as obtained from the density-functional theory (solid line, stable branches; dashed line, metastable I branch; metastable N branch, not visible on this scale) and from the computer simulations of Frenkel and Mulder (Ref. 4) [I phase: $k = 2.75$ (triangles), $k = 1/2.75$ (squares); N-phase: $k = 2.75$ (inverted triangles), $k = 1/2.75$ (circles)]. The transition density and the range of metastability is underestimated while the width is slightly overestimated by the theory.

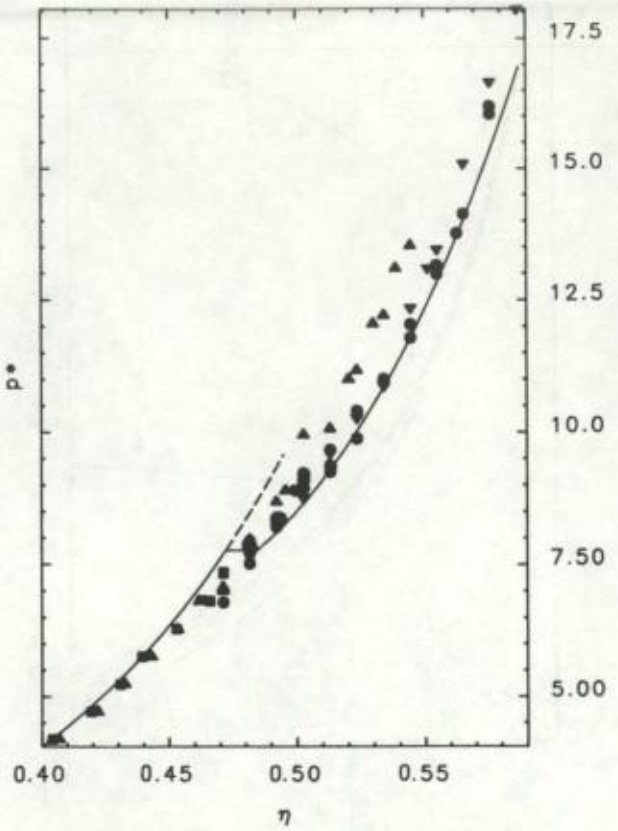

FIG. 10. Same as Fig. 9 but for $k = 3$ and $k = \frac{1}{3}$.

nematic coexistence. The theory also improves considerably on previous theoretical attempts.[9-11]

Finally, the simplicity of the theoretical expressions has been further exploited to test some of the historic milestone theories of phase transitions. It has been shown explicitly that the truncated order-parameter expansion of the free energy, which is at the basis of Landau's phenomenological theory of phase transitions,[7] largely underscores the width and the strength of the isotropic-nematic transition but yields results which are otherwise quite comparable to those obtained from the full free-energy expression. The virial expansion at the basis of Onsager's asymptotic theory[8] is, in turn, shown to become applicable only for very anisotropic molecules. These conclusions are independent of the validity of the approximations underlying the present density-functional theory and rest only on the use of truncated order parameter or virial expansions.

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