Isotropic-nematic transition of hard polar and nonpolar molecules

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A new theory to study isotropic-nematic transition is proposed. This theory requires a good knowledge of the thermodynamic properties of the isotropic phase. It allows to study nematic formation in systems possessing attractive forces. We determine isotropic-nematic equilibria for a number of hard linear models as hard spherocylinders, hard ellipsoids, and hard tangent spheres in a linear configuration. The theory predicts quite nicely the transitions when compared to simulation results. We also study the effect of an ideal dipole or quadrupole on nematic formation. Dipolar or quadrupolar forces favor the presence of a nematic phase although the effect is moderate. However, for large multipole moments no stable nematic phase was found.

I. INTRODUCTION

During the last decade, significant progress has been made in the understanding of liquid crystals.¹ Computer simulations of hard ellipsoids² (HE), hard spherocylinders^{3,4} (HSP), and of Gay-Berne model^{5,6} have been performed and nematic or even smectic order was found. The seminal work of Onsager⁷ showed that for very long models the second virial coefficient is enough for predicting an isotropicnematic transition. For shorter molecules it is necessary to go beyond the second virial coefficient approximation. Parsons⁸ and Lee^{9,10} incorporated in an approximate way the rest of the virial coefficients of the series. Tjipto-Margo and Evans¹¹ evaluated rigorously up to the third virial coefficient and estimated the rest of the virial coefficients of the series following the procedure of Barboy and Gelbart.¹² Another way of approaching the problem is by using the formalism of density functional theory.¹³ In these treatments, it is necessary to know the direct correlation function (DCF) of the system which is in general unknown. Thus, DCF is usually related to that of a hard sphere system. Most of these theoretical treatments relate the properties of the isotropic phase to those of a hard sphere system. It is clear that this procedure will not always be in general satisfactory and it will face important problems when attractive forces are also present. In fact, most of the theoretical work^{1-4,7-11} (with a few exceptions¹⁴) is focused on the study of liquid crystal formation in models of hard bodies.

During the last two decades significant progress has been made in development of theories of the isotropic phase of molecular fluids.¹⁵ Integral equations have now been solved for a number of molecular fluids^{16–20} and perturbation theories^{21–24} have provided a very useful route to the thermodynamic properties of those systems. Success has been especially significant with nonpolar molecular fluids²⁵ and some very promising results have been obtained for polar fluids.^{26–28} It would be desirable to have a theory of the isotropic-nematic transition incorporating a correct description of the isotropic phase. Moreover, it is important that this theory could be applied to systems having not only a hard

We shall apply this new theory to the study of nematic formation in HE, HSP, and in a model of tangent hard spheres in a rigid linear configuration which will be denoted as HLTS. Then, we shall study the effect of a dipole or quadrupole moment on the formation of the nematic phase. In the case of a dipolar fluid the possibility of a ferroelectric nematic^{29,30} phase is also considered.

II. THEORY

Let us consider a system of N molecules in a volume V at temperature T and with the number density $\rho = N/V$. The coordinates of the center of mass of molecule *i* are represented by \mathbf{r}_i and the orientation of the molecule *i* is represented by a set of orientational coordinates ω_i . The normalization condition for such a set of coordinates is

$$\int d\omega_i = 1. \tag{1}$$

For instance, for a linear molecule $d\omega_i$ may be written as sin $\theta d\theta d\phi/(4\pi)$, where θ and ϕ are the polar angles of the molecular axis. We shall denote the set of translational and orientational coordinates as $di = d\mathbf{r}_i d\omega_i$. The free energy of the homogeneous phase of such a system may be written as

$$\frac{A}{NkT} = \frac{A^{\text{Ideal}}}{NkT} + \frac{A^{\text{res}}}{NkT} , \qquad (2)$$

$$\frac{A^{\text{ideal}}}{NkT} = \ln(q^{\text{ideal}}\rho) - 1, \qquad (3)$$

$$\frac{A^{\text{res}}}{NkT} = \int_0^y \frac{Z-1}{y'} dy', \qquad (4)$$

where y denotes the packing fraction defined as $y = \rho V_m$ being V_m the molecular volume. The ideal molecular partition function is denoted as q^{ideal} and it has units of volume.

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core but attractive forces as well. In this work, we propose a theory which satisfy both these two conditions. It is similar in spirit to the theories proposed by Parsons⁸ and Lee.^{9,10} However, it differs from them in that no mapping to a hard sphere system is attempted and it allows to use some of the more recent theories of liquid state. Furthermore, for very long molecules the Onsager limit is recovered.

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In case the virial expansion given by $Z = 1 + \sum_{k=2}^{\infty} B_k^* y^{k-1}$ converges, the residual part of the Helmholtz free energy may be written as

$$\frac{A^{\text{res}}}{NkT} = \sum_{k=2}^{\infty} \frac{B_k^* y^{k-1}}{(k-1)},$$
(5)

where $B_k^* = B_k / V_m^{k-1}$ and B_k stand for the *k*th virial coefficient. A^{res} represents the contribution to the free energy of the system due to the forces between molecules and accounts for the nonideality of the system. Liquid state theory of the last decades has been focused in the determination of A^{res} by developing integral equations, perturbation theories or computer simulations which allow to determine A^{res} for a number of molecular fluids.

Let us now focus on a system with a nonuniform density. The free energy may be written in the absence of an external field as^{31}

$$A = kT \int \rho(1) \ln[q^{\text{ideal}}\rho(1)] d1 - kT \int \rho(1) d1$$
$$-kT \int_0^1 (1-\lambda) d\lambda \int \int \rho(1)\rho(2)c(1,2,\lambda\rho) d1 d2,$$
(6)

where $c(1,2,\lambda\rho)$ is the DCF of the system when the density of the system is given by $\lambda\rho$ being ρ the equilibrium density distribution. The last term in Eq. (6) accounts for the presence of intermolecular forces and will disappear for an ideal gas. Equation (6) provides a natural way of extending the division of Eq. (2) to a nonuniform system. In fact, we can write

$$\frac{A^{\text{ideal}}}{NkT} = kT \int \rho(1) \ln[q^{\text{ideal}}\rho(1)] d1 - \int kT\rho(1) d1, \qquad (7)$$

$$\frac{A^{\text{res}}}{NkT} = -kT \int_0^1 (1-\lambda)d\lambda \int \int \rho(1)\rho(2)c(1,2,\lambda\rho)d1d2.$$
(8)

For a uniform fluid $\rho(1) = \rho$ and Eq. (7) reduces to Eq. (3) and Eq. (8) becomes the compressibility route to the residual part of the Helmholtz free energy. In case of a nematic phase, $\rho(1)$ may be written as $\rho(1) = \rho f(\omega_1)$, where the angular distribution function $f(\omega_1)$ satisfies

$$\int f(\omega_1) d\omega_1 = 1.$$
(9)

Then, we obtain from the previous equations a general expression for the free energy of a nematic or an isotropic fluid,

$$A/(NkT) = \ln(q^{\text{ideal}}\rho) - 1 + \int f(\omega_1)\ln[f(\omega_1)]d\omega_1 + A^{\text{res}}[f(\omega)]/(NkT), \qquad (10)$$

where $A^{\text{res}}[f(\omega)]$ indicates that A^{res} is a functional of $f(\omega)$. When the fluid is isotropic $f(\omega) = 1$ and by substituting into Eq. (10), Eqs. (2) and (3) are recovered. Two kinds of theoretical treatments are found in the literature depending on the way of obtaining A^{res} . In density functional theory (DFT) treatments,^{32–34} approximations are made on Eq. (8), namely on the DCF of the isotropic or of the nematic fluid. In general, the nematic DCF is related to that of an homogeneous fluid. In the generalized Onsager theories,^{89,11} emphasis is made on the virial expansion of Eq. (8). In fact, if virial expansion converges then it is possible to write down an equation for A^{res} of the nematic fluid analogous to Eq. (5),

$$\frac{A^{\text{res}}}{NkT} = \sum_{k=2}^{\infty} \frac{b_k^* y^{k-1}}{(k-1)} \,. \tag{11}$$

In what follows B_k^* denotes the *k*th virial coefficient of the isotropic fluid, whereas b_k^* is the *k*th virial coefficient of the nematic phase. The first two virial coefficients, b_2 and b_3 , of the nematic phase may be written as

$$b_2 = \frac{-1}{2V} \int F_M(1,2) f(\omega_1) f(\omega_2) d1 d2, \qquad (12)$$

$$b_{3} = \frac{-1}{3V} \int F_{M}(1,2)F_{M}(1,3)F_{M}(2,3)f(\omega_{1})f(\omega_{2})$$
$$\times f(\omega_{3})d1d2d3, \qquad (13)$$

where $F_M(1,2) = \exp[-\beta u(1,2)] - 1$ is the Mayer function of molecules 1 and 2 interacting trough the pair potential u(1,2). Formulas for B_2 and B_3 may be obtained by substituting $f(\omega) = 1$ in Eqs. (12) and (13). Onsager⁷ treatment of isotropic-nematic equilibrium can be obtained from Eq. (5) and Eq. (11) by truncating the series of A^{res} at first order in y. Thus, only B_2 and b_2 need to be considered. This is justified for very long molecules because the rest of virial coefficients (when scaled by the appropriate power of the second virial coefficient) decays to zero. Moreover, nematic appears at a vanishing small density. So, truncation of the series at the first order power seems justified. Therefore, Onsager⁷ theory becomes exact for infinitely long molecules. However, it has ever since been accepted that for molecules with moderate elongations truncation of the virial series at the first order is not completely justified and other virial coefficients should be included. Some attempts to incorporate the third virial coefficient have been performed^{11,35} and although results improve respect to the Onsager limit, they are not completely satisfactory for medium elongations. It seems that in that case incorporation of the rest of the terms of the series of Eqs. (5) and (11) is needed.

Let us now assume the following approximation:

$$b_k = B_k b_2 / B_2. (14)$$

Then, assuming the convergence of virial expansion for isotropic and nematic phase and substituting Eq. (14) into Eq. (11) and in Eq. (10), one obtains

$$A/(NkT) = \ln(q^{\text{ideal}}\rho) - 1 + \int f(\omega_1) \ln[f(\omega_1)] d\omega_1 + \frac{A^{\text{res}}[f(\omega) = 1]}{(NkT)} \frac{b_2[f(\omega)]}{B_2}, \quad (15)$$

where the notation $b_2[f(\omega)]$ reminds us that b_2 is a functional of $f(\omega)$ [see Eq. (12)]. For the particular case of the isotropic fluid $[f(\omega)=1]$ Eq. (15) reduces to

$$A/(NkT) = \ln(q^{\text{ideal}}\rho) - 1 + A^{\text{res}}[f(\omega) = 1]/(NkT).$$
(16)

According to Eq. (16) if we would dispose of an accurate route to A^{res} of the isotropic fluid then our description of the isotropic branch should be exact. Equation (15) is only an approximation to the nematic branch even if we know exactly $A^{\text{res}}[f(\omega)=1]$.

Instead of the approximation of Eq. (14) let us assume that b_k is given by

$$b_k = B_{k,\rm HS} b_2 / B_{2,\rm HS},$$
 (17)

where $B_{k,HS}$ denotes the *k*th virial coefficient of a fluid of hard spheres. Then, substituting Eq. (14) into Eq. (11) and Eq. (10) we obtain

$$A/(NkT) = \ln(q^{\text{ideal}}\rho) - 1 + \int f(\omega_1)\ln[f(\omega_1)]d\omega_1 + \frac{A_{\text{HS}}^{\text{res}}}{(NkT)} \frac{b_2[f(\omega)]}{B_{2,\text{HS}}}, \qquad (18)$$

where $A_{\rm HS}^{\rm res}$ is the residual part of the Helmholtz free energy of a fluid of hard spheres. Equation (18) is identical to the one proposed by $Lee^{9,10}$ in his treatment of the isotropicnematic transition of hard ellipsoids (HE) and hard spherocylinders (HSP). There are two important differences between Eq. (15) and Eq. (18). The first is that in Eq. (15) the fluid phase is exactly treated whereas in Eq. (18) the treatment of the isotropic branch is only approximate. For most of molecular fluids, the exact value of A^{res} is not known yet and, therefore, some approximation has to be made to obtain it. Furthermore, Eq. (15) can be used with any kind of treatment whereas Eq. (18) implies the use of Parsons'⁸ approach. The second difference is that with Eq. (15) the incorporation of systems with attractive forces is straightforward. In general, Eq. (18) will provide a poor description of an isotropic fluid with attractive forces. From the previous discussion, we see that Eq. (18) can be obtained as a particular case of Eq. (15) if the Parsons approximation is used to describe the isotropic fluid. However, Eq. (15) is more general and allows for the incorporation of more successful theories of the isotropic phase than the Parsons approach. So, Eq. (15) can be regarded as a generalization of the successful approach proposed by Lee.9.10

Equation (15) is the central equation proposed in this work. It can be summarized by saying that properties of the nematic branch are related to those of an isotropic fluid at the same density by a simple scaling argument.

It may be argued that in our derivation of Eq. (15) convergence of the virial series was assumed. For hard bodies the virial expansion works surprisingly well (for instance, for HS very good results are obtained by summing the first ten virial coefficients³⁶). However, limits of convergence of the virial expansion are not quite clear even for hard spheres. When attractive forces are present the situation is even worse and the virial series is probably not convergent at all for most of the conditions of physical interest. In that case we still keep Eq. (15) as our basic equation although now Eq. (15) cannot probably be inferred from Eq. (14) when the virial series is not convergent. So, it must be recognized that Eq. (15) presents some ad hoc character. We shall explore this approach, although admitting that further work on its justification is needed in case that satisfactory results were obtained.

Let us now focus on the study of hard models. In that case, the second virial coefficient is just an average of the excluded volume so that we can write

$$b_2 = \frac{1}{2} \int V_{\text{exc}}(\omega_1, \omega_2) f(\omega_1) f(\omega_2) d\omega_1 d\omega_2, \qquad (19)$$

where $V_{\text{exc}}(\omega_1, \omega_2)$ is the volume excluded to the center of mass of molecule 2 with orientation ω_2 when molecule 1 is fixed with orientation ω_1 . Equation (15) reduces then for hard bodies to

$$A/(NkT) = \ln(q^{\text{ideal}}\rho) - 1 + \int f(\omega_1)\ln[f(\omega_1)]d\omega_1$$
$$+ A^{\text{res}}[f(\omega) = 1]/(NkT)$$
$$\times \frac{\int V_{\text{exc}}(\omega_1, \omega_2)f(\omega_1)f(\omega_2)d\omega_1d\omega_2}{\int V_{\text{exc}}(\omega_1, \omega_2)d\omega_1d\omega_2}.$$
(20)

In this work, we shall use a parametric form¹ for $f(\omega)$,

$$f(\omega) = C \exp[-t^2 \sin^2(\theta)], \qquad (21)$$

where C is a normalization constant which guarantees that Eq. (9) is satisfied and θ is the angle of the molecular axis with the nematic vector. According to Eq. (21) and Eq. (20), A/NkT is a function of the parameter t for a given ρ and T. The stability criterion requires that A be a minimum so that

$$\frac{\partial(A/NkT)}{\partial t} = 0. \tag{22}$$

At low densities the only solution of Eq. (22) is t=0 which corresponds to the isotropic phase. At higher densities two local minima of Eq. (22) appear (t=0 and $t=t_{nematic}$) being one of them marginally stable respect to the other. At still higher densities t=0 becomes a maximum and the only minimum correspond to $t=t_{nematic}$ so that only the nematic phase is stable. This behavior has been described in detail in Ref. 32.

The working expression of this paper for hard bodies is Eq. (20). We shall assume that $A^{\text{res}}[f(\omega)=1]$ is known and shall use the parametrization given by Eq. (21). Pressure p and compressibility factor Z are then obtained from

$$Z = \frac{pV}{NkT} = 1 + \{Z[f(\omega) = 1] - 1\} \frac{b_2}{B_2}.$$
 (23)

Coexistence between isotropic and nematic phases is obtained by equating the pressure and chemical potential of both phases. Three kinds of hard linear fluids will be analyzed, hard ellipsoids (HE), hard spherocylinders (HSP), and a model of hard tangent spheres in a linear arrangement (HLTS). For HSP with cylindrical length L and breadth σ the excluded volume $V_{\text{exc}}^{\text{HSP}}$ can be exactly being calculated and is given by¹

$$V_{\rm exc}^{\rm HSP} = 2L^2\sigma\,\sin(\theta_{12}) + 2\,\pi L\sigma^2 + 4\,\pi\sigma^3/3,$$
 (24)

where θ_{12} is the angle formed by the symmetry axes of the two rods. Equation (24) holds for prolate and oblate spherocylinders. For hard ellipsoids, we shall use the hard Gaussian overlap approximation³⁷ (HGO) so that $V_{\text{exc}}^{\text{HE}}$ will be taken from the corresponding HGO model,³⁸

$$V_{\text{exc}}^{\text{HE}} \simeq \frac{\left[1 - \chi^2 \cos^2(\theta_{12})\right]^{1/2}}{\left(1 - \chi^2\right)^{1/2}} \ 8V_m, \qquad (25)$$

where $\chi = (k^2 - 1)/(k^2 + 1)$ and k is the length to breadth ratio. The approximation given by Eq. (25) becomes worse as the elongation of the molecule increases as has been shown by Tjipto-Margo and Evans.¹¹ However, it possesses the advantage of its simplicity. Moreover, since the approximate formula of Eq. (25) is used in the numerator and denominator of the last term on the right-hand side of Eq. (20) we can expect some cancellation of errors. Since we are trying to describe the behavior of a HE (although with an approximate formula for the excluded volume coming from the HGO approximation) we shall take for $A^{\text{res}}[f(\omega)=1]$ the free energy of hard ellipsoids and not of the HGO model. Our description then corresponds to a HE although an approximate formula for the excluded volume of HE has been used.

Finally for HLTS we shall use the approximation

$$V_{\text{exc}}^{\text{HLTS}} = (m-1)^2 \sigma^3 \sin(\theta_{12}) \pi/2 + (m-1) 11 \sigma^3 \pi/6 + 4 \pi \sigma^3/3.$$
(26)

This approximation was first proposed by Boublik^{36,39} and it provides reasonable estimates of B_2 (although slightly high) for the HLTS model. Again, it has a simple form and since it is used in the numerator and denominator of Eq. (20) some cancellation of errors might occur. The integrals on the righthand side of Eq. (20) were evaluated numerically by using the Gaussian quadrature.⁴⁰

The only remaining question is the kind of approximation that will be used to describe the behavior of the fluid phase, namely $A^{\text{res}}[f(\omega)=1]$. If $Z[f(\omega)=1]$ is known then the integration of Eq. (4) yields $A^{\text{res}}[f(\omega)=1]$. There are several proposed equations of state (EOS) for hard elongated molecules. Analytical EOS have been proposed by Boublik and Nezbeda³⁶ or in the case of HLTS by Wertheim⁴¹ and Chapman *et al.*⁴² There are also some attempts to build up an EOS from the knowledge of the first virial coefficients as those proposed by Barboy and Gelbart¹² and Wojcik and Gubbins.⁴³ By analyzing the behavior of the first virial coefficients we have recently proposed⁴⁴ a new EOS for prolate and oblate hard linear models. This EOS requires a knowledge of B_2^* , B_3^* , B_4^* , and B_5^* of the molecule. Then, the EOS reads for prolate molecules Z^{pro} as

$$Z^{\text{pro}} = \frac{1 + k_1 y + k_2 y^2 + k_3 y^3}{(1 - y)^3} + [B_4^* - (k_3 + 3k_2 + 6k_1 + 10)]y^3, \quad (27)$$

where the coefficients k_1 , k_2 , and k_3 are obtained to fit the values of B_2^* , B_3^* , and B_5^* (see Ref. 44 for details). For oblate molecules Z^{obl} the EOS reads

TABLE I. Isotropic-nematic transition of hard spherocylinders (HSP). γ stands for the length to breadth ratio, so that γ is $L^* + 1$, where L^* is the reduced bond length $L^* = l/\sigma$. p^* stands for $pV_m/(kT)$. Packing fractions of isotropic and nematic phases are denoted as y_{iso} and y_{nem} , respectively. μ is the coexistence chemical potential with the ideal part given by $\ln(\rho\sigma^3) - 1$ [see Eq. (3)]. The results labeled as Lee refer to the theory of Ref. 9. Monte Carlo (MC) results are from Ref. 3.

Source	γ	y iso	y _{nem}	p*	μ/kT
This work	4	0.528	0.541	11.08	27.43
Lee	4	0.525	0.536	12.74	30.67
This work	5	0.449	0.467	6.79	19.49
Lee	5	0.454	0.468	7.71	21.35
This work	6	0.388	0.407	4.87	15.68
Lee	6	0.399	0.417	5.36	16.54
MC	6	0.	40	4.90	
This work	7	0.339	0.358	3.82	13.48

$$Z^{\text{obl}} = \frac{1 + k_1' y + k_2' y^2 + k_3' y^3}{(1 - y)^3} + [B_5^* - (3k_3' + 6k_2' + 10k_1' + 15)]y^4, \quad (28)$$

where the coefficients k'_1 , k'_2 , and k'_3 are chosen to match the known values of B_2^* , B_3^* , B_4^* .

III. RESULTS FOR HARD LINEAR MODELS

We have determined the isotropic-nematic transition for HSP, HE, and HLTS of several elongations. We shall define γ as the length to breadth ratio which for HSP is given by $\gamma = L^* + 1$, for HE is just $\gamma = k$ and for HLTS is $\gamma = m + 1$, where $L^* = l/\sigma$ is the reduced bond length and *m* is the number of tangent spheres. We show the results for HSP in Table I. For HSP with $\gamma = 6$, Frenkel³ has determined the transition by computer simulation. The densities are quite well predicted by the theory of this work [Eqs. (20)-(23)] and by the previous version of Lee.9 The pressure at the transition is better predicted in this work. For $\gamma = 4$, we predict a transition when the density of the fluid is y = 0.528. Veerman and Frenkel⁴ found a fluid-solid transition when y=0.500. The nonexistence of a fluid-nematic transition for HSP with $\gamma = 4$ is then due to the fact that the fluid-nematic transition is pre-ended by the fluid-solid transition. Properties of coexistence as densities, pressures, and chemical potentials decrease as molecular elongation increases. We show the results for HE in Table II. The theory of this work agrees remarkably well with the simulation results^{2,45} and seems to be superior to other previously proposed theories. Trends with elongations are similar to those found for HSP. This is further illustrated in Figs. 1, 2, and 3, where we show the coexistence properties as a function of γ for several hard models. Hard ellipsoids and HSP differ significantly in their coexistence properties for a given value of γ . Nematic phase appears at lower densities for HE. According to Eq. (20), $A^{\text{res}}[f(\omega)=1]$ and $V_{\text{exc}}(\omega_1,\omega_2)$ are the two ingredients of the theory. HSP and HE present very similar virial coefficients, equation of state, and free energy $A^{\text{res}}[f(\omega)=1]$ for the isotropic phase.⁴⁴ Differences in their phase diagram are due to differences in $V_{\text{exc}}(\omega_1, \omega_2)$. In Fig. 4, we show $V_{\text{exc}}/(2B_2)$ as a function of the relative orientation for HE and HSP with

TABLE II. As in Table I, but for hard ellipsoids. γ is the length to breadth ratio which for ellipsoids is given by the axes ratio, k. Results labeled as Lee refer to the theory of Ref. 10, TME to Ref. 11, CWXB to Ref. 32, and HP to Ref. 55. MC results are from Ref. 2 and 45. The order parameter S of the nematic phase is defined by $S = \langle P_2(\cos \theta) \rangle$, where the brackets denote ensemble average and P_2 is the second order Legendre polynomial.

Source	γ	${\cal Y}_{iso}$	y _{nem}	p *	μ/kT	S
This work	3	0.519	0.529	9.90	24.61	0.52
TME	3	0.465	0.481	8.11		0.64
CWXB	3	0.472	0.484	7.76	•••	0.56
HP	3	0.454	0.474	4.68	•••	0.48
MC	3	0.507	0.517	9.79	•••	0.53
This work	1/3	0.499	0.508	9.98	25.50	0.54
TME	1/3	0.428	0.437	6.08		0.46
MC	1/3	0.498	0.509	9.15		
This work	4	0.419	0.438	4.70	14.24	0.61
This work	5	0.347	0.371	3.08	10.64	0.64
TME	5	0.388	0.426	3.01	•••	0.68
CWXB	5	0.321	0.342	2.78	•••	0.64
MC	5	0.	37			
This work	1/5	0.322	0.341	3.02	11.07	0.63
TME	1/5	0.335	0.359	2.30		0.55
This work	6	0.298	0.323	2.32	8.77	0.66
This work	7	0.262	0.287	1.88	7.64	0.68
This work	10	0.192	0.214	1.25	5.91	0.71
TME	10	0.199	0.233	1.16	•••	0.75
CWXB	10	0.179	0.204	1.03	•••	0.72
HP	10	0.244	0.279	1.27		0.66
мс	10	0.:	21			

 $\gamma=6$. We see that V_{exc} changes more rapidly with orientation for HE than for HSP so that a nonuniform $f(\omega)$ will stabilize more a HE nematic phase than a HSP nematic phase. Consequently, the nematic phase appears at lower densities for HE than for HSP. We can also analyze the case of oblate



FIG. 1. Packing fractions of the isotropic and nematic phases at coexistence as a function of the length to breadth ratio γ . Results are for hard molecules. Solid lines on the top correspond to HSP and on the bottom to HLTS. The dashed line stands for prolate ellipsoids HE.



FIG. 2. As in Fig. 1, but for the coexistence pressure $(p^* = pV_m/kT)$. Symbols are the results from Tables I–III and the lines are only a guide to the eye.

ellipsoids of revolution. Equation (25) will be used for the excluded volume since this property has indeed prolateoblate symmetry (see Ref. 11). Differences in behavior of prolate-oblate HE are then due to differences in the behavior of the isotropic phase. Equation (28) will be used for describing the isotropic phase. We see in Table II that the isotropicnematic transition is very similar for prolate and oblate HE although for oblate molecules it appears at slightly smaller densities in good agreement with simulation results.^{2,3} In Fig.



FIG. 3. As in Fig. 1, but for the chemical potential at coexistence. The chemical potential μ is given in units of kT. Symbols are the results from Tables I–III and the lines are a guide to the eye.



FIG. 4. Excluded volume V_{exc} of hard linear molecules as a function of the cosine of the angle formed by the molecular axes $\mathbf{u}_1 \cdot \mathbf{u}_2$. Excluded volume is given in units of the second virial coefficients of the isotropic phase and divided by two so that the area under the curve is one half. The solid line is for HSP with $L^*=5$ ($\gamma=6$) and dashed line is for prolate HE with k=6 ($\gamma=6$).

5 we present the EOS for HE with k=3 and k=1/3 as obtained from simulation and from the theory of this work. The agreement is quite good. The behavior of the order parameter S of the nematic phase as a function of the density for HE is illustrated in Fig. 6.

We show the results for HLTS in Table III. In this case, we used two different determinations of $V_{\text{exc}}(\omega_1, \omega_2)$. The first is the approximation given by Eq. (26) which, although not exact, is reasonable and simple to use. In the second approach we determine $V_{\text{exc}}(\omega_1,\omega_2)$ numerically. Equation (26) overestimates the excluded volume of HLTS for any relative orientation but errors are small. Transitions determined from these two routes to V_{exc} are very similar. The theory of this work predicts an isotropic-nematic transition for HLTS. We see in Fig. 1 that the densities at coexistence of HLTS and HE for a given γ are quite similar. An important point to establish the presence of a nematic phase for HLTS is to be sure that the isotropic-nematic transition is not pre-ended by a fluid-solid transition. Unfortunately, little knowledge on freezing of HLTS is available except for the case m = 2. In that case the fluid-orientationally ordered solid transition appears⁴⁶ for y = 0.55 so that the isotropic-nematic transition which would occur at $y \approx 0.72$ is pre-ended by the fluid-solid equilibria. Equation (15) is not limited to hard bodies but it may be used for systems with attractive forces as well. In the next section we shall study the effect of a dipole or a quadrupole on the isotropic-nematic transition.

IV. HARD POLAR FLUIDS

In this section we shall study a linear hard model (HSP) with an embedded point dipole or quadrupole. We shall focus

on the HSP model with $L^* = 5$. The dipole-dipole u^{DD} or quadrupole-quadrupole u^{QQ} potentials are given by¹⁵

$$\mu^{\rm DD} = \frac{\mu^2}{r^3} (s_1 s_2 c - 2c_1 c_2), \tag{29}$$

$$u^{QQ} = \frac{3Q^2}{4r^5} \left[1 - 5(c_1^2 + c_2^2) - 15c_1^2c_2^2 + 2(s_1s_2c - 4c_1c_2)^2\right],$$
(30)

where μ and Q stand for the dipole and quadrupole moment, $c_i = \cos \theta_i$, $s_i = \sin \theta_i$, and $c = \cos(\phi_1 - \phi_2)$. In Eqs. (29) and (30) the polar axis is the one connecting the center of mass of both molecules. We shall use reduced multipole moments defined as $\mu^{*2} = \mu^2/(kT\sigma^3)$ and $Q^{*2} = Q^2/(kT\sigma^5)$. The



FIG. 5. Equation of state for HE obtained from the theory of this work (solid line). The symbols are Monte Carlo results of Ref. 2 for the isotropic phase (open squares) and for the nematic phase (open circles). The tie lines represent the coexistence densities as obtained from the theory of this work and from computer simulations (Ref. 2). (a) Results for prolate HE with k=3. (b) Results for oblate HE with k=1/3.



FIG. 6. Order parameter of the nematic phase $S = \langle P_2(\cos \theta) \rangle$ of HE as a function of the packing fraction y. Open and filled symbols stand for simulation results (Ref. 45) of oblate and prolate HE, respectively. Lines correspond to the theory of this work.

breadth of the spherocylinder is denoted as σ . Therefore, the total pair potential is given for a quadrupolar hard spherocylinder HSPQ by

$$u^{\rm HSPQ} = u^{\rm HSP} + u^{\rm QQ} \tag{31}$$

and for a dipolar hard spherocylinder (HSPD) by

$$u^{\text{HSPD}} = u^{\text{HSP}} + u^{\text{DD}}.$$
 (32)

The ideal dipole or quadrupole is situated on the center of mass of the molecules and is aligned with the molecular axis. All our discussions and conclusions refer to that case. According to Eq. (20), we first need to know the thermodynamic properties of the isotropic HSPQ or HSPD. This is not a trivial problem. However, Boublik has recently developed a perturbation theory for hard ellipsoids with quadrupole²⁶ (HEQ) or dipole²⁷ (HED). This perturbation theory has been extended to HSPQ fluids with good results.²⁸ We briefly summarize the theory and refer to the reader to the original papers for details.^{26-28,47} In this perturbation theory the HSP

TABLE III. As in Table I, but for hard linear tangent spheres (HLTS). γ stands for the length to breath ratio, so that $\gamma = m+1$, where m is the number of hard spheres forming the linear molecule.

-γ	y 150	y _{nem}	<i>p*</i>	μ/kT	S	$100 \Delta y/\bar{y}$
4 ª	0.417	0.429	8.20	25.71	0.64	0.71
4 ⁶	0.432	0.443	9.35	28.54	0.64	0.63
5*	0.346	0.360	4.96	18.45	0.65	0.99
5 ⁶	0.359	0.373	5.57	20.24	0.67	0.96
6*	0.295	0.310	3.54	14.94	0.67	1.24
6 ⁶	0.309	0.326	4.11	16.83	0.72	1.34
7*	0.255	0.270	2.75	12.88	0.67	1.43
7 ⁶	0.261	0.276	2.96	13.72	0.67	1.40

*Excluded volume from the approximation of Eq. (26). *Excluded volume by numerical integration.

TABLE IV. Geometrical constants I, J, K (see main text) of hard spherocylinders with a point dipole HSPD (I_D, J_D, K_D) or a point quadrupole HSPQ $(I_Q, J_Q, \text{ and } K_Q)$. No value is given for I_D and K_D since they are identically zero.

L*	J _D	IQ	. J _Q	KQ
0	0.666 66	0.000 000	4.977 77	4.179 59
1	0.206 11	-0.024 64	0.522 47	0.204 84
2	0.127 45	-0.024 12	0.287 89	0.188 76
3	0.102 10	-0.016 57	0.239 72	0.178 18
4	0.091 44	-0.011 18	0.224 53	0.173 37
5	0.087 11	-0.007 80	0.218 19	0.170 95
6	0.082 58	-0.005 67	0.215 02	0.169 55
8	0.080 46	-0.003 31	0.212 08	0.168 18
9	0.079 72	-0.002 65	0.211 31	0.167 74
10	0.079 21	-0.002 16	0.210 79	0.167 50

is taken as the reference system and the perturbation terms up to third order are evaluated. To accelerate the convergence of perturbation series a Pade approximant is used.⁴⁸ Structure of the hard reference fluid is needed to evaluate the perturbation terms. This is, in general, unknown or difficult to obtain so that the Parsons⁸ approximation is used. That means that the pair correlation function $g(r, \omega_1, \omega_2, y)$ is approximated by $g_{\rm HS}[r/d(\omega_1,\omega_2),y]$, where $g_{\rm HS}$ is the radial distribution function of hard spheres and $d(\omega_1, \omega_2)$ is the distance between the centers of mass when the two molecules are at contact for the relative orientation ω_1 , ω_2 . That uncouples orientational and radial coordinates and each perturbation term reduces to an orientational average of a certain function and a radial²⁶⁻²⁸ integration of a certain function of g_{HS} . Free energy for the isotropic phase of HSPQ is given by

$$A^{\rm HSPQ} = A^{\rm HSP} + A^{Q}_{1A} + A^{Q}_{2A} [1 - (A^{Q}_{3A} + A^{Q}_{3B})/A^{Q}_{2A}]^{-1}.$$
(33)

Defining $X_Q^* = 3/4Q^{*2}$ and $\rho^* = \rho\sigma^3$ then $A_{1A}^Q, A_{2A}^Q, A_{3A}^Q, A_{3B}^Q$ are given by

$$A_{1A}^Q/NkT = 2\pi\rho^* X_Q^* I_Q(\text{shape}) a_Q(y), \qquad (34)$$

$$A_{2A}^{Q}/NkT = -\pi\rho^* X_Q^{*2} J_Q(\text{shape}) b_Q(y), \qquad (35)$$

$$A_{3A}^{\mathcal{Q}}/NkT = \frac{\pi \rho^*}{3} X_{\mathcal{Q}}^{*3} K_{\mathcal{Q}}(\text{shape}) c_{\mathcal{Q}}(y), \qquad (36)$$

$$A_{3B}^{Q}/NkT = \frac{4}{3} \pi^{2} \rho^{*2} X_{Q}^{*3} \frac{1}{[(V_{m}/\sigma^{3})/(\pi/6)]^{5}} z_{Q}(y),$$
(37)

where I_Q , J_Q , and K_Q are geometrical quantities obtained by integration and depending on the particular shape of the considered model.²⁸ Expressions for $a_Q(y)$, $b_Q(y) c_Q(y)$, and $z_Q(y)$ are given in Eqs. (32)–(34) of Ref. 28. These functions can be obtained by numerical integration of radial distribution function of hard spheres divided by the appropriate power of the distance between the centers of mass. We present values of I_Q , J_Q , and K_Q for HSP with longer elongations in Table IV since in our previous work²⁸ only short molecules were considered. Conroy integration method^{49,50} was used in the determination of I_Q , J_Q , and K_Q . The theory may be extended to HSPD fluids. Now I_D and K_D are zero so that A_{1A} and A_{3A} vanishes. A^{HSPD} is given by

$$A^{\text{HSPD}} = A^{\text{HSP}} + A^{D}_{2A} (1 - A^{D}_{3B} / A^{D}_{2A})^{-1}.$$
 (38)

Defining $X_D^* = \mu^{*2}$ then A_{2A} and A_{3B} are given by

$$A_{2A}^{D}/NkT = -\pi\rho^{*}X_{D}^{*^{2}}J_{D}(\text{shape})b_{D}(y), \qquad (39)$$

$$A_{3B}^{D}/NkT = \frac{4}{3} \pi^{2} \rho^{*2} X_{D}^{*3} \frac{1}{[(V_{m}/\sigma^{3})/(\pi/6)]^{3}} z_{D}(y).$$
(40)

Values of J_D determined by Conroy method are shown in Table IV. Functions $b_D(y)$ and $z_D(y)$ are defined, respectively, by

$$b_D(y) = \int g_{\rm HS}(x)/x^4 \, dx, \qquad (41)$$

$$z_{D}(y) = \int \frac{1}{9(1+3)} \cos \alpha_{1} \cos \alpha_{2} \cos \alpha_{3}}{x_{12}^{2} x_{13}^{2} x_{23}^{2}} dx_{12} dx_{13} dx_{23},$$

$$(42)$$

where α_1 , α_2 , and α_3 are the internal angles of the triangle formed by the center of mass of molecules 1, 2, and 3. Furthermore, we have fitted $b_D(y)$ and $z_D(y)$ to the empirical expressions

$$b_D(y) = 0.332\ 751 + 0.431\ 728y + 0.249\ 496y^2,$$
(43)
$$z_D(y) = [0.202\ 065 + 0.548\ 44y + 0.103\ 006y^2] \frac{1}{9}.$$
(44)

Equations (33)-(44) constitute the route to obtain $A_{\text{HSPQ,HSPD}}^{\text{res}}[f(\omega)=1]$. We also need to know $b_2[f(\omega)]$ for HSPQ or HSPD. Let us first extend the concept of excluded volume to HSPQ and HSPD by defining

$$V_{\text{exc}}(\omega_1, \omega_2) = -\int (\exp\{-1/kT[u^{\text{HSP}}(\mathbf{r}, \omega_1, \omega_2) + u^{\text{QQ,DD}}(\mathbf{r}, \omega_1, \omega_2)]\} - 1)d\mathbf{r}.$$
 (45)

With this definition of V_{exc} the second virial coefficient b_2 is still given by Eq. (19). Note that in the integration of Eq. (45) the orientation of molecules 1 and 2 is fixed and the integration is over the center of mass positions. For HSPQ and HSPD, V_{exc} is a function of $(\mathbf{u}_1 \cdot \mathbf{u}_2)$, where \mathbf{u}_1 and \mathbf{u}_2 are the unit vectors situated along the molecular axes. For HSPQ, V_{exc} is symmetric around $(\mathbf{u}_1 \cdot \mathbf{u}_2)=0$ but not for HSPD. In Fig. 7 we represent V_{exc} for HSP with $L^*=5$ for several values of μ^{*2} and Q^{*2} . Presence of a quadrupole or dipole reduces the second virial coefficient of the isotropic phase (which is just the half of the area under the curve). For elongated HSP quadrupolar forces favor parallel configurations with $(\mathbf{u}_1 \cdot \mathbf{u}_2) \cong 1$. We see that dipolar forces favor antiparallel configurations⁵¹ with $(\mathbf{u}_1 \cdot \mathbf{u}_2) \cong -1$ for elongated hard spherocylinders. We emphasize that these conclusions hold for long polar molecules. If molecular hard core is rather



FIG. 7. Excluded volume [see Eq. (45) of the main text] in $4V_m$ units for multipolar HSP with $L^*=5$ as a function of the cosine of the angle between the molecular unit vectors $\mathbf{u}_1 \cdot \mathbf{u}_2$. (a) Results for quadrupolar hard spherocylinders. The solid line stands for $Q^{*2}=0$ and the dashed line stands for $Q^{*2}=4$. (b) Results for dipolar hard spherocylinders. The solid line stands for $\mu^{*2}=0$, the upper dashed line on the left-hand side stands for $\mu^{*2}=2$ and the other dashed line stands for $\mu^{*2}=4$.

spherical then these conclusions may be modified. In fact, we evaluated numerically $V_{\text{exc}}(\omega_1,\omega_2)$ for dipolar hard spheres with $\mu^{*2}=6.66$ and we found $V_{\text{exc}}(\mathbf{u}_1\cdot\mathbf{u}_2)/(4V_m)=-81$, -226, -2683 for $(\mathbf{u}_1\cdot\mathbf{u}_2)=-1$, 0, 1, respectively. We see how in that case dipole favors parallel configurations of the dipoles (in contrast with what was found for dipolar hard spherocylinders). That may explain the tendency of hard spheres with high dipole moments to form ferroelectric phases^{29,30} (solid or nematics).

In Tables V and VI, we show the isotropic-nematic tran-

TABLE V. Isotropic-nematic transition of HSP with $L^*=5$ for $Q^{*2}=0, 2, 4, 6, Q^{*2}$ is defined as $Q^2/(kT\sigma^5)$. For $Q^{*2}=6$ no transition to a nematic phase was found. $\Delta y/\bar{y}$ stands for $2(y_{nem}-y_{iso})/(y_{nem}+y_{iso})$.

Q* ²	${\cal Y}_{150}$	y _{nem}	<i>p</i> *	μ/kT	S	100 ∆y/ÿ
0	0.388	0.407	4.87	15.68	0.67	1.19
2	0.379	0.400	4.52	14.75	0.69	1.35
4	0.355	0.380	3.73	12.61	0.71	1.70
6	•••	•••				

sition for HSPQ and HSPD fluids. The effect of a dipole or quadrupole on the isotropic-nematic transition is quite similar. Equilibrium densities, pressures and chemical potentials decrease as the quadrupole or dipole moment increases. One may conclude that a dipole or quadrupole moment stabilizes the nematic phase with respect to the isotropic phase so that the transition appears at smaller densities. Transition is first order. In Fig. 8 we present the EOS and the isotropic-nematic transitions for HSP with $L^* = 5$ when no multipole moment is present and when $Q^{*2}=4$ or $\mu^{*2}=4$. The EOS of the isotropic phase is hardly affected by the presence of the multipole moment in contrast with the behavior of the nematic branch. Poniewierski and Sluckin⁵² found for HSPQ that the quadrupole decreases the densities at which appears the nematic phase. This is in agreement with our results. Unfortunately no comparison is possible for HSPQ between both theories since transition properties were not reported.⁵² Density jump and order parameter of the nematic phase at the transition increase with strength of polar forces. Overall, the effect of polar forces is relatively small. For instance when $L^*=5$, the density of the isotropic phase at the transition shifts from y = 0.388 to y = 0.355 when μ^{*2} changes from 0 to 4. Increasing molecular elongation from $L^*=5$ to $L^*=6$ ($\gamma=6$ to $\gamma=7$) with zero dipole moment changes the density at the transition from y=0.388 to y=0.339. So, the effect of elongation seems to be more important than that of dipolar of quadrupolar forces. We were unable to find an isotropic-nematic transition when $Q^{*2}=6$ or $\mu^{*2}=6$. Nematic phase becomes now unstable and its pressure decreases as the density increases. This may be due to a failure of the theory for high multipole moments. For HSP with $L^*=5$ and $\rho^* = \rho \sigma^3 = 0.07$ the theory predicts for $\mu^{*2} = 0$ and $\mu^{*2}=6 p^{*}=2.55$, 2.41 and simulation⁵³ yields $p^{*}=2.58$, 2.14 $[p^* = p/(kT/V_m)]$, where V_m is the molecular volume]. For $\mu^{*2}=6$ the predicted internal energy is U/NkT = -0.67to be compared with the simulation results U/NkT = -1.39. Although the agreement is not very good, it is at least qualitatively reasonable given the large values of L^* and μ^{*2} .

TABLE VI. Isotropic-nematic transition of HSP with $L^*=5$ for $\mu^{*2}=0, 2, 4, 6, \mu^{*2}$ stands for $\mu^2/(kT\sigma^3)$. For $\mu^{*2}=6$ no transition to a nematic phase was found.

μ^{*2}	y iso	y nem	<i>p</i> *	µ/kT	S	100 Δy/y
0	0.388	0.407	4.87	15.68	0.67	1.19
2	0.380	0.401	4.54	14.78	0.68	1.34
4	0.354	0.383	3.59	12.35	0.74	1.97
6		•••				



FIG. 8. Equation of state for polar and nonpolar hard spherocylinders with $L^*=5$. The pressure is given in reduced units $p^*=pV_m/(kT)$ and y is the packing fraction. The solid lines correspond to the EOS of the isotropic and nematic branches when no multipole moment is present. The long dashed line stand for the results of the HSPQ model with $Q^{*2}=4$. The short dashed line stand correspond to a HSPD model with $\mu^{*2}=4$. The tie lines represent the isotropic-nematic transitions as obtained from the theory of this work.

That supports the idea that nematic phase may indeed disappear for large values of the reduced multipole moment (i.e., for low temperatures). If that is the case then these systems will go directly from the isotropic phase to a smectic or solid phase but these kinds of transitions have not been considered



FIG. 9. EOS for HSP with $L^{*}=5$. $p^{*}=pV_m/(kT)$ and y is the packing fraction. The solid line on the left stands for the isotropic phase. The solid line on the nematic branch was determined from the minimization of Eq. (22) and the dashed line by functional minimization. Squares are MC results from Ref. 3. A smectic phase appears in the simulation at y=0.53.

in this work. Levesque *et al.*⁵³ have reported results for the isotropic and smectic phase for HSP with $L^*=5$ and $\mu^{*2}=6$. It would be very useful to know if a nematic phase appears in this system or as predicted in the present work the nematic phase disappears for high dipole or quadrupole moments.

In the case of the dipolar system, there is the possibility of a ferroelectric nematic phase^{29,30} with a net dipole moment per unit of volume (different number of molecules with dipoles up and down). Our trial function for $f(\omega)$ [see Eq. (21)] is symmetric around $\cos(\theta)=0$ and therefore does not

$$f(\omega) = \frac{\exp\left\{-\frac{A^{\text{res}}[f(\omega)=1]}{NkT}\frac{\int V_{\text{exc}}(\omega_1,\omega_2)f(\omega_2)d\omega_2}{B_2}\right\}}{\int \exp\left\{-\frac{A^{\text{res}}[f(\omega)=1]}{NkT}\int V_{\text{exc}}(\omega_1,\omega_2)f(\omega_2)d\omega_2\right\}d\omega_1}.$$

Equation (47) constitutes an integral equation for $f(\omega)$ and we have solved it by an iterative procedure. At high densities we find two solutions of $f(\omega)$, namely $f(\omega) = 1$ (isotropic phase) and $f(\omega)$. For a few cases we recalculate the isotropic-nematic transition by this functional minimization. Densities, pressure, and chemical potential determined in that way were similar to that found from the minimization (with respect to t) of the trial function of Eq. (21) so that all the conclusions of our previous discussions still holds. In Fig. 9, we show that EOS of the isotropic and nematic phase for HSP with $L^* = 5$. Figure 9 shows that EOS of the nematic branch as obtained by minimization of the trial function given in Eq. (21) or by functional minimization are quite similar. For all the models considered in this work, the solution of Eq. (47) was always symmetric around $\cos(\theta) = 0$ so that no evidence of ferroelectric order has been found. For HSP with $L^* = 5$ there is a nematic-smectic phase transition at high densities^{3,54} and that may explain discrepancies between the theory and the Monte Carlo results at the highest densities.

For $Q^{*2}=6$ and moderate densities we found a nematic solution of Eq. (47). However this nematic solution is mechanically unstable so that $(\partial p/\partial \rho) < 0$. At high densities no solution was found for Eq. (47). In that case $f(\omega)$ tends toward delta functions centered around $\cos(\theta)=-1$ and $\cos(\theta)=1$.

When $\mu^{*2}=6$ we were unable of finding a solution of Eq. (47) at any density [except the trivial case $f(\omega)=1$]. All these results suggest the absence of a stable nematic phase for elongated molecules with high reduced multipole moment (i.e., at low temperatures).

V. CONCLUSIONS

In this work we have proposed a theory for studying the isotropic-nematic transition. The theory follows in some respects those proposed by Parsons⁸ and Lee⁹ and, therefore, presents some ad hoc character. Nevertheless, the theory requires the knowledge of the thermodynamic properties of the

consider this possibility. In order to further investigate the possibility of a ferroelectric nematic phase we shall perform a functional minimization of Eq. (20) without imposing any symmetry on $f(\omega)$. Therefore, we look for the solution of

$$\frac{\delta A[f(\omega)]}{\delta f(\omega)} = 0 \tag{46}$$

along with the normalization condition of Eq. (9). The Euler-Lagrange equation associated to that problem is given by

isotropic phase so that it allows to incorporate the progress made in the last two decades for isotropic molecular fluids. The Onsager⁷ limit is recovered for very elongated molecules. We have applied this theory to HSP and HE and obtained good agreement with simulation results. For HLTS we predicted an isotropic-nematic transition. The analysis of the effect of dipole and quadrupole moment on nematic formation has shown that multipolar forces stabilize the nematic phase with respect to the isotropic phase. As a consequence, transition densities, pressures, and chemical potentials decrease as the strength of the multipolar forces increases. We have observed that the density jump and order parameter of the nematic phase increase with the presence of polar forces. Overall, the effect of polarity on nematic formation is moderate. The nematic phase was found to be in all the cases nonferroelectric. For high values of μ^* or Q^* (i.e., low temperatures) we did not find a stable nematic phase. That was true regardless of whether a trial function was used for $f(\omega)$ or it was obtained from minimization of a free energy functional. That suggests that nematic phase disappears for high multipole moments in favor of a more ordered phase. In this work we have focused on hard multipolar models. We were able to give a picture of the isotropic-nematic transition as a function of molecular elongation and multipolar forces. Moreover the theory presented in this work may also be applied to systems containing dispersion attractive forces.

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