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Van der Waals theory of nematogenic solutions. I. Derivation of the general equations

Martha A. Cotter and Douglas C. Wacker
Department of Chemistry, Rutgers, The State University, New Brunswick, New Jersey 08903

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In the Van der Waals theory of liquids, very short-ranged intermolecular repulsions are approximated by hard-particle exclusions and somewhat longer-ranged intermolecular attractions are subject to a self-consistent mean-field treatment. This approach, which has recently been applied to pure nematogens, is here extended to nematogenic solutions. The molecular hard cores are taken to be spherocylindrical or spherical in shape and their contribution to the free energy of the system is evaluated using scaled-particle theory. The general theory, applicable to mixtures of any number of rodlike or effectively spherical molecules is derived and its applications to various types of nematogenic systems are discussed. Finally, the way in which the theory could be modified to treat species whose molecular shapes cannot satisfactorily be approximated by spheres or spherocylinders is indicated.

I. INTRODUCTION

Nematogenic solutions are two-component or multicomponent homogeneous mixtures which exhibit a thermodynamically stable nematic mesophase over some range of temperature and composition. One or more of the components must possess a rodlike molecular shape; in the nematic phase, the long axes of the rodlike molecules tend to align parallel to a preferred direction called the director. Nematic solutions differ from isotropic liquid solutions only by their possession of this long-range orientational order. In this series of papers, we shall investigate the molecular factors which determine the equilibrium thermodynamic properties of such solutions, using an extension of the Van der Waals theory of liquids.

The term "Van der Waals theory" has been used in recent years in two related but not equivalent ways. On the one hand, it has been used to denote formally rigorous treatments[1] of systems with intermolecular pair potentials of the form $v(r_{ij}) = q(r_{ij}) + w(r_{ij})$, where $q(r_{ij})$ represents a very short-ranged repulsion,

$$w(r_{ij}) = \gamma^{\nu}\varphi(\gamma r_{ij})$$

represents a longer-ranged attraction, and ν is the dimensionality of the system. In the limit $\gamma \to 0$, it has been shown[1(c)] that for wide classes of q's and φ's, the equation of state assumes the "Van der Waalsian" form $P(\rho, T) = P^{(0)}(\rho, T) + \frac{1}{2}\alpha\rho^2$, where $P^{(0)}$ is the pressure of a reference system with $\varphi = 0$ everywhere and $\alpha = \int \varphi(\gamma r) d(\gamma r)$. On the other hand, the Van der Waals "label" has been applied to certain approximate theories of liquids based on three principal assumptions: (i) that the detailed structure of a liquid far from its critical point is determined largely by very short-ranged intermolecular repulsions; (ii) that these short-range repulsions may satisfactorily be approximated by hard-core exclusions; and (iii) that the role of longer-ranged intermolecular attractions (dispersion forces, etc.) is—to a first approximation—merely to provide a negative, spatially uniform "mean field" in which the molecules move. We use the descriptive phrase "Van der Waals" in the latter sense. From this viewpoint, the prototype Van der Waals theory of liquids is that of Longuet-Higgins and Widom.[2] They were able to predict quite successfully the thermodynamic properties of argon at its triple point using a model system of hard spheres in a mean-field potential $\bar{\psi}(\rho) = -a\rho$, where a is a positive constant. (The equation of state of the hard-sphere reference system was obtained from the molecular dynamics results of Alder and Wainwright.[3])

A Van der Waals approach was first applied to nematogenic systems by Alben,[4] who considered a system of hard rods in a mean field described by the pseudopotential $\bar{\psi}(\rho) = -W\rho$, where W is a positive constant. More recently, Gelbart and Baron,[5,6] Gelbart and Gelbart,[7] and Cotter[8-10] have utilized Van der Waals theories of nematogens in which the mean-field potential $\bar{\psi}$ acting on a molecule depends upon both the orientation of the molecule and the average orientational order in the system. When the latter approach is used[6,8] to predict the thermodynamic properties of relatively short and rigid nematogens such as PAA,[11] excellent qualitative (though not quantitative) agreement with experiment is obtained; i.e., the thermodynamic behavior of model systems with rodlike molecular hard cores and superimposed intermolecular attractions displays virtually all the qualitative features of that of the real nematogens. More important, the Van der Waals calculations clearly indicate that the orientation dependence of the very short-range intermolecular repulsions, rather than the orientation dependence of the intermolecular attractions, plays the major role in determining the stability and orientational order of nematic mesophases.

In this paper, Van der Waals theory is extended to nematogenic solutions containing any number of components with rodlike or effectively spherical molecular shapes. For the sake of convenience, the hard cores of the rodlike molecules are taken to be spherocylindrical, where a spherocylinder is a right circular cylinder capped on each end by a hemisphere of the same radius. In Sec. II, the model system is described and an equation is derived for its Helmholtz free energy as a functional of the distribution of molecular orientations. One term in this equation, the free-energy functional for the corresponding system of hard spherocylinders/spheres is evaluated in Sec. III, using scaled particle theory, and the final equations for the free energy, entropy, pressure, chemical potentials, and one-particle orientational distribution functions are presented in Sec. IV. In Sec. V, various possible applications of the general theory are discussed and the way in which it could be modified to treat species with molecular shapes other than spherocylinders or spheres is indicated.

In Paper II of this series of papers, our theory is applied to binary solutions with spherical solute molecules and rodlike solvent molecules. In Paper III, it will be applied to solutions with rodlike solvent and solute molecules.

II. MODEL SYSTEM

Our model system is an n-component mixture of N cylindrically or spherically symmetric molecules in a volume V at temperature T. Each molecule of component σ has a spherocylindrical or spherical hard core of radius $R_{a_\sigma}\, a$ and cylindrical length $R_{l_\sigma} l$ ($R_{l_\sigma}=0$ corresponds to a spherical molecule) and the pair potential $v_{\sigma\sigma'}(ij)$ between molecule i of type σ and molecule j of type σ' is given by

$$v_{\sigma\sigma'}(ij)=v^*_{\sigma\sigma'}(ij)+v^{(a)}_{\sigma\sigma'}(ij)\,,$$

where

$$v^*_{\sigma\sigma'}=\begin{cases}\infty & \text{if the hard cores of } i \text{ and}\\ & j \text{ would overlap}\\ 0 & \text{otherwise}\,,\end{cases}$$

and $v^{(a)}_{\sigma\sigma'}$ is a somewhat longer-ranged intermolecular attraction (assumed to represent primarily London dispersion forces). In the case where both components σ and σ' have spherocylindrical hard cores, both $v^*_{\sigma\sigma'}$ and $v^{(a)}_{\sigma\sigma'}$ depend on the vector $\vec{r}_{ij}$ connecting the centers of i and j and on the orientations of the molecular long axes, denoted by Ω_i and Ω_j.[12] The mole fraction of component σ ($\sigma=1,2,\ldots,n$) and the number density N/V will be denoted by y_σ and ρ, respectively.

The idealizations inherent in this model system include the complete neglect of molecular flexibility, the assumption of cylindrical symmetry for all rodlike molecules, and the approximation of short-range intermolecular repulsions by hard-core exclusions. Because of the first of these, one would not expect our theory to work very well for solutions containing nematogens with relatively long alkyl or alkoxy end chains attached to their more rigid central portions. The effects of the other two major idealizations are much harder to judge.

In the most complicated possible case, where all n components possess rodlike hard cores, the configurational partition function of the system is given by

$$Q_N=\left((4\pi)^N\prod_{\sigma=1}^{n}N_\sigma!\right)^{-1}\int d\vec{r}^N\int d\Omega^N\exp(-\beta V_N)\,, \tag{1}$$

where $\beta=1/k_BT$,

$$V_N=V^*_N+V^{(a)}_N\,,$$

$$V^*_N=\sum_{\sigma=1}^{n}\sum_{i<j=2}^{N_\sigma}v^*_{\sigma\sigma}(\vec{r}_{ij},\Omega_i,\Omega_j)+\sum_{\sigma=1}^{n}\sum_{\sigma'\neq\sigma}\sum_{i\in N_\sigma}\sum_{j\in N_{\sigma'}}v^*_{\sigma\sigma'}(\vec{r}_{ij},\Omega_i,\Omega_j)\,,$$

and

$$V^{(a)}_N=\sum_{\sigma=1}^{n}\sum_{i<j=2}^{N_\sigma}v^{(a)}_{\sigma\sigma}(\vec{r}_{ij},\Omega_i,\Omega_j)+\sum_{\sigma=1}^{n}\sum_{\sigma'\neq\sigma}\sum_{i\in N_\sigma}\sum_{j\in N_{\sigma'}}v^{(a)}_{\sigma\sigma'}(\vec{r}_{ij},\Omega_i,\Omega_j)\,.$$

We shall derive general expressions for Q_N and certain thermodynamic functions for this most complicated case. The thermodynamics of solutions containing one or more spherical components can be obtained from the general equations merely by setting the R_l's for those components equal to zero.

The angular integrations in (1) can be approximated to arbitrary accuracy by dividing the unit sphere into m arbitrarily small "sections" of solid angle $\Delta\Omega$ ($m=4\pi/\Delta\Omega$) and summing over all possible orientational distributions $\{N_{11},N_{12},\ldots,N_{nm}\}$, where $N_{\sigma k}=$ the number of molecules of type σ with orientation k (i.e., with Ω in the kth section centered about Ω_k) and $\sum_k N_{\sigma k}=N_\sigma$. This yields

$$Q_N=\left[\left(\frac{4\pi}{\Delta\Omega}\right)^N \prod_{\sigma=1}^{n} N_\sigma!\right]^{-1}$$

$$\times\sum_{N_{11}}\cdots\sum_{N_{nm}}\prod_{\sigma=1}^{n}\frac{N_\sigma!}{N_{\sigma1}!\cdots N_{\sigma m}!}\int d\vec{r}^N \exp(-\beta V_N) \tag{2}$$

$$\approx\left(\frac{\Delta\Omega}{4\pi}\right)^N [\tilde{N}_{11}!\tilde{N}_{12}!\cdots\tilde{N}_{nm}!]^{-1}$$

$$\times\int d\vec{r}^N \exp[-\beta V_N(\vec{r}^N,\tilde{N}_{11},\ldots,\tilde{N}_{nm})]\,, \tag{3}$$

where the tildes denote the set $\{N_{11},\ldots,N_{nm}\}$ corresponding to the maximum term in (2). We now apply the mean-field approximation to the intermolecular attractions by replacing $V_N^{(a)}(\vec{r}^N,\tilde{N}_{11},\ldots\tilde{N}_{nm})$ by its average value $\overline{V}_N^{(a)}(\tilde{N}_{11},\ldots,\tilde{N}_{nm})$ in Q_N; i.e., by assuming that

$$Q_N=\frac{\Delta\Omega^N \exp(-\beta\overline{V}_N^{(a)})}{(4\pi)^N\prod_\sigma\prod_k \tilde{N}_{\sigma k}!}$$

$$\times\int d\vec{r}^N \exp[-\beta V_N^*(\vec{r}^N,\tilde{N}_{11},\ldots,\tilde{N}_{nm})]\,. \tag{4}$$

We approximate $\overline{V}_N^{(a)}$, moreover, by

$$\overline{V}_N^{(a)}=\tfrac{1}{2}\,V^{-1}\sum_\sigma\sum_{\sigma'}\sum_k\sum_l \tilde{N}_{\sigma k}\tilde{N}_{\sigma' l}\int d\vec{r}\exp[-\beta V_{\sigma\sigma'}^*(\vec{r},\Omega_k,\Omega_l)]\,V_{\sigma\sigma'}^{(a)}(\vec{r},\Omega_k,\Omega_l)\,. \tag{5}$$

Substituting $\overline{V}_N^{(a)}$ from (5) into (4) and taking natural logarithms, one obtains

$$-N^{-1}\ln Q_N=\ln\left(\frac{4\pi}{\Delta\Omega}\right)+\ln\rho+\sum_\sigma\sum_k \tilde{s}_{\sigma k}\ln\tilde{s}_{\sigma k}-N^{-1}\ln\left(V^{-N}\int d\vec{r}^N\exp[-\beta V_N^*(\vec{r}^N,\tilde{N}_{11},\ldots,\tilde{N}_{nm})]\right)$$

$$+\tfrac{1}{2}\beta\rho\sum_\sigma\sum_{\sigma'}\sum_k\sum_l \tilde{s}_{\sigma k}\tilde{s}_{\sigma' l}\int d\vec{r}\exp[-\beta v_{\sigma\sigma'}^*(\vec{r},\Omega_k,\Omega_l)]v_{\sigma\sigma'}^{(a)}(\vec{r},\Omega_k,\Omega_l) \tag{6}$$

where $\tilde{s}_{\sigma k}=\tilde{N}_{\sigma k}/N$. Finally, writing $\tilde{s}_{\sigma k}=y_\sigma\tilde{f}_\sigma(\Omega_k)\Delta\Omega$ and converting from sums back to integrals yields the following equation for the configurational Hemholtz free energy per molecule:

$$N^{-1}F_c=-N^{-1}k_BT\ln Q_N$$

$$=k_BT\left[\ln\rho+\sum_{\sigma=1}^{n}\int d\Omega\tilde{f}_\sigma(\Omega)\ln[4\pi\tilde{f}_\sigma(\Omega)]-N^{-1}\ln\left(V^{-N}\int d\vec{r}^N\exp\{-\beta V_N^*[\vec{r}^N;\tilde{f}_1(\Omega),\ldots\tilde{f}_n(\Omega)]\}\right)\right] \tag{7}$$

$$+\tfrac{1}{2}\rho\sum_\sigma\sum_{\sigma'} y_\sigma y_{\sigma'}\int d\Omega\tilde{f}_\sigma(\Omega)\int d\Omega'\tilde{f}_{\sigma'}(\Omega')\int d\vec{r}\exp[-\beta v_{\sigma\sigma'}^*(\vec{r},\Omega,\Omega')]\,v_{\sigma\sigma'}^{(a)}(\vec{r},\Omega,\Omega')$$

$$=N^{-1}F_c^*[\tilde{f}_1(\Omega),\ldots,\tilde{f}_n(\Omega)]+\frac{1}{2}\sum_{\sigma=1}^{n} y_\sigma\int d\Omega\tilde{f}_\sigma(\Omega)\overline{\psi}_\sigma(\Omega)\,. \tag{8}$$

$N^{-1}F_c^*[\{f_\sigma(\Omega)\}]$ is the free energy functional for the corresponding mixture of hard rods at temperature T and density ρ (i.e., for our system with intermolecular attractions "turned off"), and

$$\overline{\psi}_\sigma(\Omega)=\rho\sum_{\sigma'=1}^{n} y_{\sigma'}\int\tilde{f}_{\sigma'}(\Omega')\,d\Omega'$$

$$\times\int d\vec{r}\,\exp[-\beta v_{\sigma\sigma'}^*(\vec{r},\Omega,\Omega')]$$

$$\times v_{\sigma\sigma'}^{(a)}(\vec{r},\Omega,\Omega')\,. \tag{9}$$

The equilibrium one-particle orientational distribution functions $\{\tilde{f}_\sigma(\Omega)\}$ $(\sigma=1,2,\ldots,n)$ must of course be determined by minimizing the functional $N^{-1}F_c[\{f_\sigma(\Omega)\}]$.

The preceding derivation of (7) and (8) is completely analogous to the derivation of the free energy functional for pure nematogens in Refs. 9 or 10. It is clear, moreover, that (8) could also be obtained by applying the statistical mechanical approach outlined in the Appendix of Ref. 5 to a mixture of hard spherocylinders in which each molecule of component σ moves about in a spatially uniform mean-field potential $\overline{\psi}_\sigma(\Omega,\rho)$ given by (9).

Before proceeding further, it is necessary to evaluate the free energy functional $N^{-1}F_c^*[\{f_\sigma(\Omega)\}]$. Although this cannot be done rigorously, an approximate expression for $N^{-1}F_c^*[\{f_\sigma(\Omega)\}]$ is derived in the following section using scaled particle theory.

III. SCALED PARTICLE THEORY OF MIXTURES OF HARD SPHEROCYLINDERS/SPHERES

The second, third, and fourth terms on the right-hand side of (6), multiplied by Nk_BT give the configurational Helmholtz free energy of a mixture of $\tilde{N}_{11}$ hard spherocylinders of type 1 (i.e., with radius $R_{a_1}a$ and cylindrical length $R_{l_1}l$) with *fixed* orientation $\Omega_1, \tilde{N}_{12}$ hard spherocylinders of type 1 with *fixed* orientation $\Omega_2, \ldots, \tilde{N}_{nm}$ hard spherocylinders of type n with *fixed* orientation Ω_m. (Thermodynamically, this is an $n \times m$ component system.) We shall evaluate this free energy using a straightforward generalization of the scaled particle theory presented in the Appendix to Ref. 8. The required free energy functional $N^{-1}F_c^*[\{f_\sigma(\Omega)\}]$ will then be obtained by adding the term $\ln(4\pi/\Delta\Omega)$, letting $\tilde{s}_{\sigma k} = y_\sigma \tilde{f}_\sigma(\Omega_k)\Delta\Omega$, and converting from sums to integrals.

The central quantity in the scaled particle theory of our mixture of hard spherocylinders with fixed orientations is the work function $W_k(\alpha, \lambda)$, defined as the reversible work of adding a scaled hard spherocylinder of radius αa, cylindrical length λl, and fixed orientation Ω_k to the system at some arbitrary point. It is related to G_c, the configurational Gibbs free energy of the mixture, by the exact equation

$$\frac{G_c}{Nk_BT} = \sum_{\sigma=1}^{n} \sum_{k=1}^{m} \tilde{s}_{\sigma k}[\ln(\tilde{s}_{\sigma k}\rho) + \beta W_k(R_{a_\sigma}, R_{l_\sigma})] . \tag{10}$$

As was done previously,[8,13] we shall approximate $W_k(\alpha, \lambda)$ for all $\alpha \geqslant 0$, $\lambda \geqslant 0$ by

$$W_k(\alpha,\lambda) = C_{00}^{(k)} + C_{10}^{(k)}\alpha + C_{01}^{(k)}\lambda + C_{11}^{(k)}\alpha\lambda + C_{20}^{(k)}\alpha^2 + (\pi a^2 lP)\alpha^2\lambda + (\tfrac{4}{3}\pi a^3 P)\alpha^3 , \tag{11}$$

where P is the hydrostatic pressure, and the coefficients $C_{ij}^{(k)}$ are obtained from

$$C_{ij}^{(k)} = (i!j!)^{-1}\left(\frac{\partial^{(i+j)} W_k^0}{\partial\alpha^i \partial\lambda^j}\right)_{\alpha=0,\lambda=0} \tag{12}$$

and

$$W_k^0 = -k_BT \ln\left(1 - \rho \sum_\sigma \sum_l \tilde{s}_{\sigma l} \mathcal{V}_{\sigma l,k}\right) \tag{13}$$

$$= -k_BT \ln\left(1 - \rho \sum_\sigma \sum_l \tilde{s}_{\sigma l}[\tfrac{4}{3}\pi a^3(R_{a_\sigma} + \alpha)^3 + \pi a^2 l(R_{a\sigma} + \alpha)^2(R_{l\sigma} + \lambda) + 2al^2(R_{a\sigma} + \alpha)R_{l_\sigma}\lambda \times |\sin\gamma(\Omega_l, \Omega_k|]\right) . \tag{14}$$

$\mathcal{V}_{\sigma l,k}$ is the volume excluded to the center of a hard spherocylinder of type σ with orientation Ω_l by the presence of the scaled spherocylinder (with orientation Ω_k) at some fixed point and $\gamma(\Omega_l, \Omega_k)$ is the angle between directions Ω_l and Ω_k.[14] [If one assumes[15] that W_k, $\partial W_k/\partial\alpha$, $\partial W_k/\partial\lambda$, $\partial^2 W_k/\partial\lambda\,\partial\lambda$, and $\partial^2 W_k/\partial\alpha^2$ are all continuous at $\alpha = 0, \lambda = 0$, then W_k^0 may be replaced by W_k in (12).] Equation (11) gives the correct result in the two limiting cases where $W_k(\alpha, \lambda)$ can be evaluated exactly; namely, when $\alpha = 0, \lambda = 0$ (Ref. 15) (i.e., when the scaled particle shrinks to a point) and when $\alpha \to \infty$ and $\lambda \to \infty$ (in which case W_k is simply the reversible PV work required to create a macroscopic spherocylindrical cavity in the fluid). Its use for intermediate values of α and λ is the central approximation of the theory and is equivalent, in a sense, to an interpolation between very large and very small values of α and λ.

After evaluating the coefficients $C_{ij}^{(k)}(\rho, \tilde{s}_{11}, \ldots, \tilde{s}_{nm})$, $W_k(R_{a_\sigma}, R_{l_\sigma})(\sigma = 1, 2, \ldots, n)$ can be obtained from (11) and substituted in (10) to give

$$\frac{G_c}{Nk_BT} = \sum_{\sigma=1}^{n}\sum_{k=1}^{m} \tilde{s}_{\sigma k} \ln\tilde{s}_{\sigma k} + \ln\left(\frac{\rho}{1 - \bar{v}\rho}\right) + \frac{B\rho}{1 - \bar{v}\rho} + \frac{C\rho^2}{(1 - \bar{v}\rho)^2} + \frac{P\bar{v}}{k_BT} , \tag{15}$$

where

$$B = \sum_{\sigma'=1}^{n}\sum_{\sigma=1}^{n} y_\sigma y_{\sigma'} v_\sigma \left[\left(1 + \frac{R_{a_{\sigma'}}}{R_{a_\sigma}}\right)\left(\frac{R_{a_{\sigma'}}}{R_{a_\sigma}}(2 + q_\sigma) + 2r_\sigma \frac{R_{l_{\sigma'}}}{R_{l_\sigma}}\Gamma_{\sigma\sigma'}\right) + \left(\frac{R_{l_{\sigma'}}}{R_{l_\sigma}} + 2\frac{R_{a_{\sigma'}}R_{l_{\sigma'}}}{R_{a_\sigma}R_{l_\sigma}} - \frac{R_{a_{\sigma'}}^2}{R_{a_\sigma}^2}\right)(1 - q_\sigma)\right] , \tag{16}$$

$$C = \sum_{\sigma=1}^{n}\sum_{\sigma'=1}^{n}\sum_{\sigma''=1}^{n} y_\sigma y_{\sigma'} y_{\sigma''} v_\sigma v_{\sigma''} \frac{R_{a_{\sigma'}}}{R_{a_{\sigma''}}}(2 + q_{\sigma''})\left[\frac{R_{l\sigma'}}{R_{l\sigma}}(1 - q_\sigma + 2r_\sigma\Gamma_{\sigma\sigma'}) + \frac{R_{a_{\sigma'}}}{R_{a_\sigma}}\left(1 + \frac{q_\sigma}{2}\right)\right] , \tag{17}$$

$$\bar{v} = \sum_{\sigma=1}^{n} y_\sigma v_\sigma ,$$

$$v_\sigma = \pi a^2 l R_{a_\sigma}^2 R_{l_\sigma} + \tfrac{4}{3}\pi a^3 R_{a_\sigma}^3 ,$$

$$q_\sigma = \tfrac{4}{3}\pi a^3 R_{a_\sigma}^3 / v_\sigma ,$$

$$r_\sigma = al^2 R_{a_\sigma} R_{l_\sigma}^2 / v_\sigma ,$$

$$\Gamma_{\sigma\sigma'} = \sum_{k=1}^{m}\sum_{l=1}^{m} \tilde{s}_{\sigma k}\tilde{s}_{\sigma' l} |\sin\gamma(\Omega_k, \Omega_l)| .$$

The pressure P is determined using (15) and the

Gibbs-Duhem equation

$$\left(\frac{\partial P}{\partial \rho}\right)_{\bar{s}_{11},\ldots,\bar{s}_{nm},T} = \rho\left(\frac{\partial G_c}{\partial \rho}\right)_{\bar{s}_{11},\ldots,\bar{s}_{nm},T} \tag{18}$$

with the result

$$\frac{P}{k_B T} = \frac{\rho}{1-\bar{v}\rho} + \frac{B\rho^2}{2(1-\bar{v}\rho)^2} + \frac{2C\rho^3}{3(1-\bar{v}\rho)^3}\ . \tag{19}$$

The configurational Helmholtz free energy of this system with fixed orientations is then obtained from (15), (19), and the thermodynamic relation $N^{-1}F = N^{-1}G - P/\rho$. Finally, adding $\ln(4\pi/\Delta\Omega)$ to the resulting expression for $N^{-1}F_c$, substituting $y_\sigma \tilde{f}_\sigma(\Omega_k)\Delta\Omega$ for $\bar{s}_{\sigma k}$, and taking the limit $\Delta\Omega \to d\Omega$, we obtain the scaled particle equation for the free energy functional $N^{-1}F_c^*[\{\tilde{f}_\sigma(\Omega)\}]$ needed in (8); namely,

$$N^{-1}F_c^*[\{\tilde{f}_\sigma(\Omega)\}] = k_B T\left[\sum_{\sigma=1}^{n} y_\sigma \ln y_\sigma + \sum_{\sigma=1}^{n} y_\sigma \int d\Omega\, \tilde{f}_\sigma(\Omega)\ln[4\pi\tilde{f}_\sigma(\Omega)] - 1 + \ln\left(\frac{\rho}{1-\bar{v}\rho}\right) + \frac{B\rho}{2(1-\bar{v}\rho)} + \frac{C\rho^2}{3(1-\bar{v}\rho)^2}\right], \tag{20}$$

where B and C are given by (16) and (17), respectively, and

$$\Gamma_{\sigma\sigma'} = \int\int \tilde{f}_\sigma(\Omega)\tilde{f}_{\sigma'}(\Omega')\,|\sin\gamma(\Omega,\Omega')|\,d\Omega\, d\Omega'\ . \tag{21}$$

[Recall that $\gamma(\Omega,\Omega')$ is the angle between directions Ω and Ω'.]

IV. GENERAL EQUATIONS

Substituting (20) in (8) yields

$$N^{-1}F_c = k_B T\left[\sum_{\sigma=1}^{n} y_\sigma \ln y_\sigma + \sum_{\sigma=1}^{n} y_\sigma \int d\Omega\, \tilde{f}_\sigma(\Omega)\ln[4\pi\tilde{f}_\sigma(\Omega)] - 1 + \ln\left(\frac{\rho}{1-\bar{v}\rho}\right) + \frac{\rho B[\{\tilde{f}_\sigma\}]}{2(1-\bar{v}\rho)} + \frac{\rho^2 C[\{\tilde{f}_\sigma(\Omega)\}]}{3(1-\bar{v}\rho)^2}\right] + \frac{1}{2}\sum_{\sigma=1}^{n} y_\sigma \int d\Omega\, \tilde{f}_\sigma(\Omega)\bar{\psi}_\sigma(\Omega)\ . \tag{22}$$

The one-particle orientational distribution functions $\tilde{f}_1(\Omega), \tilde{f}_2(\Omega), \ldots, \tilde{f}_n(\Omega)$ must be obtained by minimizing $N^{-1}F_c[f_1(\Omega), f_2(\Omega), \ldots, f_n(\Omega)]$ subject to the normalization constraints

$$\int f_\sigma(\Omega)\,d\Omega = 1 \quad (\sigma = 1, 2, \ldots, n)\ . \tag{23}$$

This produces the following set of coupled nonlinear integral equations, which must be solved numerically:

$$\begin{aligned} 0 = {} & \ln[4\pi f_\sigma(\Omega)] + 1 - \frac{\alpha_\sigma}{y_\sigma} \\ & + \frac{2r_\sigma v_\sigma \rho}{1-\bar{v}\rho}\left[\sum_{\sigma'=1}^{n} y_{\sigma'}\frac{R_{l_{\sigma'}}}{R_{l_\sigma}}\left(1 + \frac{R_{a_{\sigma'}}}{R_{a_\sigma}}\,\frac{\frac{2}{3}\sum_{\sigma''=1}^{n} y_{\sigma''}(R_{a_{\sigma'}}/R_{a_{\sigma''}})(2+q_{\sigma''})v_{\sigma''}\rho}{1-\bar{v}\rho}\right)\int f_{\sigma'}(\Omega')\,|\sin\gamma(\Omega,\Omega')|\,d\Omega'\right] \\ & + \beta\rho\sum_{\sigma'=1}^{n} y_{\sigma'}\int d\Omega'\, f_{\sigma'}(\Omega')I_{\sigma\sigma'}(\Omega,\Omega') \quad (\sigma = 1, 2, \ldots, n)\ , \end{aligned} \tag{24}$$

where α_σ is a Lagrange multiplier and

$$I_{\sigma\sigma'}(\Omega,\Omega') = \int d\vec{r}\, \exp[-\beta v^*_{\sigma\sigma'}(\vec{r},\Omega,\Omega')]\, v^{(a)}_{\sigma\sigma'}(\vec{r},\Omega,\Omega')\ .$$

Equations for all equilibrium thermodynamic quantities can be derived from (22) and (24). For example, those for the first derivatives of the free energy are

$$\frac{S_c}{Nk_B} = -\frac{F_c^*[\{\tilde{f}_\sigma(\Omega)\}]}{Nk_B T} \tag{25}$$

$$\frac{P}{k_B T} = \frac{\rho}{1-\bar{v}\rho} + \frac{\rho^2 B[\{\tilde{f}_\sigma(\Omega)\}]}{2(1-\bar{v}\rho)^2} + \frac{2\rho^3 C[\{\tilde{f}_\sigma(\Omega)\}]}{3(1-\bar{v}\rho)^3} + \tfrac{1}{2}\beta\rho\sum_{\sigma=1}^{n} y_\sigma \int d\Omega\, \tilde{f}_\sigma(\Omega)\bar{\psi}_\sigma(\Omega) \tag{26}$$

and

$$\frac{\mu_\sigma}{k_B T} = \frac{P^* v_\sigma}{k_B T} + \int d\Omega\, f_\sigma(\Omega)\ln[4\pi f_\sigma(\Omega)] + \ln\left(\frac{y_\sigma \rho}{1-\bar{v}\rho}\right) + \frac{\rho D_\sigma[\{\tilde{f}_\sigma(\Omega)\}]}{(1-\bar{v}\rho)^2} + \frac{\rho^2 E_\sigma[\{\tilde{f}_\sigma(\Omega)\}]}{(1-\bar{v}\rho)^2} + \beta\int \tilde{f}_\sigma(\Omega)\bar{\psi}_\sigma(\Omega)\,d\Omega \tag{27}$$

where P^*/k_BT represents the first three terms on the right-hand side of (26), F_c^*/Nk_BT represents the terms in curly brackets in (22),

$$D_\sigma = 6y_\sigma v_\sigma \rho(1+\tfrac{2}{3}r_\sigma\Gamma_{\sigma\sigma}) + \sum_{\sigma'\neq\sigma} y_{\sigma'} v_\sigma \rho \left[\left(1+\frac{R_{a_{\sigma'}}}{R_{a_\sigma}}\right)\left(\frac{R_{a_{\sigma'}}}{R_{a_\sigma}}(2+q_\sigma)+2r_\sigma\frac{R_{l_\sigma}}{R_{l_\sigma}}\Gamma_{\sigma\sigma'}\right)+(1-q_\sigma)\left(\frac{R_{l_\sigma}}{R_{l_\sigma}}+\frac{2R_{a_{\sigma'}}R_{l_{\sigma'}}}{R_{a_\sigma}R_{l_\sigma}}-\frac{R^2_{a_{\sigma'}}}{R^2_{a_\sigma}}\right)\right] \tag{28}$$

and

$$\begin{aligned}E_\sigma = {} & 2v_\sigma^2 y_\sigma^2\rho^2(2+q_\sigma)(1-\tfrac{1}{4}q_\sigma+r_\sigma\Gamma_{\sigma\sigma})+\frac{4}{3}\sum_{\sigma'\neq\sigma} y_\sigma y_{\sigma'}\rho^2\left[v_\sigma^2(2+q_\sigma)\frac{R_{a_{\sigma'}}}{R_{a_\sigma}}\left(\frac{R_{l_{\sigma'}}}{R_{l_\sigma}}(1-q_\sigma+2r_\sigma\Gamma_{\sigma\sigma'})+\frac{R_{a_{\sigma'}}}{R_{a_\sigma}}(1+\tfrac{1}{2}q_\sigma)\right)\right.\\ & \left. + v_\sigma v_{\sigma'}\frac{R_{a_\sigma}}{R_{a_{\sigma'}}}(2+q_{\sigma'})(1-\tfrac{1}{2}q_\sigma+2r_\sigma\Gamma_{\sigma\sigma})\right]\\ & +\frac{1}{3}\sum_{\sigma'\neq\sigma}\sum_{\sigma''\neq\sigma} y_{\sigma'}y_{\sigma''}\rho^2\left[v_\sigma v_{\sigma'}\frac{R_{a_{\sigma''}}}{R_{a_\sigma}}(2+q_{\sigma'})\left(\frac{R_{l_{\sigma''}}}{R_{l_\sigma}}(1-q_\sigma+2r_\sigma\Gamma_{\sigma\sigma''})+\frac{R_{a_{\sigma''}}}{R_{a_\sigma}}(1+\tfrac{1}{2}q_\sigma)\right)\right.\\ & + v_{\sigma'}v_{\sigma''}\frac{R_{a_\sigma}}{R_{a_{\sigma''}}}(2+q_{\sigma''})\left(\frac{R_{l_\sigma}}{R_{l_{\sigma'}}}(1-q_{\sigma'}+2r_{\sigma'}\Gamma_{\sigma\sigma'})+\frac{R_{a_\sigma}}{R_{a_{\sigma'}}}(1+\tfrac{1}{2}q_{\sigma'})\right)\\ & \left. + v_\sigma v_{\sigma''}\frac{R_{a_{\sigma'}}}{R_{a_\sigma}}(2+q_\sigma)\left(\frac{R_{l_{\sigma'}}}{R_{l_{\sigma''}}}(1-q_{\sigma''}+2r_{\sigma''}\Gamma_{\sigma'\sigma''})+\frac{R_{a_{\sigma'}}}{R_{a_{\sigma''}}}(1+\tfrac{1}{2}q_{\sigma''})\right)\right] .\end{aligned} \tag{29}$$

In order to determine the density and distribution of molecular orientations in a given system at a particular T and P, it is necessary to solve (24) and (26) simultaneously. Finally, as was noted in Sec. II, in order to treat a mixture in which one or more components have spherical molecular hard cores, it is necessary only to set $R_{l_\sigma}=0$ for all such components.

V. POSSIBLE APPLICATIONS AND EXTENSIONS

There are clearly a large number of nematogenic systems to which our theory can, in principle, be applied. Many of these fit into one of the three categories discussed briefly below.

a. Solutions of effectively spherical solutes in nematogenic solvents: The most interesting aspects of such solutions concern the solute-induced nematic → isotropic phase transition and how it depends on the size of the solute molecules and on solute-solvent attractions. As was noted in the Introduction, binary solutions of this type are considered in detail in Paper II of this series of papers, where it is shown that the calculated temperature-mole fraction phase diagrams are in rather good agreement with experimental data.

b. Mixtures of nematogens: Although the nematic ⇌ isotropic phase equilibrium in mixtures of similar homologues (e.g., MBBA-EBBA) is not very interesting,[16] it should be of interest to study mixtures of rodlike molecules with markedly different effective diameters/length-to-breadth ratios.

c. Solutions of long rodlike macromolecules (e.g., tobacco mosaic virus, PBLG, "Kevlar," nylons, biopolymers) *in suitable solvents*. Although the formation of lyotropic nematic (or cholesteric[17]) mesophases in such systems has been studied theoretically by a number of authors,[18] beginning with Onsager[19] in 1949, none of these treatments took into account the polydispersivity of the polymers used in experimental studies. Our theory, on the other hand, clearly can treat polydisperse polymer solutions and could, in fact, be used to study the effects of the distribution of molecular lengths on the properties of the ordered phase and on the nematic-isotropic phase separation.

At present, our theory applies only to mixtures of cylindrically or spherically symmetric molecules because the scaled particle derivation of Sec. III is based on hard spherocylinders. It should be possible, however, to use the scaled particle approach to evaluate the free energy functional $N^{-1}F_c^*[\{f_\sigma(\Omega)\}]$ for mixtures of hard particles with a variety of other simple molecular shapes, and thus extend the Van der Waals theory to other kinds of systems. The required modifications in the scaled particle derivation would be (i) choosing an appropriate set of scaling parameters to replace α and λ; (ii) replacing (14) by the correct equation for W_k^0 for the molecular shapes of interest. This would require deriving a general expression (valid for all σ) for $\mathcal{V}_{\sigma l,k}$ the pair excluded volume for a scaled particle with orientation Ω_k and a molecule of component σ with orientation Ω_l. (iii) replacing (11) by an appropriate expansion of W_k in terms of the chosen scaling parameters. The first term in the expansion would be $-k_BT\ln(1-\bar{v}\rho)$, where $\bar{v}$ is the average molecular volume; the last term(s) would be Pv_{sp}, where v_{sp} is the volume of the scaled particle; the coefficients of intermediate terms would be obtained from (12). (iv) replacing $W_k(R_{a_\sigma},R_{l_\sigma})$ by the appropriate symbol for the work function for a "full-grown" molecule of component σ with orientation Ω_k.

The derivation of $N^{-1}F_c^*[\{f_\sigma(\Omega)\}]$ would then proceed as in Sec. III. The remainder of the theory; i.e., (8) and its derivation, is applicable to any n-component mixture of rodlike molecules with one minor modification: if the molecular hard cores are not cylindrically symmetric, Ω represents a set of three Euler angles and 4π must be replaced by $8\pi^2$ in (1)–(8). It might be particularly interesting to modify the theory in order to consider (i) solutions of relatively flat, disklike solute molecules in nematogenic solvents and (ii) the effects of deviations from cylindrical molecular symmetry on the properties of nematogenic systems.

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[1] See, for example, (a) M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, J. Math. Phys. 4, 216 (1963); (b) J. L. Lebowitz, G. Stell, and S. Baer, J. Math. Phys. 6, 1282 (1965); (c) J. L. Lebowitz and O. Penrose, J. Math. Phys. 7, 98 (1966).

[2] H. C. Longuet-Higgins and B. Widom, Mol. Phys. 8, 549 (1964).

[3] B. J. Alder and T. E. Wainwright, J. Chem. Phys. 33, 1439 (1960).

[4] R. Alben, Mol. Cryst. Liq. Cryst. 13, 193 (1971) (section on the Steric Model, pp. 214–217).

[5] W. M. Gelbart and B. A. Baron, J. Chem. Phys. 66, 207 (1977).

[6] B. A. Baron and W. M. Gelbart, J. Chem. Phys. 67, 5795 (1977).

[7] W. M. Gelbart and A. Gelbart, Mol. Phys. 33, 1387 (1977).

[8] M. A. Cotter, J. Chem. Phys. 66, 1098 (1977).

[9] M. A. Cotter, J. Chem. Phys. 66, 4710 (1977); 67, 4268 (1977).

[10] M. A. Cotter, "The Van der Waals Approach to Nematic Liquids," in *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic, London, to be published).

[11] PAA is the commonly used abbreviation for p-azoxyanisole or, more properly, 4, 4′-dimethoxyazoxy-benzene.

[12] Ω represents the set of two angles needed to specify the orientation of a cylindrically symmetric particle.

[13] For a more detailed discussion of the scaled particle theory of hard spherocylinders, see M. A. Cotter, "Hard Particle Theories of Nematic Liquids," in *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic, London, to be published).

[14] The pair excluded volume $\mathcal{V}$ for two hard spherocylinders was first derived by Onsager in Ref. 19.

[15] When the scaled particle is sufficiently small so that it cannot simultaneously be in contact with any three ordinary molecules in the system, it can be shown that $\exp(-\beta W_k)=1-\rho\sum_\sigma\sum_l s_{\sigma l}\mathcal{V}_{\sigma l,k}+F_2^{(k)}(\alpha,\lambda,\rho)$ where

$$F_2^{(k)}=\tfrac{1}{2}\rho^2\sum_\sigma\sum_{\sigma'}\sum_l\sum_j s_{\sigma l}s_{\sigma' j}\times\int\mathcal{V}_{\sigma' j,k}\,d\vec{r}\int\mathcal{V}_{\sigma l,k}\,d\vec{r}\,g^{(2)}_{\sigma l,\sigma' j}(\vec{r}-\vec{r}\,').$$

$g^{(2)}{}_{\sigma l,\sigma' j}(\vec{r}-\vec{r}\,')$ is the pair correlation function for two molecules, one of type σ with fixed orientation Ω_l, the other of type σ' with fixed orientation Ω_j; and the integrations with respect to $\vec{r}$ and $\vec{r}\,'$ are over all positions excluded to the center of a molecule of type σ or σ', respectively, by the presence of the scaled particle at a fixed point. For a one-component system of hard spherocylinders, it can be shown that $F_2^{(k)}=\partial F_2^{(k)}/\partial\alpha=\partial F_2^{(k)}/\partial\lambda=\partial^2F_2^{(k)}/\partial\lambda\partial\alpha=\partial^2F_2^{(k)}/\partial\alpha^2=0$ at $\alpha=0,\lambda=0$. We are assuming that these quantities also vanish for our multicomponent system. (This appears to be very likely, but a general proof would be exceedingly lengthy and tedious.) For a further discussion of these points, see the work cited in Ref. 13.

[16] MBBA and EBBA are abbreviations for p-methoxybenzylidene n-butylaniline and p-ethoxybenzylidene n-butylaniline, respectively. With respect to the nematic ⇌ isotropic phase equilibrium, mixtures of these two compounds, and of a number of similar homologous pairs of nematogens, behave ideally at all compositions.

[17] With respect to their bulk thermodynamic behavior, cholesterogenic and nematogenic systems are equivalent since cholesteric twist energies are too small to be thermodynamically significant.

[18] For a discussion of this work, see J. P. Straley, Mol. Cryst. Liq. Cryst. 22, 333 (1973).

[19] L. Onsager, Ann. N. Y. Acad. Sci. 51, 627 (1949).