

On the isotropic-liquid crystal phase separation in a solution of rodlike particles of different lengths

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(Received 28 June 1983; accepted 10 October 1983)

The Onsager theory for the isotropic-anisotropic phase separation in a solution of rodlike particles is extended to the case of mixtures of such particles with different lengths. The concentration, composition, order parameters, and orientation dependent thermodynamic quantities of the coexisting phases are calculated for the case of a mixture of rods of two different lengths for different length ratios. It is found that there is a significantly higher mole fraction of the longer rods in the anisotropic phase than in the isotropic phase. The order parameter of the longer rods is higher than in the one component case, whereas the order parameter of the shorter rods first increases and then decreases as the mole fraction of the longer rods is increased. All these features are accentuated as the length ratio of the two kinds of rods increases.

I. INTRODUCTION

Zocher¹ discovered that solutions of rodlike particles exceeding a critical concentration undergo a phase separation into isotropic and anisotropic phases, coexisting in equilibrium. In the latter phase, that is usually referred to as a lyotropic liquid crystal, the particles have a preferred orientation. This phase separation was first explained by Onsager² as the result of the competition between the orientational entropy that favors disorder and the entropy effect associated with the orientation-dependent excluded volume of rodlike particles that favors order. The available experimental data for systems that approximate suspensions of long rods have been reviewed by Straley³ who concludes that the measured phase separation curves are in qualitative agreement with the Onsager theory.

Without performing the actual calculations, Onsager predicted that in the case of solutions of rodlike particles with different lengths the longer particles will collect preferentially in the anisotropic phase and that they will be more perfectly orientationally ordered than the shorter particles. The first prediction was borne out by the experimental work of Oster⁴ who studied the isotropic-anisotropic phase equilibrium in the case of monodisperse and polydisperse end-to-end aggregated tobacco mosaic virus (TMV). Oster found that in the case of normal TMV the weight average in the isotropic and anisotropic phase is the same whereas in the aggregated case the weight average molecular weight in the anisotropic phase is 50% higher than in the isotropic phase. This fractionation effect with the higher molecular weight fraction being in the anisotropic phase has also been observed for polydisperse solutions of polybenzamides⁵ and polyphenyleneterephthalamides.⁶

In the present work we extend the Onsager treatment for monodisperse systems to solutions of rodlike particles with the same diameter but two different lengths. It is found that the Onsager predictions about polydisperse solutions

(i.e., the fractionation effect and the more perfect orientational ordering of the longer particles) are indeed borne out by the quantitative elaboration of the theory.

In Sec. II we summarize the Onsager theory for the isotropic-anisotropic phase separation for a monodisperse solution of rodlike particles and in Sec. III we extend this theory to the case of a system consisting of rods of two different lengths. The predictions for the compositions, concentrations, order parameters, and thermodynamic properties of the coexisting phases for different length ratios are presented in Sec. IV. The conclusions that can be drawn from the present calculations are collected in Sec. V.

II. ONSAGER THEORY FOR THE PHASE SEPARATION IN A SOLUTION OF LONG RODS

The starting point of the Onsager theory² for the phase separation in a solution of N long rods of length L and diameter D ($L \gg D$) is the Helmholtz free energy of the solution in dialytic equilibrium with the solvent at temperature T :

$$\frac{\Delta F}{Nk_B T} = \frac{F(\text{solution}) - F(\text{solvent})}{Nk_B T} = \frac{\mu^0(T, \mu_0)}{k_B T} - 1 + \ln c + \sigma(f) + bc\rho(f). \quad (1)$$

Here $\mu^0(T, \mu_0)$ represents the standard chemical potential of the particles at temperature T in a solvent with chemical potential μ_0 , $c = (N/V)$ is the number density, $b = (\pi/4)L^2 D$ is the average excluded volume of two long rods with random orientations and σ and ρ are abbreviations for the following functionals of the one particle orientation distribution function $f(\Omega)$:

$$\sigma(f) = \int f(\Omega) \ln 4\pi f(\Omega) d\Omega, \quad (2)$$

$$\rho(f) = \frac{4}{\pi} \iint \sin\gamma(\Omega', \Omega) f(\Omega) f(\Omega') d\Omega d\Omega'. \quad (3)$$

Note that in the free energy (1) concentration contributions of c^2 and higher order have been neglected. The justification² for this is that for long rods the ratio $B_3/B_2^2 \ll 1$ (B_2 and B_3 are

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the second and third virial coefficient). Straley⁷ has argued that this truncation can be justified quantitatively only for very long rods ($L/D > 100$) although it probably produces qualitatively reliable results for considerably shorter rods ($L/D \gtrsim 20$). To obtain meaningful results for shorter rods one should start from a more sophisticated form of the free energy, as can be obtained, e.g., from scaled particle theory^{8,9} or alternative expansions of the free energy that implicitly contain powers of the concentration to all orders.¹⁰

The orientation distribution function is determined by minimizing the free energy with respect to variations in this distribution. This leads to the integral equation

$$\ln 4\pi f(\Omega) = C - bc \frac{8}{\pi} \int \sin \gamma(\Omega, \Omega') f(\Omega') d\Omega', \quad (4)$$

where C is a constant that is determined by applying the normalization condition

$$\int f(\Omega) d\Omega = 1. \quad (5)$$

The function $f^0(\Omega) = (1/4\pi)$ corresponding to a uniform distribution of angles, i.e., the isotropic phase, is a solution of Eq. (4) for all values of bc . For this isotropic orientation distribution function $\sigma = 0$ and $\rho = 1$ and thus the orientation distribution function dependent part of the free energy has the value $Nk_B T bc$. If we now consider a uniaxial anisotropic phase described by an orientation distribution function $f(\theta)$ with maxima at $\theta = 0$ and $\theta = \pi$ one easily sees from Eqs. (2) and (3) that $\sigma > 0$ and $0 < \rho < 1$. This means that for bc sufficiently large such a peaked orientation distribution function can minimize the free energy. Kayser and Raveché¹¹ showed that the bifurcation occurs for $bc = 4$. Rather than attempting to solve the integral equation (4), Onsager attacked the minimization of the free energy directly using the following trial orientation distribution:

$$f(\theta) = \frac{\alpha}{4\pi \sinh \alpha} \cosh(\alpha \cos \theta). \quad (6)$$

The functions $\sigma(\alpha)$ and $\rho(\alpha)$ can be expressed in terms of simple known functions. For small values of α one can write the power series²

$$\sigma(\alpha) = \frac{\alpha^4}{90} - \dots, \quad (|\alpha| < \pi/2), \quad (7)$$

$$\rho(\alpha) = 1 - \frac{\alpha^4}{90.4} + \dots (|\alpha| < \pi). \quad (8)$$

Minimizing the orientation dependent part of the free energy $\sigma(\alpha) + bc \rho(\alpha)$, with respect to α , one finds using Eqs. (7) and (8) that $\alpha > 0$ represents a minimum for $bc > 4$, i.e., the bifurcation point of the Onsager trial function corresponds with the exact bifurcation point.¹²

Once it has been established that above a certain density it is favorable for the system to form an anisotropic phase the concentrations of the coexisting isotropic and anisotropic phase are found by solving the coexistence conditions, i.e., the equality of (osmotic) pressure and chemical potential μ of the dissolved particles in the two coexisting phases

$$\Pi = - \left(\frac{\partial \Delta F}{\partial V} \right)_{T, \mu, N} = k_B T c (1 + bc \rho), \quad (9)$$

$$\mu = - \left(\frac{\partial \Delta F}{\partial N} \right)_{T, \mu, V} = \mu^0 + k_B T [\ln c + \sigma + 2bc \rho]. \quad (10)$$

At this point it is convenient to introduce dimensionless variables. In the following c denotes the dimensionless concentration bc , Π the dimensionless osmotic pressure ($b\Pi/k_B T$), and μ the dimensionless chemical potential

$$\frac{\mu - \mu^0}{k_B T} + \ln b.$$

Using these dimensionless variables and taking into account that in the isotropic phase $\sigma = 0$ and $\rho = 1$ the coexistence conditions can be written as

$$c_i(1 + c_i) = c_a(1 + c_a \rho), \quad (11)$$

$$\ln c_i + 2c_i = \ln c_a + \sigma + 2c_a \rho. \quad (12)$$

Here the subscripts i and a refer to the isotropic and anisotropic (lyotropic liquid crystal) phase.

The functionals σ and ρ are functions of c_a since through the minimization of the free energy the orientation distribution function depends on c_a . Numerically solving Eqs. (11) and (12), using for $f(\theta)$ the trial function (6), one obtains

$$c_i = 3.340,$$

$$c_a = 4.488,$$

$$\alpha = 18.64,$$

$$\sigma = 1.925,$$

$$\rho = 0.497.$$

The orientational order in the anisotropic phase can be conveniently described by the order parameter¹³

$$S = \langle P_2(\cos \theta) \rangle = \int f(\theta) \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) d\Omega. \quad (13)$$

From this definition it is clear that in the isotropic phase $S = 0$ and in the anisotropic phase $S > 0$. For the anisotropic phase one finds using the orientation distribution (6) with $\alpha = 18.64$ the value $S = 0.848$. Taking into account that perfect orientational order corresponds with $S = 1$ one sees that the Onsager theory predicts that the anisotropic phase that coexists with the isotropic phase is orientationally strongly ordered.

A more systematic way to solve the minimization problem of the free energy is to start from the integral equation (4) and expand the kernel $\sin \gamma$ in Legendre polynomials.^{11,14} For symmetry reasons, only even Legendre polynomials are necessary:

$$\sin \gamma = \frac{\pi}{4} - \sum_{n=1}^{\infty} d_{2n} P_{2n}(\cos \gamma), \quad (14)$$

where¹⁴

$$d_{2n} = \frac{\pi(4n+1)(2n-3)!!(2n-1)!!}{2^{2n+2} n!(n+1)!}. \quad (15)$$

Substituting Eq. (14) in Eq. (4) and using the addition theorem of spherical harmonics one obtains

$$f(\theta) = \frac{\exp \left[\sum_{n=1}^{\infty} \alpha_{2n} P_{2n}(\cos \theta) \right]}{Z}, \quad (16)$$

TABLE I. Convergence of the concentration, order parameter, and orientation dependent free energy terms of the coexisting isotropic and anisotropic phase using the expansion of $\sin \gamma$ in Legendre polynomials $P_{2n}(\cos \gamma)$ truncated at different values of n . The results labeled Onsager refer to the results obtained with the Onsager trial distribution function.

n	c_i	c_a	S	σ	ρ	Π	μ
1	3.504	3.872	0.574	0.756	0.794	15.79	8.263
2	3.327	4.031	0.735	1.320	0.638	14.39	7.855
3	3.297	4.140	0.778	1.523	0.585	14.16	7.786
4	3.291	4.179	0.789	1.584	0.570	14.12	7.774
5	3.291	4.189	0.792	1.599	0.566	14.12	7.772
6	3.290	4.191	0.792	1.601	0.565	14.12	7.772
7	3.290	4.191	0.792	1.601	0.565	14.12	7.772
Onsager	3.340	4.488	0.848	1.925	0.497	14.49	7.886

where Z is the normalization factor and

$$\alpha_{2n} = \frac{8}{\pi} bcd_{2n} \langle P_{2n} \rangle, \quad n = 1, 2, 3, \dots \quad (17)$$

The values α_{2n} that satisfy Eq. (17) are found by solving the coupled consistency equations

$$\int f(\theta) P_{2n}(\cos \theta) d\Omega - \frac{\alpha_{2n}}{\frac{8}{\pi} bcd_{2n}} = 0, \quad n = 1, 2, 3, \dots \quad (18)$$

In order that this expansion method is of practical value it should converge after a few terms. In order to check this we performed calculations in which the expansions in Eqs. (14)–(18) are truncated after $n = 1, 2, 3, 4, 5, 6$, and 7 , respectively.

The results of these calculations are collected in Table I. From these results it appears that the convergence is indeed rather rapid. Indeed taking into account only the first three terms in Eq. (14), i.e., up to $P_6(\cos \gamma)$ one obtains results that are already reasonably accurate. Calculations of comparable accuracy as reported here using a slightly different approach for the calculation of the thermodynamic properties have been carried out by Kayser and Raveché¹¹ who obtain¹⁵

$$c_i = 3.291, \quad c_a = 4.223, \quad \Pi = 14.1164, \quad \mu = 7.7716.$$

Except for the slight difference between the respective values of c_a (for which we have no explanation) the agreement seems to be perfect.

A different expansion method in Legendre polynomials was used by Lasher.⁷ He expands the orientation distribution

$$f(\theta) = \frac{1}{4\pi} \left[1 + \sum_{n=1}^{\infty} a_{2n} P_{2n}(\cos \theta) \right] \quad (19)$$

and the coefficients a_{2n} , $n = 1, 2, 3, \dots$ are obtained by minimizing directly the free energy.

Truncating the series at $n = 7$ the following results were obtained:

$$c_i = 3.30, \quad c_a = 4.16, \quad S = 0.784, \quad \sigma = 1.56, \quad \rho = 0.577.$$

Comparing these results to those given in Table I it appears that they correspond to the level of accuracy obtained with three to four terms in the series expansion (16).

For the sake of reference we have also included in Table I the results obtained with the Onsager trial distribution function. As already noted by Onsager the trial function (6) is too sharply peaked causing σ to be too high and ρ to be too

low. As can be seen from the osmotic pressure coexistence equation (11) this causes c_a to be too high. However, considering the fact that the trial function (6) contains only one parameter it produces truly remarkable results.

III. EQUATIONS DETERMINING PHASE SEPARATION IN A SOLUTION OF LONG RODS OF TWO DIFFERENT LENGTHS

The appropriate extension of the free energy (1) for a solution of N_1 rods of length L_1 and N_2 rods of length L_2 both with the same diameter D in dialytic equilibrium with the solvent at temperature T is given by

$$\begin{aligned} \frac{\Delta F}{Nk_B T} &= \frac{F(\text{solution}) - F(\text{solvent})}{Nk_B T} \\ &= \frac{(1-x)\mu_1^0(T, \mu_0) + x\mu_2^0(T, \mu_0)}{k_B T} \\ &\quad - 1 + \ln c + (1-x)\ln(1-x) + x \ln x \\ &\quad + (1-x)\sigma_1 + x\sigma_2 + c\{(1-x)^2 b_{11} \rho_{11} \\ &\quad + 2x(1-x)b_{12} \rho_{12} + x^2 b_{22} \rho_{22}\}. \end{aligned} \quad (20)$$

Here $N = N_1 + N_2$ is the total number of particles, $c = (N/V)$ is the total number density, $(1-x)$ is the molefraction of the rods 1, x is the mole fraction of the rods 2, $b_{jk} = (\pi/4) L_j L_k D$ is the average excluded volume of a pair of rods of type j and k with random orientations, and σ_j and ρ_{jk} are abbreviations for the following functionals of the one particle orientation distribution functions $f_1(\Omega)$ and $f_2(\Omega)$.

$$\sigma_j = \int f_j(\Omega) \ln 4\pi f_j(\Omega) d\Omega, \quad j = 1, 2, \quad (21)$$

$$\rho_{jk} = \frac{4}{\pi} \iint \sin \gamma(\Omega, \Omega') f_j(\Omega) f_k(\Omega') d\Omega d\Omega', \quad j, k = 1, 2. \quad (22)$$

Introducing the notation

$$q = \frac{L_2}{L_1} \quad (23)$$

and

$$b = b_{11} = \frac{\pi}{4} L_1^2 D, \quad (24)$$

one can write

$$b_{12} = qb \quad \text{and} \quad b_{22} = q^2b.$$

In the following, the rods 2 will be taken to be the longer one, i.e., $q > 1$.

Like in the one component case the orientation dependent distribution functions are determined by minimizing the free energy with respect to variations of these distribution functions. This leads to the coupled integral equations

$$\ln 4\pi f_1(\Omega) = C_1 - \frac{8}{\pi} bc \int \sin \gamma(\Omega, \Omega') \times [(1-x)f_1(\Omega') + xqf_2(\Omega')] d\Omega', \quad (25)$$

$$\ln 4\pi f_2(\Omega) = C_2 - \frac{8}{\pi} bcq \int \sin \gamma(\Omega, \Omega') [(1-x)f_1(\Omega') + xqf_2(\Omega')] d\Omega', \quad (26)$$

where C_1 and C_2 are constants that are determined by applying the appropriate normalization conditions

$$\int f_j(\Omega) d\Omega = 1, \quad j = 1, 2.$$

Once the minimization problem has been solved, the compositions and concentrations of the coexisting phase are found by solving the coexistence conditions, i.e., the equality of the osmotic pressure Π and the chemical potentials μ_1 and μ_2 of the dissolved particles in the two coexisting phases

$$\Pi = - \left(\frac{\partial \Delta F}{\partial V} \right)_{T, \mu_0, N_1, N_2} = k_B T c [1 + bc [(1-x)^2 \rho_{11} + 2x(1-x)q \rho_{12} + x^2 q^2 \rho_{22}]], \quad (27)$$

$$\mu_1 = - \left(\frac{\partial \Delta F}{\partial N_1} \right)_{T, \mu_0, V, N_2} = \mu_1^0 + k_B T \{ \ln c + \ln(1-x) + \sigma_1 + 2bc [(1-x)\rho_{11} + xq\rho_{12}] \}, \quad (28)$$

$$\mu_2 = - \left(\frac{\partial \Delta F}{\partial N_2} \right)_{T, \mu_0, V, N_1} = \mu_2^0 + k_B T \{ \ln c + \ln x + \sigma_2 + 2bcq [(1-x)\rho_{12} + xq\rho_{22}] \}. \quad (29)$$

At this point it is again convenient to introduce dimensionless variables that are chosen as in Sec. II with the volume b as defined by Eq. (24). Using these dimensionless variables and taking into account that in the isotropic phase $\sigma_j = 0$

and $\rho_{jk} = 1$ the coexistence equations can be written as

$$c_i (1 + c_i [(1-x_i)^2 + 2x_i(1-x_i)q + x_i^2 q^2]) = c_a (1 + c_a [(1-x_a)^2 \rho_{11} + 2x_a(1-x_a)q \rho_{12} + x_a^2 q^2 \rho_{22}]), \quad (30)$$

$$\ln c_i + \ln(1-x_i) + 2c_i [(1-x_i) + x_i q] = \ln c_a + \ln(1-x_a) + \sigma_1 + 2c_a [(1-x_a)\rho_{11} + x_a q \rho_{12}], \quad (31)$$

$$\ln c_i + \ln x_i + 2c_i q [(1-x_i) + x_i q] = \ln c_a + \ln x_a + \sigma_2 + 2c_a q [(1-x_a)\rho_{12} + x_a q \rho_{22}]. \quad (32)$$

The functionals σ_j and ρ_{jk} are functions of x_a and c_a since through the minimization of the free energy the orientation distribution functions depend on x_a and c_a . Note that in the three coexistence equations (30)–(32) there appear four intensive thermodynamic variables x_i , c_i , x_a , c_a . This means that one variable can be freely chosen (in the actual calculations we will take this to be x_i). This is in fact a reflection of the Gibbs phase rule that says that the number of thermodynamic degrees of freedom f is given by $f = 2 + c - p$, where c is the number of components and p is the number of phases. Here with $c = 2$ and $p = 2$ one finds $f = 2$. However since we are dealing with an athermal system the temperature does not enter as a true variable and thus the effective number of degrees of freedom is one.

IV. EVALUATION OF THE COMPOSITION, CONCENTRATION, ORDER PARAMETERS, AND ORIENTATION DEPENDENT FREE ENERGY TERMS OF THE COEXISTING PHASES

We performed the calculations starting from the coupled integral equations (25) and (26). Expanding $\sin \gamma$ in even Legendre polynomials and substituting this expansion in Eqs. (25) and (26) one obtains

$$f_1(\theta) = \frac{\exp\left(\sum_{n=1}^{\infty} \alpha_{2n} P_{2n}(\cos \theta)\right)}{Z_1}, \quad (33)$$

$$f_2(\theta) = \frac{\exp\left(\sum_{n=1}^{\infty} q\alpha_{2n} P_{2n}(\cos \theta)\right)}{Z_2}, \quad (34)$$

TABLE II. Composition, concentration, order parameters, and orientation dependent free energy terms of the coexisting isotropic and anisotropic phase calculated using the expansion of $\sin \gamma$ in Legendre polynomials $P_{2n}(\cos \gamma)$ up to $n = 7$.

x_i	c_i	x_a	c_a	S_1	$L_2/L_1 = 2$		σ_1	σ_2	ρ_{11}	ρ_{12}	ρ_{22}
					S_2	S_2					
0.0	3.290	0.0	4.191	0.792	1.601	...	0.565
0.1	2.301	0.496	2.773	0.862	0.953	0.953	2.064	3.152	0.462	0.382	0.277
0.2	1.900	0.588	2.240	0.807	0.937	0.937	1.704	2.852	0.542	0.447	0.320
0.3	1.632	0.643	1.916	0.747	0.918	0.918	1.397	2.581	0.616	0.510	0.364
0.4	1.432	0.689	1.688	0.690	0.897	0.897	1.154	2.348	0.679	0.567	0.406
0.5	1.276	0.737	1.516	0.639	0.876	0.876	0.972	2.154	0.728	0.614	0.443
0.6	1.150	0.786	1.383	0.597	0.855	0.855	0.838	1.996	0.764	0.652	0.476
0.7	1.047	0.838	1.275	0.563	0.837	0.837	0.739	1.866	0.792	0.681	0.504
0.8	0.960	0.892	1.186	0.536	0.820	0.820	0.666	1.761	0.812	0.705	0.528
0.9	0.886	0.946	1.111	0.513	0.805	0.805	0.609	1.674	0.828	0.724	0.548
1.0	0.823	1.0	1.048	...	0.792	0.792	...	1.601	0.565

TABLE III. Composition, concentration, order parameters, and orientation dependent free energy terms of the coexisting isotropic and anisotropic phase calculated using the expansion of $\sin \gamma$ in Legendre polynomials $P_{2n}(\cos \gamma)$ up to $n = 7$.

x_i	c_i	x_a	c_a	S_1	$L_2/L_1 = 5$		σ_1	σ_2	ρ_{11}	ρ_{12}	ρ_{22}
					S_2	σ_2					
0.0	3.290	0.0	4.191	0.792	1.601	...	0.565
0.1	0.770	0.741	0.601	0.685	0.978	...	1.160	3.919	0.680	0.511	0.193
0.2	0.520	0.631	0.453	0.445	0.951	...	0.464	3.107	0.871	0.709	0.284
0.3	0.384	0.574	0.367	0.298	0.902	...	0.208	2.406	0.943	0.821	0.395
0.4	0.303	0.612	0.308	0.247	0.866	...	0.144	2.076	0.961	0.860	0.459
0.5	0.249	0.674	0.266	0.224	0.842	...	0.118	1.903	0.968	0.877	0.496
0.6	0.211	0.742	0.235	0.211	0.826	...	0.105	1.796	0.972	0.887	0.520
0.7	0.184	0.810	0.212	0.202	0.814	...	0.097	1.724	0.974	0.893	0.536
0.8	0.162	0.876	0.194	0.196	0.805	...	0.092	1.672	0.976	0.898	0.549
0.9	0.145	0.939	0.180	0.192	0.789	...	0.087	1.633	0.977	0.901	0.558
1.0	0.132	1.0	0.168	...	0.792	1.601	0.565

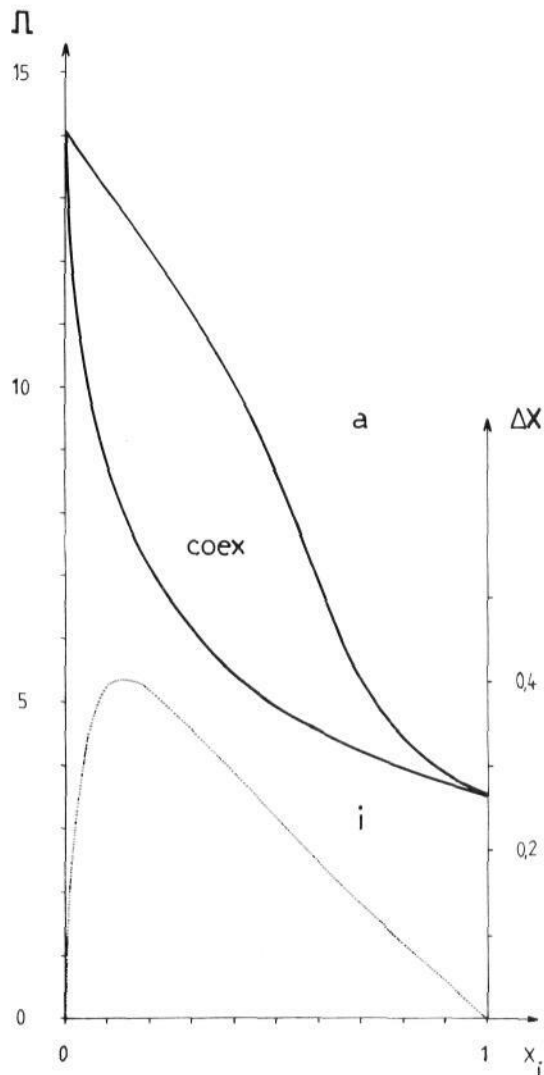


FIG. 1. Characteristics of the coexisting isotropic and anisotropic phase for the system $(L_2/L_1) = 2$. Drawn line: $\Pi - x$ diagram. Dotted line: $\Delta x = x_a - x_i$ plotted as function of x_i .

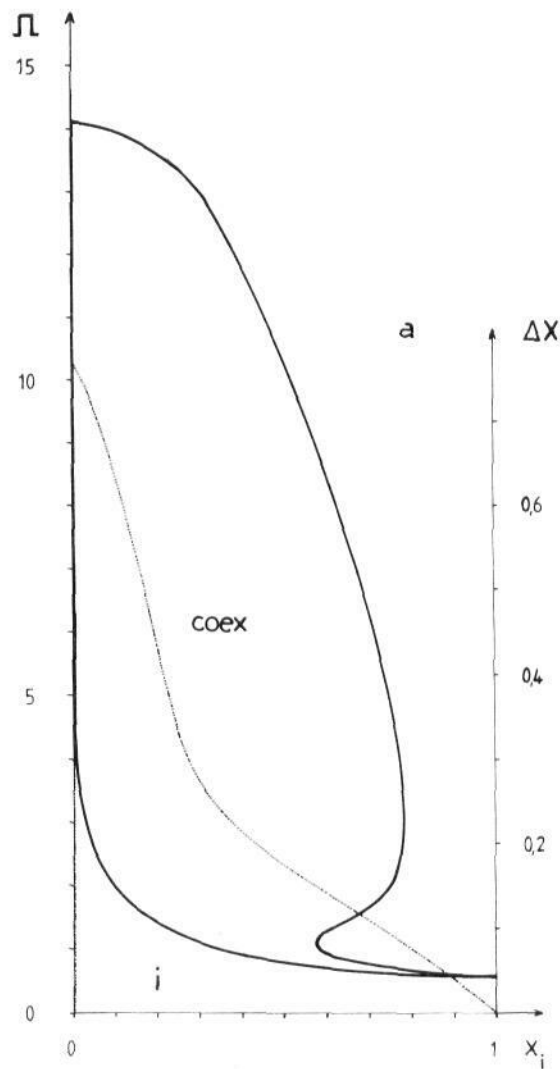


FIG. 2. Characteristics of the coexisting isotropic and anisotropic phase for the system $(L_2/L_1) = 5$. Drawn line: $\Pi - x$ diagram. Dotted line: $\Delta x = x_a - x_i$ plotted as function of x_i .

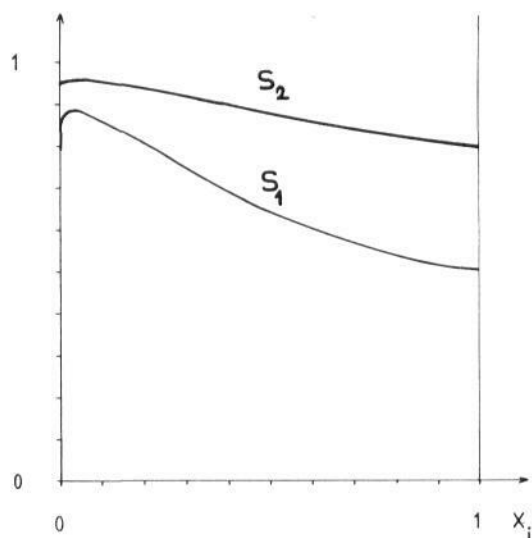


FIG. 3. Order parameters S_1 and S_2 of the shorter and longer rods in the anisotropic phase plotted as function of x_i in the coexisting isotropic phase for the system $(L_2/L_1) = 2$.

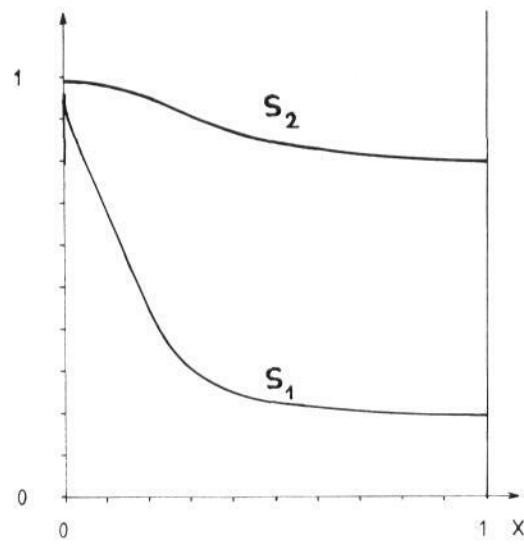


FIG. 4. Order parameter S_1 and S_2 of the shorter and longer rods in the anisotropic phase plotted as function of x_i in the coexisting isotropic phase for the system $(L_2/L_1) = 5$.

where Z_1 and Z_2 are normalization factors and

$$\alpha_{2n} = \frac{8}{\pi} bcd_{2n} [(1-x)\langle P_{2n} \rangle_1 + xq\langle P_{2n} \rangle_2]. \quad (35)$$

The coefficients d_{2n} appearing in the above equation are given by Eq. (15). The values for α_{2n} that satisfy Eq. (35) are found by solving the coupled consistency equations

$$\int [(1-x)f_1(\theta) + xqf_2(\theta)] P_{2n}(\cos \theta) d\Omega - \frac{\alpha_{2n}}{\frac{8}{\pi} bcd_{2n}} = 0, \quad n = 1, 2, 3, 4, \dots \quad (36)$$

The required integrals are calculated using 32 point Gaussian integration and the consistency equations are solved by the Newton method. In Tables II and III we present the results for the composition, concentration, order parameter and orientation dependent free energy terms for the coexisting phases obtained by solving the coexistence equations (30)–(31) with the Newton method for the length ratios $q = 2$ and $q = 5$. In these calculations $\sin \gamma$ has been expanded in even Legendre polynomials up to $P_{14}(\cos \gamma)$, meaning that the orientation distribution functions are determined by seven parameters $\alpha_2, \alpha_4, \dots, \alpha_{14}$.

In order to clearly display the noted fractionation that occurs between the isotropic and anisotropic phase we have plotted in Figs. 1 and 2 the $\Pi - x$ diagram of the coexisting phases and the difference in mole fractions $\Delta x = x_a - x_i$ for $L_2/L_1 = 2$ and $L_2/L_1 = 5$ based on the calculations where $\sin \gamma$ is expanded in even Legendre polynomials up to $P_{14}(\cos \gamma)$.

The behavior of the order parameters S_1 and S_2 of the longer and shorter rods is presented in Figs. 3 and 4. The noteworthy feature here is that the order parameter of the shorter rods decreases rather rapidly with increasing mole fraction of the longer rods. Especially for the higher ratios L_2/L_1 does the order parameter of the shorter rods eventual-

ly drop to quite low values (≈ 0.2 compared to ≈ 0.8 in the monodisperse case).

V. CONCLUSION

In this work we have considered the extension of the Onsager theory for phase separation in a solution of long rods to the case of long rods of two different lengths. We have paid particular attention to the minimization problem of the free energy as it appears that the final results for the concentration and particularly the composition depend very sensitively on it. In particular the results obtained by using the expansion of $\sin \gamma$ in even Legendre polynomials and truncating at $P_2(\cos \gamma)$ show qualitatively the same features as accurate calculations¹⁶ with more terms but quantitatively differ rather more from these accurate calculations than in the case of the one component system.

Considering the results for the compositions and concentrations of the coexisting phases the most remarkable feature is indeed the extent of the fractionation between the two coexisting phases. Especially for large length ratios and low mole fractions of long rods in the isotropic phase the effect is striking. It would appear that this effect could be potentially useful for the separation of long rodlike polymers.

Less dramatic but nonetheless remarkable is the fact that the volume fraction in the isotropic phase required for the onset of phase separation is lower in the binary case than in the corresponding one component case with particles with the average length¹⁷

$$L_{\text{eff}} = (1-x)L_1 + xL_2. \quad (37)$$

A simple calculation indicates that the ratio of the volume fractions for the onset of the phase separation in the binary case (ϕ_i) and in the one component case with particles with the average length (ϕ_i^{eff}) is given by

$$\frac{\phi_i}{\phi_i^{\text{eff}}} = \frac{c_i [(1-x_i) + x_i q]^2}{3.290}. \quad (38)$$

Using the data given in Tables V and VI one finds

$$\frac{\phi_i}{\phi_i^{\text{eff}}} = 0.846 \text{ for } \frac{L_2}{L_1} = 2 \text{ and } x_i = 0.1,$$

$$\frac{\phi_i}{\phi_i^{\text{eff}}} = 0.467 \text{ for } \frac{L_2}{L_1} = 5 \text{ and } x_i = 0.1.$$

This finding that polydispersity actually facilitates the phase transition is in agreement with the observation of Oster⁴ that in the aggregated TMV case the phase transition occurs at a much lower concentration than in the normal case.

Comparing the ratio of the volume fraction in the anisotropic phase (ϕ_a) with the volume fraction in the coexisting isotropic phase (ϕ_i):

$$\frac{\phi_a}{\phi_i} = \frac{c_a [(1 - x_a) + qx_a]}{c_i [(1 - x_i) + qx_i]}, \quad (39)$$

one finds using the data given in Tables V and VI:

$$\frac{\phi_a}{\phi_i} = 1.64 \text{ for } \frac{L_2}{L_1} = 2 \text{ and } x_i = 0.1,$$

$$\frac{\phi_a}{\phi_i} = 2.21 \text{ for } \frac{L_2}{L_1} = 5 \text{ and } x_i = 0.1.$$

The corresponding value for the one component system is 1.27. This increase in the volume fraction ratio between the anisotropic and isotropic phase in the binary case over the one component case is not in agreement with the observations of Oster⁴ who actually finds that the ratio decreases for the case of aggregated TMV compared to normal TMV.

A further noteworthy feature of the present calculations can be discerned from Fig. 2. From the results displayed in that figure it follows that a solution with a binary mixture of long rods with length ratio (L_2/L_1) = 5 with the mole fraction x of the longer rods lying between 0.57 and 0.76 will show the following phase behavior when the overall concentration is increased: monophasic isotropic–biphasic–monophasic anisotropic–biphasic–monophasic anisotropic. So when increasing the concentration a biphasic equilibrium enters a second time.

In addition to the virial expansion method of Onsager² to account for the isotropic–anisotropic phase transition in a solution of rodlike particles, there exists a lattice model due to Flory¹⁸ to deal with this problem. Like in the Onsager theory, in the Flory treatment there is a critical volume fraction, that is inversely proportional to the aspect ratio L/D , above which the system splits into an isotropic and an anisotropic phase. Recently Flory and Ronca¹⁹ have presented an improved treatment of the original lattice model and they find for the concentrations and order parameter of the coexisting phases

$$c_i = 7.89, \quad c_a = 11.57, \quad S = 0.95 \quad (\text{Flory–Ronca}).$$

These values are to be compared with the results that follow from the Onsager theory

$$c_i = 3.29, \quad c_a = 4.19, \quad S = 0.79 \quad (\text{Onsager}).$$

We see that although qualitatively the Onsager and Flory theory display the same behavior, quantitatively they differ.

Flory and co-workers have extended the original lattice model for a monodisperse solution of rods to a polydisperse system²⁰ and applied it to the study of phase equilibria in solutions of rods with two different lengths,²¹ the most probable distribution of lengths²² and the Poisson distribution of lengths.²³ Further, Moscicki and Williams²⁴ have applied the theory of Flory and co-workers to a system of rods with a Gaussian distribution of lengths. Although, as is not surprising after comparing the results for the monodisperse case, the results are quantitatively different, all the qualitative features about the biphasic equilibrium are in agreement. The only major difference is that we have observed no indication of a triphasic equilibrium (isotropic–anisotropic 1–anisotropic 2) as has been found by Abe and Flory.²²

ACKNOWLEDGMENT

One of us (R. V.) thanks the “Nationaal Fonds voor Wetenschappelyk Onderzoek” (Belgium) for financial support.

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