Density functional theory applied to the isotropic–nematic transition in model liquid crystals

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The isotropic–nematic phase transition is investigated for several model liquid crystals using the density functional method. The models considered are hard ellipsoids of revolution (both prolate and oblate cases), hard spherocylinders, and two additional fluids characterized by pair potentials of a generalized Maier–Saupe type. The direct pair correlation functions for the isotropic phase are obtained by numerical solution of the hypernetted-chain (HNC) and Percus–Yevick (PY) integral equation theories. It is shown that second order density functional theory is strongly dependent upon the approximation used for the isotropic direct pair correlation function. In all cases the density functional results are qualitatively consistent with conclusions based upon orientational stability criteria.

I. INTRODUCTION

In previous articles[1-3] we have solved the hypernetted-chain (HNC) and Percus–Yevick (PY) integral equation theories for several model fluids which form nematic phases. These include models characterized by potentials of the Maier–Saupe type,[1-4] as well as fluids of hard ellipsoids of revolution[2,5] and spherocylinders.[3,6,7] In this earlier work stability criteria[1-3,8] were examined in order to determine the absolute stability limit of the isotropic phase. The stability criterion applied essentially amounted to determining the state points at which the reciprocal Kerr constant $K^{-1} = 0$. Of course this condition determines the spinodal line rather than points on the thermodymamic coexistence curve. The purpose of the present paper is to locate the true isotropic–nematic phase transitions by applying the density functional approach.

In recent years density functional theory has been widely and fruitfully employed in the study of the freezing transition[9-16] in both simple[9-14] and molecular[15,16] systems. The density functional method has also been used in investigations of the isotropic–nematic[17-21] and nematic–smectic[22] phase transitions for several model liquid crystals. Also it is worth noting that the much earlier work of Onsager,[23] Lasher,[24] and Workman and Fixman[25] on the isotropic–nematic transition for systems of hard rods and spherocylinders is closely related to what is now called density functional theory.

A key ingredient in the density functional formalism is the direct pair correlation function commonly denoted $c^{(2)}(12)$. For example, in order to apply the density functional approach to determine the isotropic–nematic transition it is necessary to know $c^{(2)}(12)$ for the isotropic phase. In general the determination of $c^{(2)}(12)$ for nonspherical particles is a nontrivial task and this has posed a problem in the application of the density functional method to such systems. However, our recently developed methods[1-3,26] for solving integral equation theories now provide HNC and PY

results for $c^{(2)}(12)$ for nonspherical models, and it is these approximations for $c^{(2)}(12)$ which are used in the present calculations. For the models considered it is found that density functional theory predicts isotropic–nematic transitions at state points which lie close to the spinodal curves determined by the orientational stability condition.

II. THEORY

Density functional theory has been clearly discussed several times in the recent literature[10-14] and the essentials of the approach are well known. Therefore, in the present paper we shall simply quote the general result and discuss its application to the problem of interest.

In the density functional analysis the grand potential $\Omega = -PV$ (P is the pressure and V the volume of the sample) is treated as a functional of the singlet distribution function $\rho(1)$. The central equation obtained[10-14] for the difference in the grand potential between two states can be expressed in the form

$$
\begin{aligned}
\beta\Delta\Omega = \beta\Omega[\rho] - \beta\Omega[\rho_0] = \int d(1) \Bigg\{ \rho(1)\ln\left(\frac{\rho(1)}{\rho_0(1)}\right) \\
- [\rho(1) - \rho_0(1)]\Bigg\} - \frac{1}{2}\int d(1)d(2)c^{(2)}(12;[\rho_0]) \\
\times [\rho(1) - \rho_0(1)][\rho(2) - \rho_0(2)] - \frac{1}{6} \\
\times \int d(1)d(2)d(3)c^{(3)}(123;[\rho_0])[\rho(1) - \rho_0(1)] \\
\times [\rho(2) - \rho_0(2)][\rho(3) - \rho_0(3)] + \cdots, \quad (1)
\end{aligned}
$$

where $\beta = 1/kT$, $c^{(3)}(123)$ is the direct three-body correlation function, and $[\rho]$ is used to indicate functional dependence on $\rho(1)$. Also in Eq. (1), $(1) \equiv (\mathbf{r}_1,\omega_1)$ and $d(1) = d\mathbf{r}_1\,d\omega_1$ where $\mathbf{r}_1$ and ω_1 describe the position and orientation of particle 1, respectively. We remark that the higher order terms in the $\beta\Delta\Omega$ expansion depend upon the higher order direct correlation functions. Since reliable approximations are not presently available for the three-body and high-

er order direct correlation functions, we follow previous authors[17,20] and truncate Eq. (1) after the second order term.

In order to apply Eq. (1) to the isotropic–nematic transition we make the identifications

$$\rho(1) = \rho_N(1) \tag{2}$$

and

$$\rho_0(1) = \rho_I(1) = n_I/4\pi = \bar{n}_I, \tag{3}$$

where the subscripts I and N denote the isotropic and nematic phases, respectively, and $n_I = N/V$ is the number density of the isotropic phase. Keeping terms to second order Eq. (1) then yields

$$\beta\Delta\Omega = \int d(1) \left\{ \rho_N(1)\ln\left(\frac{\rho_N(1)}{\bar{n}_I}\right) - [\rho_N(1) - \bar{n}_I] \right\}$$

$$- \frac{1}{2}\int d(1)d(2)\, c_I^{(2)}(12;\bar{n}_I)$$

$$\times [\rho_N(1) - \bar{n}_I][\rho_N(2) - \bar{n}_I]. \tag{4}$$

In order to find coexisting isotropic and nematic phases Eq. (4) is minimized with respect to $\rho_N(1)$. Coexistence occurs when the condition[10]

$$\beta\Delta\Omega = 0 \tag{5}$$

is satisfied.

In the nematic phase the singlet distribution function can be expanded in the form

$$\rho_N(1) = \rho_N(\omega) = \bar{n}_N \left[1 + \sum_{\substack{m > 2 \\ \text{even}}} a_m\, P_m(\cos\theta) \right], \tag{6}$$

where $\bar{n}_N = n_N/4\pi$, θ describes the orientation of the molecular symmetry axis with respect to the director, and the $P_m(\cos\theta)$ are the usual Legendre polynomials. The coefficients a_m are given by

$$a_m = (2m + 1)\overline{P}_m, \tag{7}$$

where

$$\overline{P}_m = \frac{1}{n_N}\int \rho_N(\omega)P_m(\omega)d\omega \tag{8}$$

defines the usual order parameters. It is convenient to rewrite Eq. (6) in the form

$$\rho_N(\omega) = \bar{n}_I \left[\frac{n_N - n_I}{n_I} + 1 + \frac{n_N}{n_I}\sum_{m > 2} a_m\, P_m(\cos\theta) \right]$$

$$= \bar{n}_I \left[1 + \sum_{m > 0} b_m\, P_m(\cos\theta) \right]$$

$$= \bar{n}_I\, F(\cos\theta), \tag{9}$$

where

$$b_0 = \frac{n_N - n_I}{n_I} \tag{10}$$

is the fractional change in density associated with the isotropic–nematic transition, and

$$b_m = \left(\frac{n_N}{n_I}\right) a_m \quad \text{if } m \geqslant 2. \tag{11}$$

We now assume axially symmetric particles and expand the direct correlation function for the isotropic phase in the form[1–3,26]

$$c_I^{(2)}(\omega_1,\omega_2,\mathbf{r}) = \sum_{mnl} c^{mnl}(r)\Phi^{mnl}(\omega_1,\omega_2,\hat{\mathbf{r}}), \tag{12}$$

where $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$, $\hat{\mathbf{r}} = \mathbf{r}/|\mathbf{r}|$, and the $\Phi^{mnl}(12)$ are rotational invariants as defined by Eqs. (5) and (36) of Ref. 26. We note that expansion (12) has been frequently employed in our earlier work.[1–3,26] Using Eqs. (9), (12), and the orthogonality properties of the $\Phi^{mnl}(12)$, Eq. (4) can be reduced to the expression

$$\frac{\beta\Delta\Omega}{V} = \frac{n_I}{2}\int_{-1}^{+1} dx\, F(x)\ln F(x)$$

$$- n_I b_0 - \frac{n_I^2}{2}\sum_{m>0}\frac{\tilde{c}^{mm0}(0)}{(2m+1)^2}b_m^2, \tag{13}$$

where $x = \cos\theta$, $F(x)$ is as defined in Eq. (9), and

$$\tilde{c}^{mm0}(0) = 4\pi\int_0^\infty r^2 c^{mm0}(r)dr \tag{14}$$

is the Fourier transform of $c^{mm0}(r)$ evaluated at $k = 0$. Equation (13) can be minimized with respect to the coefficients b_m using standard variational methods. We note that the minimization must be carried out subject to the physical constraint that $F(x)$ be positive for all x.

III. RESULTS AND DISCUSSION

Fluids of hard ellipsoids and spherocylinders can be conveniently characterized by specifying the length-to-breadth ratio a/b, and the reduced density $n_I^* = n_I\, b^3$. In our earlier work[2,3] HNC and PY results were obtained for a wide range of a/b values and densities. The present density functional calculations for hard particles were carried out using both HNC and PY values for the $\tilde{c}^{mm0}(0)$, and terms to order $m = 6$ were included in Eq. (13). It was found that the existence or nonexistence of an isotropic–nematic transition strongly depends upon the approximation used for the direct correlation function in the isotropic phase. Indeed, for densities where we were able to obtain numerical solutions of the PY equations, the PY values did not give a transition for any of the systems considered in the present calculations. The HNC results, on the other hand, readily lead to isotropic–nematic transitions provided that the particles are sufficiently anisotropic.

The density functional calculations were in fact unambiguous. In the cases where no phase transition was found minimization of Eq. (13) yielded only the trivial isotropic solution $b_m = 0$ for all values of n_I^* for which HNC and/or PY results could be obtained numerically. The behavior of Eq. (13) for the fluids where transitions are observed is quite remarkable and is illustrated in Figs. 1(a) and 1(b). For these systems as well minimization of Eq. (13) gives the isotropic result $b_m = 0$ over most of the density range considered. However, very close to the transition all the b_m coefficients "jump" to finite positive values in a discontinuous manner. The density is then increased slightly until the coexistence condition $\beta\Delta\Omega/V = 0$ is met, precisely determining the location of the isotropic–nematic transition. We note
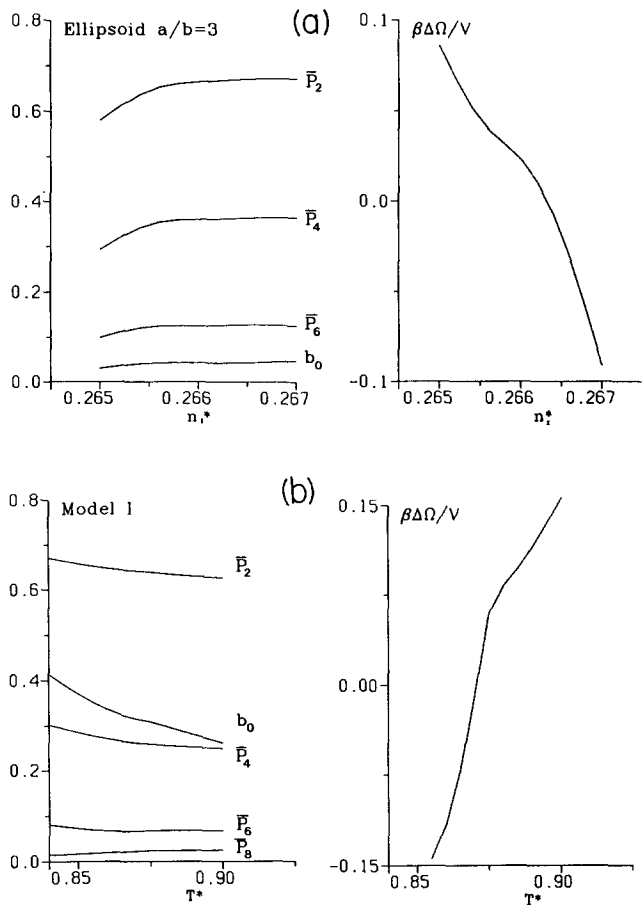
FIG. 1. The values of $\beta \Delta\Omega / V$, b_0, and the order parameters given by minimization of Eq. (13) in the vicinity of the phase transition for (a) ellipsoids and (b) model I. The discontinuous behavior is evident in the plots.

Based upon this analysis the following conclusions were reached. For the hard prolate ellipsoids[2] and spherocylinders[3] considered the PY theory did not give the long-range orientational correlations necessary to destabilize the isotropic phase. On the other hand, the HNC theory did predict a nematic phase for both models if $a/b \geqslant 3$. We have also carried out a single calculation for oblate ellipsoids with $a/b = 1/3$ and the orientational stability criteria yield results which are very similar to the prolate case. Qualitatively, the present density functional calculations are totally consistent with the stability analysis.

The fact that the PY and HNC approximations give different results is not surprising if one examines the density dependence of the $\tilde{c}^{mm0}(0)$. This is illustrated in Fig. 2 where we have plotted HNC and PY results for $n_I \tilde{c}^{mm0}(0)$ ($m = 2,4,6$) for ellipsoids with $a/b = 3$. [When considering this figure it is interesting to recall that at the level of Onsager theory the $\tilde{c}^{mm0}(0)$ are positive density independent constants,[17(a)] and hence the $n_I \tilde{c}^{mm0}(0)$ will be simple linearly increasing functions of n_I.] It can be seen from Fig. 2 that both the HNC and PY values increase with n_I^* for all three projections. However, the HNC results deviate more rapidly from the low density linear behavior and increase very steeply in the vicinity of the phase transition [note that Eq. (16) is satisfied when $n_I \tilde{c}^{220}(0) = 5$]. These steep increases can in fact be related to the growth of long-range orientational correlations.[1-3] It is possible that the PY theory would eventually give a transition if numerical solutions could be obtained at higher values of n_I^*. It is likely, however, that such a transition would lie above the freezing density. Finally, we note that the $n_I \tilde{c}^{mm0}(0)$ curves for other fluids of ellipsoids and spherocylinders with $a/b \geqslant 3$ (or $a/b = 1/3$ in

that the behavior is very similar for the simple temperature dependent models discussed below.

It is useful at this point to very briefly recall our earlier work[1-3] which attempted to investigate the phase behavior of the present models by determining the absolute stability limit of the isotropic phase. The general condition for stability of the isotropic phase can be derived[8] and expressed in the form[1-3]

$$\left[1 - \frac{n_I}{2m+1} \, \tilde{c}^{mm0}(0) \right] \geqslant 0. \tag{15}$$

Furthermore, it is not difficult to show[1-3] that it is the growth (i.e., with increasing density or decreasing temperature) of long-range orientational correlations which lead to the violation of this condition and the destabilization of the isotropic phase. In our actual calculations[1-3] the $m = 2$ case was used and the stability limit was taken to be the state point at which the reciprocal Kerr constant

$$\beta A K^{-1} = \left[1 - \frac{n_I}{5} \, \tilde{c}^{220}(0) \right] = 0, \tag{16}$$

where A is a molecular constant independent of state parameters. However, it can be seen from Figs. 2 and 3 below that the violation of Eq. (15) occurs essentially simultaneously for all values of m.
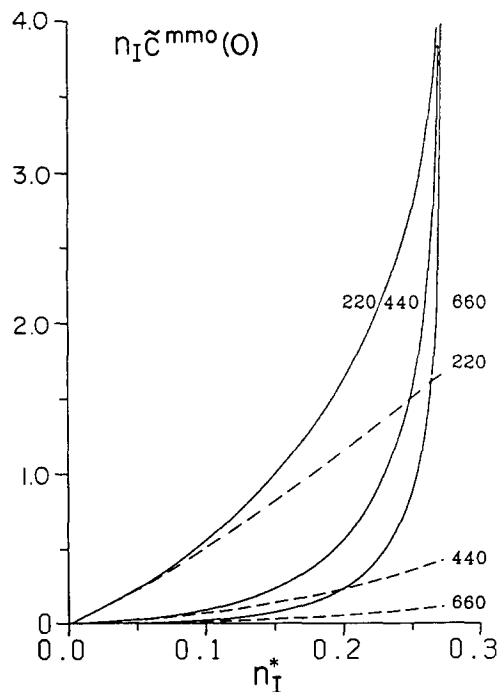

FIG. 2. The density dependence of $n_I \tilde{c}^{mm0}(0)$ for ellipsoids with $a/b = 3$. The solid and dashed curves are HNC and PY results, respectively.

TABLE I. Summary of results for hard ellipsoids and spherocylinders. The order parameters quoted are the values at the isotropic–nematic transition density.

a/b	n_I^* (isotropic–nematic)			$n_I\chi_T/\beta$	b_0	Order parameters		
	SL[a]	DFT[b]	MC[c]			$\bar{P}_2$	$\bar{P}_4$	$\bar{P}_6$
			(A) Ellipsoids					
3	0.276	0.2662	0.323	0.038	0.0437	0.657	0.358	0.127
1/3	0.090	0.0878	0.108	0.037	0.0372	0.638	0.350	0.131
5	0.122	0.1124	⋯	0.063	0.072	0.649	0.356	0.129
			(B) Spherocylinders					
3	0.238	0.231	⋯	0.023	0.041	0.635	0.356	0.130
6	0.079	0.073	0.089	0.044	0.043	0.625	0.333	0.120

[a] The stability limit as determined by Eq. (16).
[b] The results given by density functional theory with HNC direct correlation functions.
[c] Monte Carlo results from Refs. 5 and 27.

the oblate case) are very similar to those shown in Fig. 2, and that the remarks made above apply equally to those systems.

For the systems which exhibit isotropic–nematic phase changes, the thermodynamic transition densities and stability limits together with the values (calculated at the transition density) of other properties of interest are given in Table I. The quantity $n_I\chi_T/\beta = [1 - n_I\tilde{c}^{000}(0)]^{-1}$ is the reduced isothermal compressibility of the isotropic fluid. We emphasize again that all results given in Table I were obtained using the HNC direct correlation functions since no phase changes were found with PY values. From Table I it can be seen that the transition densities obtained in the density functional calculations lie quite close to the stability limits given by Eq. (16). The fractional density changes b_0 found are rather small which is consistent with the fact that these hard models are not very compressible at the transition densities (note the values of $n_I\chi_T/\beta$ in Table II). Also we observe that for all three fluids the values of the order parameters at the transition density are similar.

For prolate ellipsoids with $a/b = 3$ it is possible to compare the present theory with Monte Carlo simulations,[5] and with previous density functional calculations[19-21] in which different approximations for $c_I^{(2)}(12)$ were used. The Monte Carlo transition density is given in Table II and we note that the present value is about 20% lower than the Monte Carlo

result. The fractional density change reported in Ref. 5 (i.e., 0.02) is smaller than the value we obtain. It is not clear whether the discrepancies between the present calculations and the Monte Carlo results are due to the HNC theory, or to the neglect of the three-body and higher order terms in Eq. (1). Singh and Singh[19] report the value 0.195 for the transition density of this system obtained using a direct correlation function constructed from the PY result for hard spheres. The values of b_0, $\bar{P}_2$, and $\bar{P}_4$ given in Ref. 19 are 0.040, 0.547, and 0.197, respectively. We remark that other authors[16(d),20] have pointed out errors in the work of Singh and Singh which seriously alter the results obtained for the isotropic fluid to plastic crystal transition. However, these errors pertain to the treatment of the solid state and we would not expect them to have influenced the results reported in Ref. 19 for the isotropic–nematic transitions (cf. Ref. 20). Recently, additional density functional calculations using other approximations for the direct correlation function have been reported by Marko[20] and by Baus et al.[21] The transition density and fractional density change obtained by Marko[20] are 0.313 and 0.003, respectively. The corresponding values reported by Baus et al.[21] are 0.300 and 0.025.

Monte Carlo results have also been reported[5] for oblate ellipsoids with $a/b = 1/3$ and it can be seen from Table I that (as for prolate particles) the present transition density is lower than the Monte Carlo value. It was observed in Ref. 5 that if a reduced density which takes the difference in volume of prolate and oblate ellipsoids into account (e.g., multiply the oblate densities in Table I by 3) is used then the prolate ($a/b = 3$) and oblate ($a/b = 1/3$) transitions occur at essentially the same value. We note that this is also true of the density functional results.

For spherocylinders with $a/b = 6$ the Monte Carlo isotropic–nematic transition density recently obtained by Frenkel[27] is also included in Table I. Again we see that second order density functional theory combined with the HNC direct correlation functions gives a transition density which is about 14% lower than the true value. It is also worth noting that the transition densities given by Onsager–Lasher[23,24] theory [cf. Eq. (10) of Ref. 24] for spherocylinders with $a/b = 3$ and 6 are 1.051 and 0.168, respectively. These values are obviously much higher than the present results.

In addition to the fluids of hard particles discussed above, density functional calculations were carried out for "soft" models defined[1,4] by pair potentials of the type

TABLE II. Summary of results for the Luckhurst–Romano models with $n_I^* = n_I\sigma^3 = 0.79$ for model I and $n_I^* = 0.7496$ for model II. The order parameters given are the values at the isotropic–nematic transition temperature.

Models	T^* (isotropic–nematic)			$n_I\chi_T/\beta$	b_0	Order parameters			
	SL[a]	DFT[b]	MC[c]			$\bar{P}_2$	$\bar{P}_4$	$\bar{P}_6$	$\bar{P}_8$
I	0.790	0.875	0.890	0.265	0.312	0.638	0.257	0.067	0.023
II	1.125	1.280	1.130	0.275	0.346	0.647	0.266	0.067	0.023

[a] As in Table I.
[b] As in Table I.
[c] Monte Carlo results from Ref. 4.

$$u(12) = u_0(r) + u_2(r)P_2(\cos \gamma)$$

$$= u_0(r) + u_2(r)\Phi^{220}(12), \tag{17}$$

where γ is the angle between the symmetry axis. In the earlier Monte Carlo simulations of Luckhurst and Romano,[4] and in our subsequent HNC calculations[1] $u_0(r)$ was taken to be the usual Lennard-Jones interaction and two different forms were considered for $u_2(r)$. These were

$$u_2(r) = -4\lambda\epsilon\left(\frac{\sigma}{r}\right)^6 \quad \text{(model I)} \tag{18}$$

and

$$u_2(r) = -4\lambda\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} + \left(\frac{\sigma}{r}\right)^6\right] \quad \text{(model II)}, \tag{19}$$

where ϵ and σ are the Lennard-Jones parameters, and λ is a variable determining the strength of the anisotropic interaction. In Ref. 1 the models defined by Eqs. (18) and (19) are referred to as models I and II, respectively, and we shall continue this designation here.

For models I and II it is convenient to introduce the reduced temperature $T^* = kT/\epsilon$ and the reduced density $n_I^* = n_I\sigma^3$. These reduced parameters together with λ are sufficient to determine the state of the system. As in our previous work[1] the value $\lambda = 0.15$ is used in the present calculations. Also as in Ref. 1 the densities considered are $n_I^* = 0.79$ for model I and 0.7496 for model II since these are the densities for which Luckhurst and Romano[4] have reported isotropic–nematic transition temperatures.

For these models the density functional theory was applied using reference HNC (RHNC) values[1] for the $\tilde{c}^{mm0}(0)$. The temperature dependence of $\tilde{c}^{mm0}(0)$ at fixed density is shown in Fig. 3 for model I. Terms up to $m = 8$ were included in the calculations. Equation (13) was minimized at fixed n_I^* for different values of T^* and the results obtained for model I are illustrated in Fig. 1. At high temperature minimization of Eq. (13) gives only the isotropic solution $b_m = 0$. However, close to the transition temperature the order parameters jump to finite positive values. The condition $\beta\Delta\Omega/V = 0$ can then be easily satisfied by a small decrease in T^*. Model II gives results analogous to those shown in Fig. 1(b). Obviously, this behavior is qualitatively similar to the systems of hard particles described above except that we are now considering temperature instead of density dependence. Also we remark that the temperature dependence of the $\tilde{c}^{mm0}(0)$ shown in Fig. 3 is much like the density dependences found for systems of hard particles which show isotropic–nematic transitions. Specifically, the $\tilde{c}^{mm0}(0)$ are positive and increase at an increasing rate as T^* is decreased. This parallels the increasing density behavior observed for fluids of hard ellipsoids and spherocylinders (cf. Fig. 2).

Numerical values for the properties of interest for models I and II are given in Table II. For both models the thermodynamic transitions given by the density functional calculations occur at temperatures which are considerably higher than the absolute stability limits given by the HNC theory. The transition temperatures obtained are in reasonably good agreement with the Monte Carlo values.[4] Finally we note that the fractional changes in density found for both models I and II are about an order of magnitude larger than those obtained for hard ellipsoids and spherocylinders (cf. Table I). This is not surprising in view of the fact that for these soft models the isothermal compressibilities are also nearly an order of magnitude larger than the compressibilities for the fluids of hard particles.
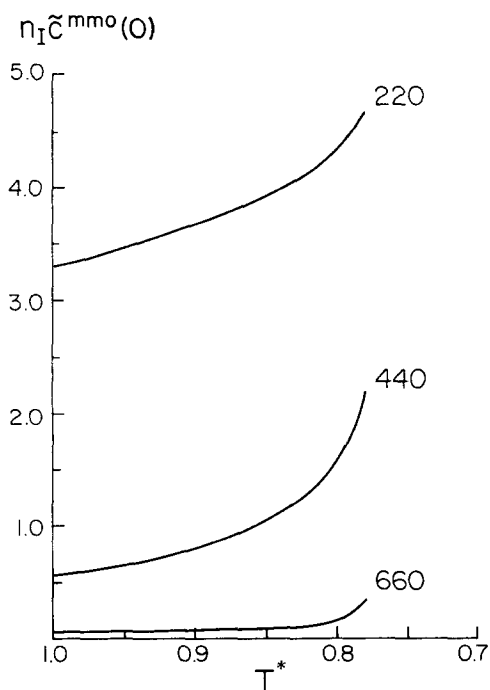
IV. SUMMARY AND CONCLUSIONS

The density functional method has been applied in order to obtain the isotropic–nematic transition densities for fluids of hard ellipsoids and spherocylinders. The required direct pair correlation functions for the isotropic phase were determined by means of numerical solutions of the HNC and PY integral equation theories. It is shown that for fluids of hard nonspherical particles even the qualitative results given by density functional theory are strongly dependent upon the approximation used for the direct correlation function. A striking example of this is that PY results do not give an isotropic–nematic transition for any of the fluids considered. The HNC approximation does lead to phase transitions for hard prolate ellipsoids and spherocylinders if $a/b \geqslant 3$. This is also true for hard oblate ellipsoids with $a/b = 1/3$. We emphasize that in this regard the present density functional calculations are consistent with the orientational stability analysis described in Refs. 2 and 3.

In addition to the hard models, we have also considered two soft potentials which were originally the subject of a Monte Carlo study by Luckhurst and Romano.[4] For these systems second order density functional theory coupled with the HNC approximation gives transition temperatures con-

$n_I \tilde{c}^{mmo}(0)$

FIG. 3. The temperature dependence of $n_I\tilde{c}^{mm0}(0)$ for model I. The curves are HNC results.

sistent with the stability analysis and in relatively good agreement with the Monte Carlo values.

ACKNOWLEDGMENTS

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