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Equation of state for nematic liquid crystals

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Taking the point of view that a nematic is an ordinary simple liquid, whose anisotropic properties can be treated in terms of perturbation theory, an equation of state for nematic liquid crystals is derived, based on both anisotropic repulsion between (slightly) nonspherical molecular hard cores and anisotropic attractive forces. The spatial order in the liquid is, in a first approximation, thought to be determined by a hard-sphere repulsion. The orientational ordering is considered to result from the effect of the eccentricity of the molecular hard core and the superimposed attractive interaction, both of which are taken into account by means of perturbation theory. A molecular field approximation and, in order to account for short-range orientational correlations, a two-site cluster approximation, are both applied to the orientational molecular coordinates. Expressions for the equilibrium thermodynamics quantities are derived. Extensive numerical model calculations are reported and compared with experimental data for *p*-azoxyanisole (PAA) and the results of Cotter. As a special case an equation of state for the Maier-Saupe model (spherical molecules) is presented. If short-range orientational order is taken into account, quantitative agreement with the experimental data for PAA can be obtained.

I. INTRODUCTION

The nematic phase is characterized by long-range orientational order, i.e., the long molecular axes tend to align along a preferred direction. The origin of nematic order is still a subject of controversy. Two mechanisms that can bring about the alignment have been proposed. One school of thought[1,2] ascribes the nematic structure primarily to the anisotropy of the intermolecular attractive forces, particularly the Van der Waals forces between anisotropically polarizable molecules. The intermolecular repulsions are assumed to be isotropic, at least to a first approximation, and serve to provide a positive pressure. These theories were worked out at constant volume, rather than at constant pressure. In other theories[3-5] the nematic order results primarily from the short-range highly anisotropic repulsive forces between rodlike molecules. The high density of the liquid is established by the intermolecular attractions, which are assumed to be isotropic. Neither of these extreme approaches can account for the quantitative behavior of real nematogens. The hard-rod models are athermal and give values for the order parameter and the density change at the nematic-isotropic transition that are too high. The Maier-Saupe model fails to predict the correct density dependence of the order parameter, as shown by the experiments of McColl and Shih.[6] These experiments revealed large differences between the temperature dependence of the order parameter at constant density and at constant pressure. They also demonstrated the importance of both attractive and repulsive intermolecular forces in establishing nematic order.

A number of authors[7-9] have tried to reconcile the two extreme points of view by incorporating both anisotropic intermolecular repulsions and attractions in their models. From the statistical-mechanical point of view Cotter's approach[9] seems to be the most promising. In her model the short-range intermolecular repulsions are represented by repulsions between hard spherocylinders, having the dimensions of a molecule. The anisotropic intermolecular attractions are treated self-consistently in the mean-field approximation. Using scaled-particle theory an equation of state is derived, which permits a description of the various influences of density, pressure, and temperature on the nematic-isotropic transition. Although her model calculations display many qualitative features of the common nematogen *p*-azoxyanisole (PAA), quantitative comparison with the experimental data suggests that her treatment exaggerates the effect of the elongated molecular hard cores rather strongly. From the physical point of view this is not surprising at all because mutual excluded volumes of spherocylinders are strongly nonadditive. This means that an equation of state which is derived on the basis of the excluded volume of only a few spherocylinders is bound to exaggerate the influence of the excluded volume, if we substitute the real length-to-breadth ratio; e.g., the density is underestimated but the relative density change is overestimated. This situation gets worse with increasing length-to-breadth ratio. Experimentally the relative density change at the nematic-isotropic transition is very small, while the density of the liquid is that of a normal liquid. This suggests that a nematic can be looked upon as a normal liquid, where its anisotropic properties can be treated in terms of perturbation theory.

In view of the foregoing it seems logical to derive an equation of state for nematics, starting from a system of molecules with a hard core that deviates only slightly from a sphere. The liquid aspects of nematics can then be treated in terms of the theory of simple liquids, which is quite well developed. The purpose of this paper is to present an equation of state based on the following point of view. The spatial ordering in the liquid is considered to be determined by the hard-core repulsion, which is, to a first approximation, replaced by a hard-sphere repulsion. As is well known, hard spheres form a good reference system for simple liquids.[10] The orientational ordering is thought to result from the effect of the eccentricity of the hard core and the superimposed anisotropic attractive interaction, both of which are taken into account by means of perturbation theory. The orientational molecular coordinates are treated in two ways. First a molecular-field approximation is applied. Secondly, the effect of short-range orientational order is investigated, using a two-particle orientational distribution function, as provided by a two-site cluster variation method.[11] This short-range order is also essential for the calculation of pretransitional phenomena in the isotropic phase.[11] As a special case an equation of state is presented, involving the assumptions of Maier and Saupe, i.e., the neglect of all steric effects. Until now the Maier-Saupe model has been worked out at constant volume, rather than at constant pressure. The derived equation of state enables one to consider and compare both approaches.

This paper is organized in the following way. The model is described in Sec. II. Expressions for the relevant equilibrium thermodynamic properties, such as the free energy and the equation of state are given. In Sec. III extensive numerical calculations are reported for systems of spherical and slightly nonspherical molecules. The relative influence of anisotropic attraction and steric hindering on the nematic-isotropic transition is investigated. In the model calculations two particular choices of the attractive interaction are considered. The results are compared with the experimental data for PAA and with Cotter's results.[9] The effect of short-range orientational order on the equation of state is also investigated. Finally, a summary with conclusions is given in Sec. IV.

II. MODEL

The model system which we will consider consists of N axially symmetric, nonspherical molecules, which are contained in a volume V. Apart from the infinite hard-core repulsion the molecules interact with each other through anisotropic attractive forces. If the molecules are assumed to have an anisotropic polarizability, they interact through the Van der Waals dispersion forces. The attractive interaction energy has the following form:

$$u_{\text{att}}(r_{ij},\Omega_i,\Omega_j)=u_0(r_{ij})+u_2(r_{ij})P_2(\cos\theta_{ij})\,, \tag{2.1}$$

where Ω_i denotes the orientation of the long axis of molecule i, θ_{ij} the angle between the orientations of two molecules, and r_{ij} the intermolecular distance. P_2 is the second Legendre polynomial.

A. Steric hindering

First we will derive an expression for the configurational entropy due to the eccentricity of the molecular hard core. Consider a system of N hard particles with fixed orientations, such that N_k molecules have an orientation between Ω_k and $\Omega_k+d\Omega_k$, $k=1,2,\ldots,p$. The partition function for this system without attractive forces reads

$$Q_N(N_1,\ldots,N_p)=N!\left(\prod_{k=1}^{p}N_k!\right)^{-1}\prod_{k=1}^{p}\left(\frac{d\Omega_k}{4\pi}\right)^{N_k}Z_N\,, \tag{2.2}$$

with

$$Z_N=\frac{1}{N!}\int\cdots\int d\vec{r}\cdots d\vec{r}_N\prod_{i>j}\xi[r_{ij}-D(\Omega_i,\Omega_j)]\,, \tag{2.2a}$$

where $D(\Omega_i,\Omega_j)$ is the closest distance of approach of two molecules with orientations Ω_i and Ω_j and ξ is defined as

$$\begin{aligned}\xi(x)&=0\,,\quad x<0\,,\\ &=1\,,\quad x>0\,.\end{aligned}$$

Strictly speaking, the closest distance of approach D also depends on the direction of the intermolecular distance vector $\vec{r}_{ij}$. Including this dependence would confront us with the serious problem of short-range correlations between positional and orientational molecular coordinates, a prohibitively difficult task. $D(\Omega_i,\Omega_j)$ should therefore be interpreted as a mean closest distance of approach, averaged over all directions of the distance vector $\vec{r}_{ij}$, at fixed Ω_i and Ω_j. For small eccentricity this approximation is allowed. The total configurational integral Q_N is obtained by summing $Q_N(N_1, \ldots, N_p)$ over all possible distributions $\{N_1, N_2, \ldots, N_p\}$. Describing the orientational distribution by a continuous function $f(\Omega)$ such that

$$N_k = Nf(\Omega_k)d\Omega_k \, ,$$

we find, in the maximum-term approximation (see Ref. 5),

$$\ln Q_N = -N\int d\Omega f(\Omega) \ln[4\pi f(\Omega)] + \ln Z_N \, . \qquad (2.3)$$

The first term of this expression refers to the mixing entropy and the second term to the packing entropy. The mixing entropy term arises from the fact that molecules of different orientations are treated as molecules of different kinds.

Following Bellemans[12] we will express the free energy of the system in terms of the properties of an assembly of hard spheres, which are fairly well known. We write

$$D(\Omega_i\, , \Omega_i) = D_0[1 - \alpha(\Omega_i, \Omega_j)] \, , \qquad (2.4)$$

where α is defined such that the average over all orientations

$$\langle \alpha(\Omega, \Omega') \rangle = \frac{1}{N^2} \sum_{i,j} N_i N_j \, \alpha(\Omega_i\, , \Omega_j)$$

$$= \int\int d\Omega \, d\Omega' f(\Omega) f(\Omega') \alpha(\Omega, \Omega')$$

vanishes in the isotropic phase. D_0 is called the diameter of the equivalent hard sphere of the reference system. Expanding $\xi[r_{ij} - D(\Omega_i, \Omega_j)]$ in terms of α we have

$$\xi[r_{ij} - D(\Omega_i, \Omega_j)] \approx \xi(r_{ij} - D_0) + D_0 \alpha(\Omega_i\, , \Omega_j) \times \delta(r_{ij} - D_0) \, , \qquad (2.5)$$

where $\delta(r)$ denotes Dirac's δ function. Expanding Z_N and keeping only terms linear in $\langle \alpha(\Omega, \Omega') \rangle$, we obtain

$$\ln Q_N \approx \ln Q_N^0 + D_0 \sum_{i>j} \langle \alpha(\Omega_i, \Omega_j) \rangle \frac{1}{Q_N^0 N!} \int d\vec{r}_1 \cdots d\vec{r}_N \, \delta(r_{ij} - D_0) \prod_{\substack{k>l \\ kl \neq ij}} \xi(r_{kl} - D_0) - N\int d\Omega f(\Omega) \ln[4\pi f(\Omega)] \, , \qquad (2.6)$$

with Q_N^0 denoting the configurational integral of the reference hard-sphere system:

$$Q_N^0 = \frac{1}{N!} \int d\vec{r}_1 \cdots d\vec{r}_N \prod_{i>j} \xi(r_{ij} - D_0) \, . \qquad (2.7)$$

When the radial-distribution function g_{HS} of the reference hard-sphere system is defined in the usual way, (2.6) can be rewritten

$$\ln Q_N \approx \ln Q_N^0 + \tfrac{1}{2} N\rho D_0 \langle \alpha(\Omega, \Omega') \rangle \times \int d\vec{r}_{12} \, \delta(r_{12} - D_0) \, g_{\text{HS}}(r_{12}) \xi^{-1}(r_{12} - D_0) - N\int d\Omega f(\Omega) \ln[4\pi f(\Omega)] \, , \qquad (2.8)$$

where ρ is the number density. Realizing that by definition

$$\xi(r_{ij} - D_0) = \exp[-\beta u_{\text{HS}}(r_{ij})] \, , \qquad (2.9)$$

where u_{HS} is the infinite repulsive interaction between hard spheres, and defining

$$\tau(r) = g_{\text{HS}}(r) \exp[\beta u_{\text{HS}}(r)] \, , \qquad (2.10)$$

the integral in (2.8) reduces to

$$\int d\vec{r} \, \delta(r - D_0) \tau(r) = 4\pi D_0^2 \tau(D_0) \, . \qquad (2.11)$$

Since the hard-sphere model has not been solved rigorously, we have to resort to some approximation. A successful approximation is due to Percus and Yevick[13] which leads to an integral equation for $\tau(r)$ that can be solved explicitly[14]:

$$\tau(r) = \lambda_1 + 6\eta\lambda_2(r/D_0) + \tfrac{1}{2}\eta\lambda_1(r/D_0)^3 \quad (r < D_0) \, , \qquad (2.12)$$

with $\eta = \frac{1}{6}\pi D_0^3 \rho \equiv \rho v_0$, the packing fraction, where v_0 is the volume of a hard sphere. The constants λ_1 and λ_2 are given by

$$\lambda_1 = (1 + 2\eta)^2/(1 - \eta)^4 \, , \quad \lambda_2 = -(1 + \tfrac{1}{2}\eta)^2/(1 - \eta)^4 \, . \qquad (2.13)$$

Applying the expressions (2.12) and (2.13) the contribution to the entropy due to the eccentricity of the molecular hard core reads, apart from the Boltzmann factor k,

$$\delta \ln Q_N \equiv \ln Q_N - \ln Q_N^0 = 12N \frac{\eta(1 + \frac{1}{2}\eta)}{(1 - \eta)^2} \langle \alpha(\Omega, \Omega') \rangle - N\int d\Omega f(\Omega) \ln[4\pi f(\Omega)] \, . \qquad (2.14)$$

Next, $\alpha(\Omega_i, \Omega_j)$ is expanded in Legendre polynomials. Neglecting possible differences between heads and tails of the molecules and truncating the series after the first term, we have

$$\alpha(\Omega_i,\Omega_j)=\alpha_2 P_2(\cos\theta_{ij})\,, \tag{2.15}$$

where θ_{ij} denotes the angle between the long molecular axes of the molecules i and j. The Helmholtz free energy F_{HS} and the corresponding equation of state for the reference hard-sphere system are known in closed form and read (see, e.g., Refs. 10 and 15)

$$\frac{\beta F_{\text{HS}}}{N}=\log\frac{\rho}{(1-\eta)^{\lambda+1}}-\frac{2\lambda}{1-\eta}+\frac{\frac{1}{2}(\lambda+3)}{(1-\eta)^2}+\frac{3}{2}\lambda-\frac{5}{2}\,, \tag{2.16}$$

$$\beta p_{\text{HS}}/\rho=(1+\eta+\eta^2+\lambda\eta^3)/(1-\eta)^3\,, \tag{2.17}$$

with $\beta=1/kT$ and $\lambda=0$ or -3; $\lambda=0$ corresponds to the compressibility equation of state, derived from fluctuations in the grand canonical ensemble; $\lambda=-3$ corresponds to the pressure or virial equation of state, which can be derived from the virial theorem. The discrepancy between the results of the two equations arises from the approximate form of the radial distribution function $g(r)$, and is often considered as a measure of the degree of failure of a theory.

It easily follows that the configurational free energy F_{HC} that originates from repulsive interactions can be written

$$\beta F_{\text{HC}}=\beta F_{\text{HS}}-12N\frac{\eta(1+\frac{1}{2}\eta)}{(1-\eta)^2}\alpha_2\langle P_2(\cos\theta_{12})\rangle+N\int d\Omega f(\Omega)\ln[4\pi f(\Omega)]\,. \tag{2.18}$$

B. Attractive forces

A system of hard particles cannot satisfactorily describe all thermodynamic properties of liquid crystals. For instance, it is athermal and it does not yield a vapor-pressure line. Attractive forces must be added in order to establish the high liquid densities, a liquid-gas transition and so on. A simple and useful approach[10] in order to account for attractive interactions is to consider the hard-particle system as a reference system and to treat the attraction as a perturbation. The intermolecular potential is written as the sum of the hard-core potential and an attractive perturbation:

$$U_N(\vec{r}_1\Omega_1,\ldots,\vec{r}_N\Omega_N)=U_{\text{HC}}(\vec{r}_1\Omega_1,\ldots,\vec{r}_N\Omega_N)+U_{\text{att}}(\vec{r}_1\Omega_1,\ldots,\vec{r}_N\Omega_N)\,. \tag{2.19}$$

The partition function Q_N satisfies

$$\log Q_N=\log\operatorname{Tr}\exp(-\beta U_N)=\log Q_N^{\text{HC}}+\log\langle\exp(-\beta U_{\text{att}})\rangle_{\text{HC}}\,, \tag{2.20}$$

where Q_N and Q_N^{HC} are configurational integrals for a system of molecules with fixed orientations [consistent with $f(\Omega)$] and the average $\langle\ \rangle_{\text{HC}}$ is also evaluated for such a system.

Generally it is very hard to calculate this thermal average, and we have to resort to some approximation, in our case a high-temperature expansion[16]:

$$\log\langle\exp(-\beta U_{\text{att}})\rangle_{\text{HC}}=-\beta\langle U_{\text{att}}\rangle_{\text{HC}}+\cdots\,, \tag{2.21}$$

with

$$\langle U_{\text{att}}\rangle_{\text{HC}}=\sum_{i>j}\frac{1}{V^2}\int d\vec{r}_i\,d\Omega_i\,d\vec{r}_j\,d\Omega_j\times u_{\text{att}}(\vec{r}_{ij}\Omega_i\Omega_j)f(\Omega_i)f(\Omega_j)\times g_{\text{HC}}(\vec{r}_{ij},\Omega_i\Omega_j)\,, \tag{2.22}$$

where g_{HC} is the hard-particle pair correlation function and $f(\Omega)$ a one-particle distribution function for the orientations. Subsequent terms in the high-temperature expansion involve higher-order (than the second) distribution functions and will be neglected.

In the foregoing we considered molecular hard cores that deviate only slightly from a sphere. This means that, in a first-order approximation, we may evaluate the attractive perturbation energy with the hard-sphere distribution function g_{HS}. The average over the orientational coordinates then only involves the one-particle distribution function $f(\Omega)$, which implies that we have effectively introduced the molecular-field approximation for the treatment of the orientational coordinates.

If we assume that the attractive interaction has the form (2.1), the total internal energy reads

$$\langle U_{\text{att}}\rangle=\tfrac{1}{2}N\rho\int d\vec{r}\,g_{\text{HS}}(r)[u_0(r)+u_2(r)\times\langle P_2(\cos\theta_{12})\rangle]\,. \tag{2.23}$$

The integral cannot be performed easily, because a simple expression for the hard-sphere radial distribution function g_{HS} is not available. The Laplace transform of $rg_{\text{HS}}(r)$, however, is given explicitly by Wertheim[14]:

$$G_{\text{HS}}(\eta,t)=\frac{1}{D_0^2}\int_0^\infty dr\,r g_{\text{HS}}(r)e^{-tr/D_0}=\frac{te^{-t}L(t)}{12\eta[L(t)e^{-t}+S(t)]}\,, \tag{2.24}$$

with

$$L(t)=12\eta[(1+2\eta)+(1+\tfrac{1}{2}\eta)t]\,,$$
$$S(t)=(1-\eta)^2t^3+6\eta(1-\eta)t^2+18\eta^2t-12\eta(1+2\eta)\,, \tag{2.25}$$

and D_0 denoting the diameter of the hard sphere. If we assume that $ru_i(r)$ $(i=0,2)$ possesses a continuous inverse Laplace transform[17]

$$ru_i(r)=D_0\int_0^\infty dt\, e^{-tr/D_0}V_i(t)\quad (i=0,2)\,, \tag{2.26}$$

(2.23) can be written

$$\langle U_{\text{att}}\rangle = 12\eta N\int_0^\infty dt\, G_{\text{HS}}(\eta,t)[V_0(t)+V_2(t) \times\langle P_2(\cos\theta_{12})\rangle]\,, \tag{2.27}$$

with $\eta=\frac{1}{6}\pi D_0^3\rho$.

In the model calculations two particular choices of the attractive potential will be considered. First, we shall consider

$$u_{\text{att}}(r_{ij},\Omega_i\Omega_j)=-\frac{1}{r_{ij}^6}[J_0+J_2P_2(\cos\theta_{ij})]\,, \tag{2.28}$$

corresponding to the Van der Waals dispersion forces. We then have

$$V_i(t)=-J_it^4/D_0^6 4!\quad (i=0,2)\,, \tag{2.29}$$

and the internal energy reads

$$\langle U_{\text{att}}\rangle = -\tfrac{1}{2}N\eta\,\frac{J_0+J_2\langle P_2(\cos\theta_{12})\rangle}{D_0^6} \times\int_0^\infty dt\, t^4G_{\text{HS}}(\eta,t)\,. \tag{2.30}$$

The integral must be evaluated numerically for each η. It seems attractive, therefore, to use a second somewhat simpler potential, e.g.,

$$u_{\text{att}}(r_{ij},\Omega_i\Omega_j)=-(1/V)[V_0+V_2P_2(\cos\theta_{ij})]\,, \tag{2.31}$$

where the interaction constants V_0 and V_2 have been divided by the volume V in order to get an extensive expression for the total attractive interaction energy

$$\langle U_{\text{att}}\rangle = -\tfrac{1}{2}N\rho[V_0+V_2\langle P_2(\cos\theta_{12})\rangle]\,. \tag{2.32}$$

This simple potential leads to the same one-particle pseudopotential as was used recently by Cotter.[9]

C. Thermodynamic equilibrium

In this section we will give expressions for some equilibrium thermodynamic properties of the system of molecules that interact through both repulsive and attractive forces, as described distinctly in Secs. II A and II B, applying the molecular-field approximation to the orientational coordinates. Employing the relations (2.1), (2.18), and (2.20)–(2.23), we obtain for the total Helmholtz free energy F

$$\beta F=\beta F_{\text{HS}}+N\int d\Omega\, f(\Omega)\ln 4\pi f(\Omega) - 12N\,\frac{\eta(1+\frac{1}{2}\eta)}{(1-\eta)^2}\,\alpha_2S^2 + \tfrac{1}{2}N\beta\rho\int d\vec{r}\, g_{\text{HS}}(r)[u_0(r)+u_2(r)S^2]\,. \tag{2.33}$$

In this expression S is the long-range order parameter, defined by

$$S=\int d\Omega\, P_2(\cos\theta)f(\Omega)\,. \tag{2.34}$$

The one-particle orientational distribution function $f(\Omega)$ must still be determined. At a particular temperature T and pressure p the equilibrium distribution results from minimization of the Gibbs free energy $G=F+pV$ with respect to variations of $f(\Omega)$. From (2.33) the form of $f(\Omega)$ is readily derived,

$$f(\Omega)=\frac{1}{4\pi Z}\exp[B_2(\eta,T)SP_2(\cos\theta)]\,, \tag{2.35}$$

with

$$B_2(\eta,T)=\frac{24\eta(1+\frac{1}{2}\eta)}{(1-\eta)^2}\,\alpha_2-\beta\rho\int d\vec{r}\, u_2(r)g_{\text{HS}}(r) \tag{2.36}$$

with Z denoting a normalization constant, such that $\int f(\Omega)d\Omega=1$. The terms in $B_2(\eta,T)$ correspond to the two mechanisms that bring about the nematic order, viz., the steric hindering between nonspherical molecules and the anisotropic attraction between anisotropic polarizabilities. With the form (2.35) for $f(\Omega)$, (2.34) is an implicit equation for S.

From Eq. (2.33) we can evaluate all thermodynamic quantities, e.g., the equation of state is given by

$$\frac{\beta p}{\rho}=\frac{\beta p_{\text{HS}}}{\rho}+\tfrac{1}{2}\eta\,\frac{\partial}{\partial\eta}\left(\beta\rho\int dr\, u_0(r)g_{\text{HS}}(r)-B_2(\eta,T)\right), \tag{2.37}$$

with p_{HS} given by (2.17). At a particular temperature T and pressure p, (2.34) and (2.37) from two coupled equations in ρ (or η) and S, which must be solved simultaneously. The nematic-isotropic transition at constant pressure is located by equating the pressures and chemical potentials of the two phases:

$$\begin{aligned}\mu_{\text{nem}}(\eta_c,T_c,S_c)&=\mu_{\text{iso}}(\eta_{ic},T_c)\,,\\ p_{\text{nem}}(\eta_c,T_c,S_c)&=p_{\text{iso}}(\eta_{ic},T_c)\,,\end{aligned} \tag{2.38}$$

with S_c determined by (2.34). If the pressure is kept fixed, we have, in fact, four equations in the four unknowns η_c, η_{ic}, T_c, and S_c. Choosing

v_0 to be the estimated molecular volume of a particular nematogen, the only parameters that have to be specified are the eccentricity α_2 and the strengths of the isotropic and anisotropic attractive interaction (2.1). The isotropic interaction strength can be estimated from the latent heat of vaporization, because

$$\Delta H \simeq \Delta U \simeq \tfrac{1}{2}\rho_{\text{liq}} \int d\vec{r}\, g_{\text{HS}}(r) u_0(r), \tag{2.39}$$

where the difference between enthalpy H and internal energy U has been neglected.

The eccentricity parameter α_2 can, in principle, be related to the dimensions of the molecular hard core. In the case of spherocylinders an expression for α_2 can also be obtained by equating (2.36) with the corresponding expression in Ref. 5, because in the limit of small length-to-breadth ratios the equation of state mentioned in Ref. 5 reduces to ours. We find

$$\alpha_2 = \tfrac{5}{64}(l/d - 1)^2, \tag{2.40}$$

where l is the length and d the breadth of the molecular hard core.

D. Short-range orientational order

In the preceding part the Helmholtz free energy of the system was written

$$\beta F = \beta F_{\text{HS}} + \tfrac{1}{2}N\beta\rho \int d\vec{r}\, g_{\text{HS}}(r) u_0(r) + \beta F_{\text{orient}}, \tag{2.41}$$

where the orientational free energy F_{orient} was given in the molecular-field approximation, i.e.,

$$\beta F_{\text{orient}} = N \int d\Omega\, f(\Omega) \ln 4\pi f(\Omega) - \tfrac{1}{2}N B_2(\eta, T) S^2. \tag{2.42}$$

In using only a one-particle distribution function for the molecular orientations, short-range orientational correlations were neglected. In order to account for nearest-neighbor correlations between molecular orientations, at least a two-particle orientational distribution function is required. In a recent paper[11] we described a cluster-variation method, which provides such a distribution in a rather crude but simple way. This method gives the following expression for F_{orient}:

$$\beta F_{\text{orient}} = -\tfrac{1}{2}N\gamma \ln Z_{12} + N(\gamma - 1)\ln Z_1, \tag{2.43}$$

with

$$Z_{12} = \int d\Omega_1\, d\Omega_2 \exp\!\left(\frac{B_2(\eta, T)}{\gamma} P_2(\cos\theta_{12}) + \frac{\gamma - 1}{\gamma} B_2(\eta, T)\bar{S} \times [P_2(\cos\theta_1) + P_2(\cos\theta_2)]\right), \tag{2.44}$$

and

$$Z_1 = \int d\Omega \exp[B_2(\eta, T)\bar{S} P_2(\cos\theta)]. \tag{2.45}$$

θ_{12} is the angle between the orientations Ω_1 and Ω_2 of two molecules that are nearest neighbors, γ is the number of nearest neighbors, and $\bar{S}$ is a variational parameter to be determined self-consistently by minimizing the orientational free energy. From the total Helmholtz free energy F, which reads [compare (2.33)]

$$\beta F = \beta F_{\text{HS}} + \tfrac{1}{2}N\beta\rho \int d\vec{r}\, g_{\text{HS}}(r) u_0(r) - \tfrac{1}{2}N\gamma \ln Z_{12} + N(\gamma - 1)\ln Z_1, \tag{2.46}$$

all thermodynamic quantities are readily derived.

III. RESULTS AND DISCUSSION

In this section extensive numerical results are presented for various model systems and compared with available experimental data for a common nematogen, p-azoxyanisole (PAA). In Sec. III A a model system is considered, consisting of molecules with a spherical hard core. This corresponds to the assumptions of the Maier-Saupe theory. An interesting comparison with Cotter's[9] model of hard spherocylinders is made. In Sec. III B a model system is investigated, consisting of molecules with a slightly nonspherical hard core. In Secs. III A and III B the molecular-field approximation is applied in dealing with the orientational coordinates. This means that the numerical results of these sections have been obtained using the formulas of Sec. II C. In Sec. III C finally, the same model systems will be discussed, but the orientational averages will be evaluated, using a two-particle orientational distribution function, as described in Sec. II D. A short account of this work has already been reported.[18]

In Secs. III A and III B the nematic-isotropic transition in the model systems was determined from (2.38) and (2.34) with $f(\Omega)$ given by (2.35). The pressure p is kept fixed at about 1 atm, i.e., $pv_0/k = 1.69\,^\circ\text{K}$, where k is Boltzmann's constant and v_0 is chosen to be the estimated volume of a PAA molecule, 230 Å^3.[19] If the interaction strengths of the attractive interaction [V_0, V_2 in (2.31)] or [J_0, J_2 in (2.28)] and the eccentricity parameter α_2 are given, solution of (2.38) and (2.34) yields the packing fractions η_c and η_{ic} of the nematic and the isotropic phase, the transition temperature T_c, and the long-range order parameter S_c. All remaining thermodynamic quantities can then be calculated.

In Sec. III C a similar procedure is followed, but now based on the free energy (2.46) as given by

TABLE I. Comparison of the nematic-isotropic transition for different equations of state $\lambda = 0, -1, -3$; S_c is the order parameter, η_c the nematic packing fraction, $\Delta\eta/\eta_c$ the density change at the transition temperature T_c. $V_0/v_0k = 30\,000$ °K; $V_2/v_0k = 3000$ °K; $\alpha_2 = 0$.

Quantity	$\lambda = 0$	$\lambda = -1$	$\lambda = -3$
T_c	373 °K	382	407
S_c	0.440	0.440	0.441
η_c	0.567	0.580	0.618
$\frac{\Delta\eta}{\eta_c}$	0.0054	0.0055	0.0059

the two-site cluster approximation.

The model calculations were based on the compressibility equation of state, i.e., $\lambda = 0$ in (2.37). The reason is twofold. In the first place, this equation gives, for a system of hard spheres without attractive forces, better agreement with the computer-simulation results[15,20] than the pressure equation ($\lambda = -3$). Secondly, Cotter's[9] equation of state for a system of hard spherocylinders reduces to ours ($\lambda = 0$) in the limit of vanishing cylindrical length. The discrepancy between the pressure and compressibility equations of state is often considered as a test for the consistency of a theory, in this case the Percus-Yevick approximation. In order to estimate this degree of consistency the nematic-isotropic transition was determined from (2.38) and (2.34) for a fixed set of interaction constants, using the compressibility and pressure equation of state. Table I summarizes the results where we used the uniform attractive interaction (2.31) with fixed interaction constants. The results for $\lambda = -1$, corresponding to an empirical equation of state,[21] are also shown, because this equation gives, for hard spheres, the best agreement with the computer-simulation results. Use of the compressibility equation of state ($\lambda = 0$) appears to introduce only small errors.

A. Case $\alpha_2 = 0$: spherical molecules

In this section the molecular hard core is assumed to be spherical ($\alpha_2 = 0$), in agreement with the assumptions of the Maier-Saupe theory. Until now the Maier-Saupe theory has been worked out[1,2] at constant volume. This means that properties of the phase transition at constant pressure, as it takes place in experiments, can only be estimated by relating them to experimentally determined quantities, e.g., the compressibility. Application of the equation of state of Sec. II C with $\alpha_2 = 0$ enables an investigation of many thermodynamic quantities of the nematic-isotropic transition in the Maier-Saupe model, both at constant volume and at constant pressure. We will apply the molecular-field approximation to the attractive interaction (2.31), which allows an interesting comparison with the results of Cotter.[9] All differences between Cotter's results and ours are caused by the assumptions about the effective shape of the molecular hard core, which is a spherocylinder and a sphere, respectively.

In Table II we compare the properties of the nematic-isotropic transition in the model systems of hard spheres and hard spherocylinders[9] with the available experimental data for PAA. The an-

TABLE II. Comparison of the nematic-isotropic transition in PAA and in the model systems of hard spheres and of hard spherocylinders (Cotter, Ref 9); S_c is the order parameter, η_c the nematic packing fraction; $\Delta\Sigma/Nk$ is the entropy difference between the two phases; $\Gamma(T_c)$ is defined in (3.1). $(V_0/v_0k)_{\text{spheres}} = 39\,000$ °K; $(V_2/v_0k)_{\text{spheres}} = 3130$ °K; $\alpha_2 = 0$. $(V_0/v_0k)_{\text{spherocyl}} = 25\,000$ °K; $(V_2/v_0k)_{\text{spherocyl}} = 2000$ °K.

Quantity	Spheres	Spherocylinders	PAA	References
T_c	408 °K	410	409	1
S_c	0.437	0.542	~0.40	23
η_c	0.593	0.454	0.62	1, 19
$\frac{\Delta\eta}{\eta_c}$	0.0038	0.040	0.0035	1
$\frac{\Delta\Sigma}{Nk}$	0.542	0.887	0.218	24
$\Gamma(T_c)$	1.00	3.90	~4.0	6
$\left(\frac{dT_c}{dp}\right)_{p=1\text{ bar}}$	19.7 °K/kbar	175	43	1, 24

isotropic interaction strength V_2 was chosen such that the transition temperature of PAA at atmospheric pressure was reproduced. In this table the parameter Γ is a measure for the relative sensitivity of the order parameter to volume changes (at constant temperature) and temperature changes (at constant volume). It is defined as

$$\Gamma = \frac{V}{T}\,\frac{(\partial S/\partial V)_T}{(\partial S/\partial T)_V} = -\left(\frac{\partial \ln T}{\partial \ln V}\right)_S = \left(\frac{\partial \ln T}{\partial \ln \eta}\right)_S . \qquad (3.1)$$

A constant order parameter S in the differentiation of (3.1) implies $B_2(\eta, T) = \text{const}$ [see (2.35)]. With the definition (2.36) of $B_2(\eta, T)$ and the potential (2.31) we have for the special case of spherical molecules

$$B_2(\eta, T) = \rho V_2/kT = (\eta/T)(V_2/v_0 k), \qquad (3.2)$$

which implies $\Gamma = 1$. The pressure dependence of the transition temperature dT_c/dp is determined by Clausius-Clapeyron's law. Cotter[9] chose the interaction strengths V_0 and V_2 such as to reproduce T_c and $\Gamma(T_c)$ quantitatively. The other quantities deviate appreciably from the experimental values. Except for Γ, the overall agreement with experiment of the hard-sphere model is better than that of Cotter's model, although her basic assumption of a spherocylindrical molecular shape seems more realistic than a spherical shape. It should be noted, however, that the predicted S_c for spherocylinders will become much worse, if the excluded volume of two spherocylinders is taken into account more accurately. This excluded volume $b(\Omega_i, \Omega_j)$ for spherocylinders with cylindrical length L and diameter D, which is equal to[22]

$$b(\Omega_i, \Omega_j) = \tfrac{4}{3}\pi D^3 + 2\pi L D^2 + 2L^2 D|\sin\theta_{ij}|, \qquad (3.3)$$

was approximated by Cotter, using

$$\sin\theta_{ij} \simeq \tfrac{1}{4}\pi - \tfrac{5}{32}\pi P_2(\cos\theta_{ij}). \qquad (3.4)$$

As a result the predicted value of the order parameter has been lowered by roughly 25%.[9]

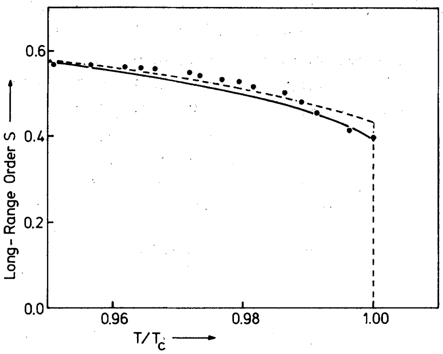

FIG. 1. Order parameter S as a function of the reduced temperature at constant pressure; dashed curve: calculated values for the hard-sphere model with $V_0/v_0 k$ and $V_2/v_0 k$ as in Table II; solid curve: calculated values for a nonspherical model with $V_0/v_0 k$ and $V_2/v_0 k$ as in Table VI; the dots are the observed values of Rowell *et al.* (Ref. 25) for PAA.

Figure 1 gives the temperature dependence of the order parameter S at constant pressure for the hard-sphere model (dashed curve). The interaction constants have the same value as in Table II. The experimental NMR data[25] for PAA are also shown.

In the calculations, reported above, the spatially uniform attractive interaction (2.31) was used in order to allow a comparison with Cotter's model of spherocylinders. It should be mentioned, however, that for hard spheres similar results can be obtained with the distance-dependent interaction (2.28), which corresponds to the Van der Waals dispersion forces. Equations (2.38), which locate the nematic-isotropic transition, were therefore solved for a few fixed values of $B_2(\eta_c, T_c)$ (and thus fixed S_c) in the range of interest, viz., $B_2 > B_2$ (constant-volume transition) = 4.541 with $S > 0.429$.[1] This was done for both the uniform and the distance-dependent interaction. The interaction constants V_0, V_2 and J_0, J_2 were chosen such as to reproduce the transition temperature of PAA at atmospheric pressure. The results are summarized in Table III. The distance-dependent inter-

TABLE III. Comparison of the nematic-isotropic transition in model systems with uniform (A) and distance-dependent (B) attractive interactions. S_c is the order parameter, η_c the nematic packing fraction, $\Delta\eta/\eta_c$ the density change at the transition; Γ is defined in (3.1); $\Gamma_A = 1$.

$B_2(\eta_c, T_c)$	S_c	$(\eta_c)_A$	$(\eta_c)_B$	$\left(\frac{\Delta\eta}{\eta_c}\right)_A$	$\left(\frac{\Delta\eta}{\eta_c}\right)_B$	Γ_B
4.55	0.437	0.594*	0.688	0.0037*	0.0021	1.77
4.56	0.445	0.539	0.640	0.0079	0.0046	1.72
4.57	0.453	0.509	0.612*	0.0120	0.0071*	1.69*
4.58	0.460	0.489	0.594	0.0159	0.0095	1.67
4.59	0.467	0.474	0.580	0.0198	0.0120	1.66
4.60	0.473	0.462	0.569	0.0236	0.0144	1.65

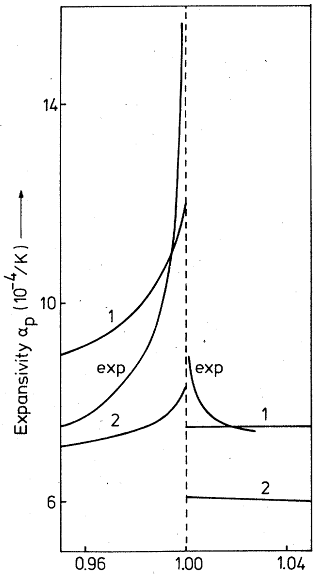

FIG. 2. Expansivity α_p as a function of the reduced temperature. Curve 1: distance-dependent interaction (2.28); curve 2: uniform interaction (2.31). Experimental data are of Maier and Saupe (Ref. 1).

action gives slightly higher densities, and a higher value of Γ, which is caused by the density dependence of the radial distribution function g_{HS}. In Fig. 2 the isobaric expansivity α_p has been drawn for both potentials. The experimental data[1] are also given. From Table III we chose for each potential the set of interaction constants that gives the best packing fraction at the transition (PAA: $\eta_c = 0.62$). The properties corresponding to these cases are marked with an asterisk. The behavior of α_p (and similarly of the isothermal compressibility and isobaric specific heat), as calculated from the hard-sphere model, agrees qualitatively with the observed behavior. Quantitative comparison with the experimental data near the transition does not seem useful, given the large uncertainties in the experimentally observed quantities. In the isotropic phase, away from the transition, such a comparison is possible and the agreement for both the uniform and the distance-dependent interaction is quite reasonable, given the sensitivity of the second derivatives of the free energy to the details of the model and the statistical-mechanical approximations. The values predicted by the model of spherocylinders[9] compare less favorably with the experimental values.

B. Case $\alpha_2 \neq 0$: nonspherical molecules

In this section we investigate the effect of a slightly nonspherical molecular shape ($\alpha_2 \neq 0$) on the nematic-isotropic transition. The spatially uniform attractive interaction (2.31) is used and the orientational coordinates are treated in the molecular-field approximation.

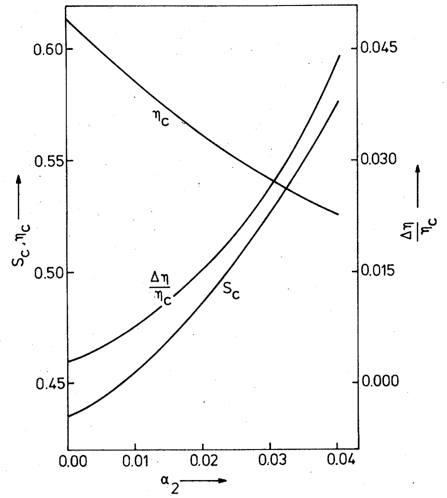

FIG. 3. Order parameter S_c, the packing fraction η_c, and the relative density change $\Delta\eta/\eta_c$ at the transition as a function of α_2 for $V_0/v_0k = 30\,000$ °K and $V_2/v_0k = 2000$ °K .

Figure 3 shows the packing fraction, order parameter, and relative density change at the nematic-isotropic transition as a function of the eccentricity parameter α_2 for a given set of interaction strengths $V_0/(v_0k)$ and $V_2/(v_0k)$. It appears that even small values of α_2 have a strong influence on the thermodynamic properties at the transition. With increasing eccentricity α_2 of the molecular shape the steric hindering becomes more effective, shifting the phase transition to lower densities with increasing density change and jump of the order parameter.

Next, a model calculation was carried out, based on the experimental data for PAA. In Table IV a number of properties at the nematic-isotropic transition are compared in the model system and in PAA. The parameters V_0, V_2, and α_2 were chosen such as to reproduce quantitatively the transition temperature and the parameter Γ, defined in (3.1) for PAA. The contribution of steric hindering to the nematic order can be evaluated from (2.36) by comparing the two terms. Steric hindering appears to contribute 41% to $B_2(\eta_c, T_c)$.

The improvement of the model of slightly nonspherical molecules with respect to the hard-sphere model (see Table II) appears in the relative sensitivity of the order parameter to density and temperature changes, as measured by the parameter Γ. The results for the order parameter and the density change at the transition have wor-

TABLE IV. Comparison of the nematic-isotropic transition in PAA and in the model system of slightly nonspherical molecules; the meaning of the quantities is as in Table II. $V_0/v_0k = 39\,000\,°K$; $V_2/v_0k = 1850\,°K$; $\alpha_2 = 0.0168$.

Quantity	Model	PAA
T_c	409 °K	409
S_c	0.473	~0.40
η_c	0.596	0.62
$\frac{\Delta\eta}{\eta_c}$	0.0102	0.0035
$\frac{\Delta\Sigma}{Nk}$	0.590	0.218
$\Gamma(T_c)$	3.96	~4.0
$\left(\frac{dT_c}{dp}\right)_{p=1\,\mathrm{bar}}$	48.6 °K/kbar	43

sened somewhat, but still agree better with experiment than the results for spherocylinders (see Table II). The improvement with respect to the model of hard spheres is demonstrated even better in Fig. 4 where the dependence of the order parameter on temperature is shown at constant density rather than at constant pressure (curves A and B). Starting at atmospheric pressure and a temperature of about 397 °K, the temperature is raised while keeping the density fixed, as in the experiments of McColl and Shih.[6] The nematic-isotropic transition is shifted to a higher temperature, as compared to the transition at atmospheric pressure, viz., to 413.5 °K in the hard-sphere model (curve A) and to 438.9 °K in the model of nonspherical molecules (curve B), whereas the experimental value is 437.5 °K. During this process the pressure has been raised from 1 to 210 and 560 bar in the model systems, in the experiment to 640 bar. The theoretical curve for the model of nonspherical molecules has roughly the correct shape. Very close to the transition temperature its downward curvature is not sufficient, but this is expected to be a consequence of the molecular-field approximation, which was applied to the orientational coordinates.

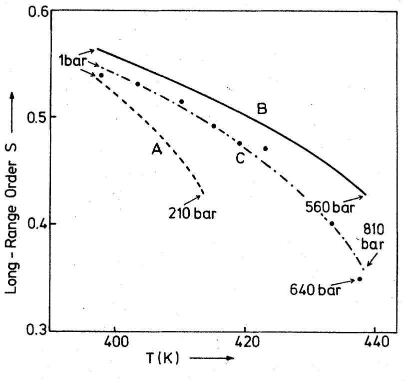

FIG. 4. Order parameter S as a function of temperature at constant volume. The theoretical curves A and B refer, respectively, to model systems of hard spheres and of slightly nonspherical molecules. They have been obtained employing a molecular-field approximation for orientational coordinates with $V_0/v_0k = 39\,000\,°K$; $(V_2/v_0k)_{\mathrm{spher}} = 3130\,°K$; $(V_2/v_0k)_{\mathrm{nonspher}} = 1850\,°K$; $(\alpha_2)_{\mathrm{spher}} = 0$; $(\alpha_2)_{\mathrm{nonspher}} = 0.0168$. The theoretical curve C refers to a model system of slightly nonspherical molecules using the two-site cluster approximation; V_0, V_2, and α_2 are as in Table VI. The experimental points are those of McColl and Shih (Ref. 6) at a molar volume of 225 cm^3 ($\eta = 0.63$).

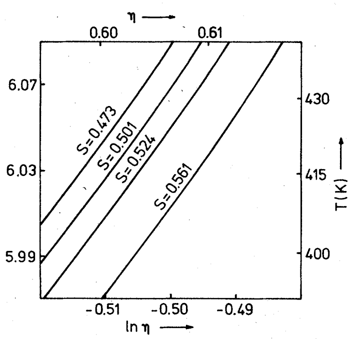

FIG. 5. Relationship between the temperature T and the packing fraction η at four fixed values of the order parameter S; V_0, V_2, and α_2 are as in Table IV.

McColl and Shih[6] investigated the manner in which the density depends on temperature at constant order parameter by plotting $\ln T$ vs $\ln V$ for several values of the order parameter. The plots were linear and the slope, which is equal to Γ, defined in (3.1), appeared to be nearly constant. Figure 5 shows these plots for the model system of nonspherical molecules with the same value for V_0, V_2, and α_2 as in Table IV. The plots were obtained from (2.36) with $u_2(r) = -V_2/V$. Except at the highest densities and temperatures, the slope of the plots is approximately equal to 4.

C. Short-range orientational order

In Secs. III A and III B the molecular-field approximation was applied in dealing with the orientational coordinates of the molecules. In using only a one-particle orientational distribution function $f(\Omega)$, short-range orientational correlations were neglected. In this section the influence of nearest-neighbor correlations between molecular orientations on the nematic-isotropic transition is investigated, applying a two-particle orientational distribution, as described in Sec. II D.

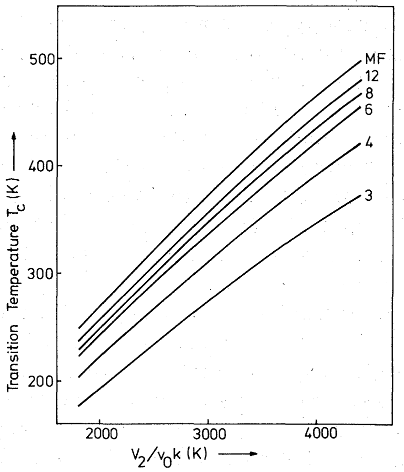

FIG. 6. Nematic-isotropic transition temperature T_c as a function of $V_2/(v_0k)$ for several numbers of nearest neighbors γ, and for the mean-field approximation (MF). $V_0/v_0k = 30\,000$ °K; $\alpha_2 = 0$.

First, the effect of short-range orientational order on the nematic-isotropic transition temperature of the model systems of Secs. II A and II B was investigated. Figure 6 shows the transition temperature T_c as a function of the strength of the anisotropic attraction V_2/v_0k. The isotropic attraction V_0/v_0k is kept fixed, and the eccentricity parameter α_2 is taken to be zero, i.e., the molecular hard cores are considered to be spherical, as in Sec. III A. The curves are drawn for several numbers of nearest neighbors γ, and the mean-field results are also given. In the Maier-Saupe theory the anisotropic interaction strength V_2 is proportional to the square of the anisotropy of the molecular polarizability. Experimentally De Jeu and Van der Veen[26] found some qualitative trends, similar to those in Fig. 6, in the transition temperatures of nematics as a function of their anisotropic polarizability. In Fig. 7 the transition temperature is drawn, for fixed V_0 and V_2, as a function of the eccentricity parameter α_2 for several numbers of nearest neighbors, and for the mean-field approximation. In both figures short-range orientational order appears to reduce the transition temperature in comparison with the mean-field approximation.

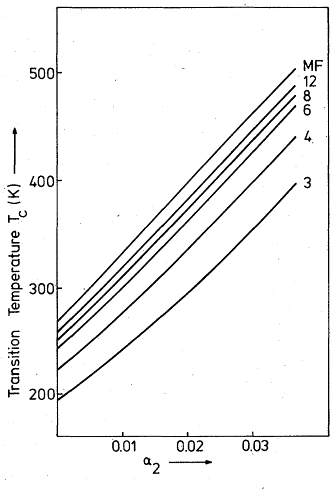

FIG. 7. Nematic-isotropic transition temperature as a function of α_2 for $\gamma = 3, 4, 6, 8, 12$ and for the mean-field approximation (MF). $V_0/v_0k = 30\,000$ °K; $V_2/v_0k = 2000$ °K.

TABLE V. Temperature T_c, order parameter S_c, nematic packing fraction η_c, relative density change $\Delta\eta/\eta_c$, and entropy change $\Delta\Sigma/Nk$ at the nematic-isotropic transition in a model system of slightly nonspherical molecules, as predicted by the two-site cluster approximation for various numbers of nearest neighbors γ, and by the mean-field approximation (MF). $V_0/v_0k = 30\,000$ °K; $V_2/v_0k = 2500$ °K; $\alpha_2 = 0.0150$.

γ	T_c	S_c	η_c	$\frac{\Delta\eta}{\eta_c}$	$\frac{\Delta\Sigma}{Nk}$
3	309°K	0.341	0.609	0.0021	0.173
4	351	0.391	0.586	0.0048	0.310
6	379	0.426	0.572	0.0077	0.437
8	390	0.440	0.566	0.0092	0.494
12	400	0.452	0.561	0.0106	0.546
MF	416	0.473	0.553	0.0133	0.637

In Table V a number of properties at the nematic-isotropic transition are compared for several numbers of nearest neighbors for a given set of V_0, V_2, and α_2. The mean-field results are also given. The discontinuities in the order parameter, the density and the entropy decrease if short-range orientational order is included.

Next, some model calculations were carried out, based on the experimental data for PAA. Table VI summarizes a number of properties at the nematic-isotropic transition for a model system of slightly nonspherical molecules. For the reader's convenience the experimental data for PAA are once more given. V_0, V_2, and α_2 were chosen such as to reproduce quantitatively T_c and Γ for PAA. The number of nearest neighbors γ was taken to be four, because the two-site cluster approximation strongly underestimates the effect of short-range orientational order, getting worse with increasing number of nearest neighbors. Therefore, a rather low effective number of nearest neighbors was selected for our calculations. We remark that the value of α_2 used in this table corresponds, for spherocylinders, to a molecular length-to-breadth ratio of about 1.5 [compare (2.40)].

TABLE VI. Comparison of the nematic-isotropic transition in PAA and in the model system of nearly spherical molecules, as predicted by the two-site cluster approximation for $\gamma=4$. Γ is defined in (3.1); the other quantities are as in Table V. $V_0/v_0k=45\,000\,^\circ\mathrm{K}$; $V_2/v_0k=2300\,^\circ\mathrm{K}$; $\alpha_2=0.016\,74$.

Quantity	Model	PAA
T_c	409 °K	409
S_c	0.393	~0.40
η_c	0.621	0.62
$\frac{\Delta\eta}{\eta_c}$	0.0039	0.0035
$\frac{\Delta\Sigma}{Nk}$	0.295	0.218
$\Gamma(T_c)$	3.96	~4.0
$\left(\frac{dT_c}{dp}\right)_{p=1\,\mathrm{bar}}$	35.8 °K/kbar	43

The relative contributions of steric and energetic effects to the molecular alignment can be evaluated from the expression (2.36) for $B_2(\eta_c, T_c)$ and appear to be of comparable magnitude, viz., steric effects contribute 40%, energetic effects 60%. A similar conclusion was drawn by McColl and Shih[6] from their experiments on PAA.

Figure 1 (solid curve) shows the calculated temperature dependence of the long-range order parameter at a constant pressure of about 1 atm ($pv_0/k=1.69\,^\circ\mathrm{K}$). The agreement with the experimental data for PAA,[26] which have also been plotted, is quite satisfactory.

Figure 4 (curve C) gives the relationship between the long-range order parameter and the temperature at constant density rather than at constant pressure. The nematic-isotropic transition is now shifted to 438.4 °K at a pressure of 810 bar. The curve for S agrees excellently with the experimental data. The isobaric expansivity α_p (and similarly the isothermal compressibility and isobaric specific heat) and the relationship between the density and temperature at some fixed values of the order parameters S ($\ln T$ vs $\ln\eta$ plots) show a similar behavior as in the preceding parts of this section (see Figs. 2 and 5).

IV. SUMMARY AND CONCLUSIONS

In Sec. II we derived an equation of state, based on both anisotropic attractive forces and anisotropic repulsive forces between molecules with a slightly nonspherical hard core. Both the attractive interaction and the anisotropic repulsion due to the eccentricity of the molecular shape are treated as perturbations to a hard-sphere repulsion. A system of hard spheres acts as a reference system, which is treated in the Percus-Yevick approximation. To the orientational molecular coordinates both the molecular-field approximation and the two-site cluster approximation can be applied. In the latter case short-range correlations between molecular orientations are taken into account.

In Sec. III extensive numerical results were presented for various model systems and compared with the experimental data for PAA. As a special case, first a system of molecules with a spherical hard core was considered, corresponding to the assumptions of the Maier-Saupe theory. Like the model of spherocylinders with fixed length-to-breadth ratio this model contains only two adjustable parameters. The main deficiency of this model appears to be, that it cannot account for the rather strong volume dependence of the order parameter, as measured by the parameter Γ, defined in (3.1). Apart from this quantity, the hard-sphere model gives results that are in better agreement with the experimental data than the results of Cotter's model of hard spherocylinders.

In Sec. III B the steric hindering of elongated molecules was taken into account by considering a system of slightly nonspherical molecules. The thermodynamic properties of the model system agreed quite reasonably with those of the real system (PAA), e.g., the high packing fraction, the temperature dependence of the order parameter (both at constant pressure and at constant density), nearly linear $\ln T$ vs $\ln\eta$ plots (at constant order parameter), and the pressure dependence of the transition temperature. The order parameter and the density change at the transition, and also the latent heat were still too high, which was due to the neglect of short-range orientational correlation. In Sec. III C the molecular-field approximation was abandoned for the treatment of the orientational molecular coordinates. Employing a two-particle orientational distribution function, as provided by the two-site cluster approximation, essentially quantitative agreement with the experimental data of PAA was obtained, except for the higher derivatives of the free energy, e.g., α_p. Although the two-site cluster approximation introduces the number of nearest neighbors, this number cannot be considered as an adjustable parameter. Generally a molecule will, on the average, be surrounded by five or six molecules. Because, however, this approximation underestimates the effect of short-range correlations, we selected four to be the number of nearest neighbors in order to get as close as possible to a realistic estimation of the contribution of short-range order.

At first sight, the assumption of a slightly nonspherical molecular shape as a starting point for a molecular theory of nematics does not seem to be very convincing. Hard rods seem more appropriate. The success of our model, however, is striking and cannot be ignored. A possible explanation might be that our model allows for an alternative interpretation of the slightly nonspherical hard core in terms of microclusters.[1] The shape of these microclusters, which consist of a molecule with a few nearest neighbors whose orientations are highly correlated, will resemble a sphere more closely than the shape of a single molecule does. All thermodynamic properties are expressed in terms of the packing fraction $\eta = \rho v_0$, where ρ and v_0 can be interpreted as the density and volume, respectively, of microclusters or of single molecules. Keeping the pressure fixed, we chose a value of v_0 in pv_0/k, which was the estimated volume of a PAA molecule. It appeared, however, that the results are nearly insensitive to a change of v_0 by a factor of 5 or so. For this reason the results may be interpreted in terms of microclusters.

A deficiency of our model might be the molecular interpretation of the eccentricity parameter α_2, in contrast to the hard-rod models which contain the molecular length-to-breadth ratio explicitly. As has already been argued, however, the molecular statistical theories, using the explicit length-to-breadth ratio, overestimate the effect of the excluded volume considerably. Quantitative agreement can only be obtained if one abandons the real length-to-breadth ratio and uses an effective one instead. In that case the equation of state for hard spherocylinders probably also will produce reasonable quantitative results, provided the length-to-breadth ratio is used as an adjustable parameter.

Finally attention should be paid to the question whether it is justified to assume that short-range correlations between molecular orientations and the orientations of $\vec{r}_{ij}$, in first instance, can be neglected as has been done in the Eq. (2.2) and (2.23). Quite recently, Gelbart and Gelbart[27] derived an effective one-body pseudopotential for a system of hard spherocylinders interacting through an attractive pair potential similar to (2.28). Averaging over the excluded volume of two molecules they found that the orientation dependence of the pseudopotential is mainly due to the coupling between the isotropic attractions and the anisotropic hard-core repulsions. Apart from the problem of the strong nonadditivity of excluded volumes, which presents difficulties in interpreting the results of Gelbart and Gelbart for systems with liquid densities, we do not think that their quite interesting results contradict our assumption as soon as one adopts the point of view that our model should be interpreted in terms of microclusters.

In conclusion, it can be stated that the derived equation of state, based upon both anisotropic attractive and repulsive forces, agrees quite well with experiment. The underlying idea is to consider the nematic as an ordinary liquid, whose anisotropic properties can be treated by means of perturbation theory. Hard-rod theories, using a scaled-particle treatment, probably will also give good agreement with experiment as soon as the actual length-to-breadth ratio is abandoned. Because of the strong nonadditivity of mutual excluded volumes a "renormalized" length-to-breadth ratio should be taken instead. The molecular statistical problem then is to calculate this "renormalized" ratio. This problem is outside the scope of this paper. In our opinion the solution of this problem is far beyond present statistical mechanical methods.

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