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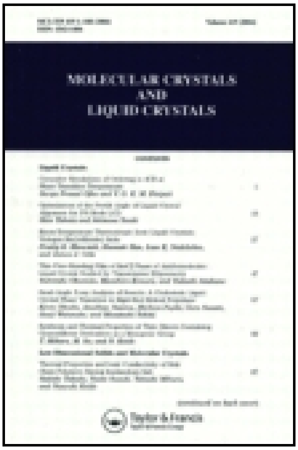

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Simplified Onsager Theory of Lyotropic Liquid Crystals

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Simplified Onsager Theory of Lyotropic Liquid Crystals

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The Onsager theory for isotropic–anisotropic phase separation in a solution of rodlike particles is revised. The Onsager trial function of orientation distribution,

$$f(\theta) = \frac{\alpha}{4\,\pi \sinh \alpha} \cosh\,(\alpha \cos \theta), \quad \alpha > 0$$

is replaced by

$$f(\theta) = \frac{2p + 1}{4\pi} \cos^{2p}\theta, \quad p = 0, 1, 2, 3, \ldots .$$

Here θ means the angle between the axis of rodlike particles and the symmetry axis of the anisotropic phase. The new distribution function is simpler; nevertheless, the numerical results obtained with it are closer to the "exact" values obtained by Lekkerkerker *et al.* on the basis of a series of Legendre polynomials.

Keywords: lyotropic liquid crystals, Onsager theory, rodlike particle

1. INTRODUCTION

Zocher[1] discovered that solutions of rodlike particles exceeding a critical concentration undergo a phase separation into isotropic and anisotropic phases, coexisting in equilibrium. Stanley[2] found that a solution of two percent tobacco mosaic virus forms two phases. In the anisotropic phase, which is usually called a lyotropic liquid crystal, the particles have a preferred orientation. This phase separation was first explained by Onsager[3] as the result of the competition between the orientational entropy, which favors disorder, and the orientation-dependent excluded volume of rodlike particles, which favors order. The Onsager theory is based on the assumption that the length to diameter ratio, L/D, of the rodlike particle is sufficiently large. In fact, the theory agrees with recent observations made by Nakamura and Okano[4] using bacterial virus fd for which L/D is approximately 100. The statistical physics of lyotropic liquid crystals is reviewed by Odijk.[5]

2. THEORY OF ISOTROPIC SOLUTION OF RODLIKE PARTICLES

Van't Hoff's Law for the osmotic pressure ΔP of a dilute solution, where n solute particles are in a volume V at temperature T, is of the form

$$\Delta P = nkT/V, \tag{1}$$

k being the Boltzmann constant. This law is related to the mixing entropy between the solute particles and solvent molecules:

$$\Delta S = kn\,[1 + \ln(N/n)],$$

where N is the number of solvent molecules in the volume V ($n << N$). Let v_0 denote the volume per solvent molecule: $v_0 = V/N$. Then the excess free energy

$$\Delta F = -T\Delta S$$

due to the mixing entropy can be expressed, in terms of V, n, T, as follows

$$\Delta F = kTn\,[1 + \ln(V/nv_0)].$$

Equation (1) agrees with the thermodynamic relation

$$\Delta P = -\,(\partial \Delta F/\partial V)_{n,\,T}. \tag{2}$$

Van't Hoff's Law resembles the equation of the state of an ideal gas. The gas pressure is replaced by osmotic pressure, the gas volume by the solution volume, and the number of molecules in the gas by the number of particles of solute.

Van't Hoff's formula is applicable to dilute solutions where interactions between solute particles are negligible. When these interactions are not negligible, the formula for the osmotic pressure

$$\Delta P = kT\left[\frac{n}{V} + \frac{n^2}{V^2}B + \frac{n^3}{V^3}C + \cdots\right] \tag{3}$$

still resembles the equation of the state of a real gas. Here B and C, which are functions of the temperature in general, are called the second and the third virial coefficient, respectively. It is to be noted, however, that the intermolecular potential in a gas should be replaced by an effective potential energy between solute particles surrounded by solvent molecules.

When the solute particle is a long rigid rod of length L and diameter D (L<<D), the second virial coefficient is given by one half of the excluded volume:

$$B = \mathrm{DL}^2 \langle \sin \gamma \rangle.$$

Here γ is the angle between two rods, and angular brackets mean the average over the orientation distribution of solute particles. For the isotropic distribution

$$\langle \sin \gamma \rangle = \int_0^\pi \sin \theta \; 2\pi \sin \theta \; d\theta / 4\pi = \pi/4.$$

The next term in Equation (3), which is proportional to $n^3V^{-3}D^3L^3$, can be neglected by virtue of the condition D<<L. Hence we have

$$\Delta P = kT\left(\frac{n}{V} + \frac{\pi}{4}DL^2\frac{n^2}{V^2}\right). \tag{4}$$

According to Equation (2), this osmotic pressure is related to the free energy given by

$$\Delta F = nkT\,[\text{const.} + \ln(DL^2\, n/V) + (\pi/4)\, DL^2\, n/V]. \tag{5}$$

Here "const." is a term which is independent of V and n.

3. SIMPLIFIED TRIAL FUNCTION FOR THE ORIENTATION DISTRIBUTION

For an anisotropic solution of rodlike particles, the author proposes the trial function

$$f(\theta) = \frac{2p+1}{4\pi}\cos^{2p}\theta, \qquad \text{where } p = 0, 1, 2, 3, \ldots. \tag{6}$$

for the orientation distribution of solute particles. The case $p=0$ corresponds to the isotropic distribution. This function is normalized as

$$\int_0^\pi f(\theta)\; 2\pi \sin\theta \; d\theta = 1. \tag{7}$$

Our trial function is simpler than Onsager's

$$f(\theta) = (\alpha/4\pi \sinh \alpha) \cosh(\alpha \cos\theta), \qquad \alpha > 0.$$

Nevertheless, numerical results obtained on the basis of Equation (6) are closer to the "exact" values obtained by Lekkerkerker *et al.*[6] on the basis of a series of Legendre polynomials (see Table II).

The orientational order parameter, $\langle P_2(\cos\theta)\rangle$, is calculated to be

$$\int_0^\pi \frac{1}{2}(3\cos^2\theta - 1)\, f(\theta)\; 2\pi \sin\theta \; d\theta = \frac{2p}{2p+3}. \tag{8}$$

Let σ denote the orientational entropy (divided by $-k$):

$$\sigma = \int_O^{\pi} f(\theta) \ln [4\pi f(\theta)] \, 2\pi \sin \theta \, d\theta.$$

Then

$$\sigma = \ln (2p + 1) - \frac{2p}{2p + 1}. \tag{9}$$

Hence the excess free energy, Equation (5), is generalized to

$$\Delta F = nkT \, [\text{const.} + \ln (\mathrm{DL}^2 \, n/V) + \sigma + \langle \sin \gamma \rangle \, \mathrm{DL}^2 \, n/V]. \tag{10}$$

Here $\langle \sin \gamma \rangle$, which is equal to $\pi/4$ in the isotropic phase, is the following

$$\int_O^{2\pi} \int_O^{\pi} \int_O^{\pi} \sin \gamma f(\theta_1) f(\theta_2) \, 2\pi \sin \theta_1 \sin \theta_2 d\theta_1 d\theta_2 d(\phi_2 - \phi_1),$$

γ being the angle between two axial orientations (θ_1, ϕ_1) and (θ_2, ϕ_2):

$$\cos \gamma = \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos(\phi_2 - \phi_1). \tag{11}$$

4. NUMERICAL CALCULATIONS

Table I gives the calculated value of $\langle \sin \gamma \rangle$ for each $2p$, together with the values of order parameter Equation (8) and orientational entropy Equation (9).

The power index $2p$ which minimizes ΔF, Equation (10), is the following:

$2p = 0$. for $0.205 < V/n\mathrm{DL}^2$,

$2p = 12$ for $0.19 < V/n\mathrm{DL}^2 < 0.205$,

$2p = 14$ for $0.17 < V/n\mathrm{DL}^2 < 0.19$.

Figure 1 shows $\Delta F/nkT$ − const. or

$$\ln (\mathrm{DL}^2 \, n/V) + \sigma + \langle \sin \gamma \rangle \, \mathrm{DL}^2 \, n/V \tag{12}$$

thus obtained as a function of $V/n\mathrm{DL}^2$. A part of the common tangent line between two points of contact, for which

$$0.178 \leqq V/n\mathrm{DL}^2 \leqq 0.232,$$

indicates coexistence between the isotropic phase and an anisotropic phase with

TABLE I

Calculated values for each $2p$

$2p$	$\langle P_2(\cos\theta)\rangle$	σ	$\langle \sin\gamma\rangle$
0	0.000	0.000	0.785
2	0.400	0.432	0.712
4	0.571	0.809	0.630
6	0.667	1.089	0.566
8	0.727	1.308	0.525
10	0.769	1.489	0.477
12	0.800	1.642	0.4465
14	0.824	1.775	0.421
16	0.842	1.892	0.401

$2p = 14$, the osmotic pressures in both phases being equal on account of Equation (2). The ratio of the density of solute particles in the anisotropic phase to that in the isotropic phase is

$$(n/V)_A/(n/V)_I = 0.232/0.178 = 1.30. \tag{13}$$

5. COMPARISON WITH RESULTS OBTAINED BY PREVIOUS AUTHORS

In Table II the present results for density ratio, order parameter, orientational entropy, and $4\langle\sin\gamma\rangle/\pi$ in the coexisting anisotropic phase, are compared with the

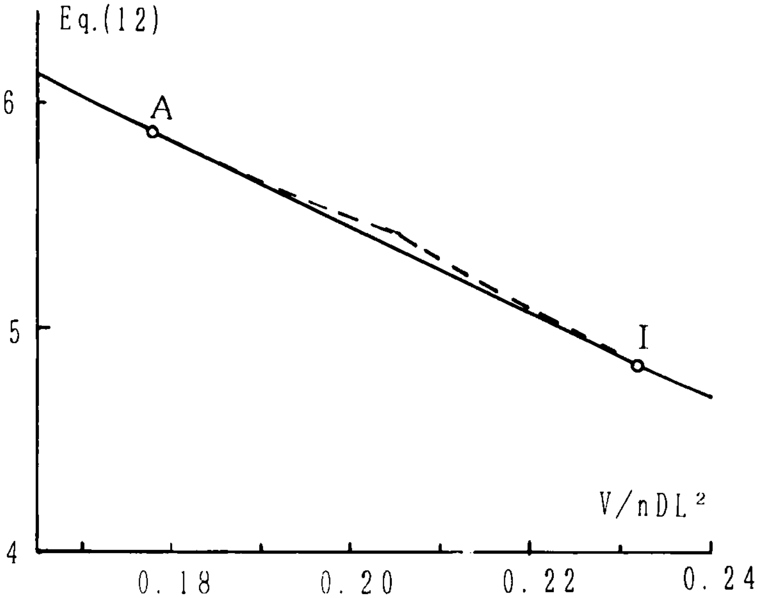

FIGURE 1 The free energy, Equation (12), as a function of the specific volume, V/nDL^2. Points A and I are anisotropic and isotropic phases coexisting in equilibrium.

TABLE II

Comparison with results by other authors

	density ratio	$\langle P_2(\cos\theta)\rangle$	σ	$\langle\sin\gamma\rangle 4/\pi$
Onsager	1.34	0.848	1.92	0.497
present result	1.30	0.824	1.77	0.536
"exact"	1.274	0.792	1.601	0.565
Lasher	1.26	0.784	1.56	0.577

results obtained by Onsager and with "exact" values obtained by Lekkerkerker *et al.* using a particular expansion of $f(\theta)$ in Legendre polynomials. Our results lie between Onsager's and "exact" values.

Lasher[7] expands directly the orientation distribution in a series of Legendre polynomials:

$$f(\theta) = \frac{1}{4\pi}\left[1 + \sum_{n=1}^{\infty} a_n P_{2n}(\cos\theta)\right]$$

and the coefficients a_n, $n=1, 2, 3, \ldots$, are obtained by minimizing the free energy. His results obtained by truncating the series at $n=7$ are included in Table II.

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