

Classification
 Physics Abstracts
 61.30 — 64.70E

Phase transition in a solution of rodlike particles with different lengths

R. Deblieck and H. N. W. Lekkerkerker

Fakulteit Wetenschappen, Vrije Universiteit Brussel, 1050 Brussel, Belgium

(Reçu le 3 mars 1980, accepté le 13 juin 1980)

Résumé. — La théorie d'Onsager décrivant la transition de phase isotrope-nématique dans une solution de particules allongées est généralisée au cas de solutions contenant des particules allongées de longueurs différentes. Dans le cas d'un mélange de particules longues et courtes, nous montrons que la fraction molaire des particules longues dans la phase anisotrope est significativement plus élevée que dans la phase isotrope; simultanément il y a un accroissement de l'ordre orientationnel de ces particules. Ceci explique le fractionnement qui s'effectue entre la phase isotrope et la phase anisotrope de solutions polydisperses de polymères en forme de bâtonnets allongés.

Abstract. — The Onsager theory for the isotropic-nematic phase transition in a solution of rodlike particles is extended to the case of mixtures of such rods with different lengths. It is found that there is a significantly higher molefraction of long rods in the anisotropic phase than in the isotropic phase and a concomitant enhancement of the orientational order of these particles. This explains the fractionation that occurs between the isotropic and anisotropic phase of polydisperse solutions of rodlike polymers.

1. **Introduction.** — It is well known that a solution of rodlike particles such as Tobacco Mosaic Virus, at a critical density, exhibit a phase transition whereby spontaneous alignment of the rods occurs [1]. The first theoretical treatment of this transition was given by Onsager [2]. He studied the monodisperse case in detail obtaining the critical density at which the transition occurs and the corresponding orientational order in the nematic phase. As for the polydisperse case, he wrote down the relevant thermodynamic functions for the isotropic phase and indicated how to treat the anisotropic phase without really working out the details. He nevertheless already noted that the long rods will be more perfectly oriented than the short ones.

In the present work we extend the Onsager treatment for the monodisperse system to polydisperse solutions. In particular we will solve the general equations for mixtures of rods with two different length/diameter (L/D) ratios.

2. **Thermodynamic equations.** — The Helmholtz free energy, in the second virial approximation, for a solution of rodlike particles with m different L/D ratios, in dialytic equilibrium with the isothermal bulk solvent reads :

$$\frac{\beta[F(\text{solution}) - F(\text{solvent})]}{N} = \sum_{i=1}^m x_i \varphi_i(T, \mu_0) - 1 + \ln \rho + \sum_{i=1}^m (x_i \ln x_i + x_i \sigma_i) + \rho \sum_{i,j=1}^m x_i x_j B_{ij} \quad (1)$$

where $\beta = (kT)^{-1}$, N is the total number of particles, ρ is the total number density, x_i is the molefraction of particles of kind i and $\varphi_i(T, \mu_0)$ represents the free energy contribution of the kinetic energy of the particles of kind i in a solvent with chemical potential μ_0 . Further, σ_i and B_{ij} are functionals of the one particle orientational distribution function $f_i(\Omega)$, describing the two main entropy contributions, the orientational entropy S^{or} and the packing entropy S^{pack} , the competition of which causes an ordering transition to take place :

$$\frac{S^{\text{or}}}{kN} = - \sum_{i=1}^m x_i \sigma_i = - \sum_{i=1}^m x_i \int_{\Omega} d\Omega f_i(\Omega) \ln(4 \pi f_i(\Omega)) \quad (2)$$

$$\frac{S^{\text{pack}}}{kN} = - \rho \sum_{i,j=1}^m x_i x_j B_{ij} = + \frac{1}{2} \rho \sum_{i,j=1}^m x_i x_j \iint_{\Omega \Omega'} d\Omega d\Omega' \beta_{ij}(\Omega, \Omega') f_i(\Omega) f_j(\Omega') \quad (3)$$

where $\beta_{ij}(\Omega, \Omega')$ is the first irreducible cluster integral, which for hard particles is nothing else but the excluded volume and for spherocylinders of kinds i and j , with orientations Ω and Ω' is given by [2]

$$- \beta_{ij}(\Omega, \Omega') = \frac{4}{3} \pi D^3 + \pi(L_i + L_j) D^2 + 2 L_i L_j D |\sin \gamma(\Omega, \Omega')| \quad (4)$$

where γ is the angle of intersection of the two particles.

The truncation of the virial expansion of the excess Helmholtz free energy after the linear term in the density is clearly valid only when the density is sufficiently low so that higher order terms are negligible. Unfortunately for many purposes, the isotropic to nematic phase transition in hard rod systems occurs at such low densities only when the L/D ratio of the hard rods is quite large. Based on estimates of the ratio $\rho_c B_3/B_2$ (where ρ_c is the critical density and B_2 and B_3 are the second and third virial coefficients) Straley [3] 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 of order 20 to 50). For the intended purpose of the present work i.e. the study of the qualitative features of transitions in mixtures in which the shorter rods have $L/D = 20$ the Onsager-truncation can thus be used.

Orientalional disorder maximizes the orientational entropy whereas orientational order reduces the excluded volume and hence leads to an increase of the packing entropy. The equilibrium orientational distributions are determined by minimizing the free energy with respect to variations in these distributions, subject to the appropriate normalization conditions. One gets readily :

$$\ln(4 \pi f_i(\Omega)) = \chi_i - 1 + \rho \sum_{j=1}^m \int_{\Omega'} d\Omega' \beta_{ij}(\Omega, \Omega') f_j(\Omega') \quad (5)$$

where χ_i is an undetermined Lagrange multiplier, which is evaluated by applying the normalization condition. The conditions for coexistence of the isotropic and anisotropic phase are simply that the osmotic pressure Π and the chemical potentials $\mu_i, i = 1, 2, \dots, m$ must be equal in both phases :

$$\begin{aligned} \Pi^{\text{iso}}(\rho^{\text{iso}}, x_1^{\text{iso}}, x_2^{\text{iso}}, \dots, x_m^{\text{iso}}) &= \Pi^{\text{an}}(\rho^{\text{an}}, x_1^{\text{an}}, x_2^{\text{an}}, \dots, x_m^{\text{an}}) \\ \mu_i^{\text{iso}}(\rho^{\text{iso}}, x_1^{\text{iso}}, x_2^{\text{iso}}, \dots, x_m^{\text{iso}}) &= \mu_i^{\text{an}}(\rho^{\text{an}}, x_1^{\text{an}}, x_2^{\text{an}}, \dots, x_m^{\text{an}}) \\ & i = 1, 2, \dots, m \quad (6) \end{aligned}$$

The osmotic pressure Π and the chemical potentials μ_i are easily calculated by application of the usual thermodynamic relations :

$$\beta \Pi = - \left(\frac{\partial \beta F}{\partial V} \right)_{T, \mu_0, N, \{x_j\}} = \rho + \rho^2 \sum_{i,j=1}^m x_i x_j B_{ij} \quad (7)$$

$$\beta \mu_i = \left(\frac{\partial \beta F}{\partial N_i} \right)_{T, \mu_0, \{N_{j \neq i}\}} = \varphi_i(T, \mu_0) + \ln \rho_i + \sigma_i + 2 \rho \sum_{j=1}^m x_j B_{ij} \quad (8)$$

In the next section we will specifically solve these coexistence equations for a mixture of rods with two different L/D ratios.

3. The phase transition. — In order to solve the coexistence relations one has to know the orientational distribution functions (i.e. one has to solve the set of coupled integral equations (5)). We expand the orientation dependent part of the kernel $\beta_{ij}(\Omega, \Omega')$ in terms of even Legendre polynomials [4]

$$|\sin \gamma(\Omega, \Omega')| = \frac{\pi}{4} - \frac{5\pi}{32} P_2(\cos \gamma) - \frac{9\pi}{256} P_4(\cos \gamma) - \dots$$

which truncated after P_2 , is known [5] to exhibit qualitatively correct behaviour for the monodisperse case. Using this approximation and applying the addition theorem for Legendre polynomials we get :

$$f_i(\Omega) = \frac{1}{4 \pi Z_i} \times \exp \left[\frac{5\pi}{16} \rho L_i D \sum_{j=1}^2 x_j L_j \langle P_2 \rangle_j P_2(\cos \theta) \right] \quad (9)$$

where Z_i is the normalization constant, θ is the angle between the long axis of the rods and the nematic axis and $\langle P_2 \rangle_j$ is the order parameter of the j th species

$$\langle P_2 \rangle_j = \int_{\Omega} d\Omega P_2(\cos \theta) f_j(\Omega) .$$

It is obvious from (9) that the phase transition is coupled i.e., there is only one transition even though there is more than one rodlike species.

The set of coexistence relations (7) and (8) was solved by a common tangent construction. We first select an osmotic pressure Π lying between the transition pressure of the respective monodisperse systems

$$\Pi_{\text{long}}^{\text{tr}} < \Pi < \Pi_{\text{short}}^{\text{tr}} .$$

For this selected osmotic pressure we calculate from equation (7) for every composition x the corresponding number densities ρ^{iso} and ρ^{an} in the isotropic and anisotropic phase respectively. This then allows us to calculate the Gibbs free energy per particle at the selected osmotic pressure as a function of composition

in both phases

$$\beta g = \sum_{i=1}^2 x_i \varphi_i(T, \mu_0) + \ln \rho + \sum_{i=1}^2 (x_i \ln x_i + x_i \sigma_i) + 2 \sum_{i,j=1}^2 x_i x_j B_{ij} \quad (10)$$

From equilibrium thermodynamic (see e.g. [6]) one knows that the intercepts of the tangent of the Gibbs

free energy per particle at constant pressure at $x_1 = 1$ and $x_2 = 1$ are equal to the chemical potentials of components 1 and 2 respectively. Thus the construction of a common tangent to the Gibbs free energy per particle in the isotropic and anisotropic phase ensures that the chemical potentials are equal in both phases. The composition of the coexisting phases are found as the abscissa of the points of contact. This procedure is schematically represented in figure 1.

Table I. — Compositions, volume fractions and chemical potentials of the coexisting phases and the order parameters in the anisotropic phase. x : molefraction of the long rods, ϕ : total volume fraction occupied by the rods,

$\beta\mu_{0,i} = \varphi_i(T, \mu_0) - \ln \pi D^3$.
 (a) $(L/D)_1 = 20$; $(L/D)_2 = 30$.
 (b) $(L/D)_1 = 20$; $(L/D)_2 = 100$.

Table Ia.

x^{iso}	x^{an}	ϕ^{iso}	ϕ^{an}	$\langle P_2 \rangle_1$	$\langle P_2 \rangle_2$	$\pi D^3 \beta \Pi$	$\beta (\mu_1 - \mu_{0,1})$	$\beta (\mu_2 - \mu_{0,2})$
0.0000	0.0000	0.1824	0.1965	0.545	-	0.1856	5.176	-
0.0500	0.0797	0.1748	0.1897	0.543	0.700	0.1708	4.692	5.464
0.1000	0.1512	0.1684	0.1836	0.536	0.694	0.1586	4.264	5.647
0.2000	0.2754	0.1581	0.1730	0.516	0.677	0.1398	3.546	5.508
0.3000	0.3835	0.1501	0.1643	0.494	0.658	0.1257	2.928	5.251
0.4000	0.4821	0.1436	0.1570	0.473	0.639	0.1147	2.371	4.991
0.5000	0.5749	0.1381	0.1508	0.455	0.629	0.1054	1.836	4.707
0.6000	0.6640	0.1334	0.1455	0.434	0.605	0.0984	1.324	4.532
0.7000	0.7505	0.1294	0.1409	0.424	0.590	0.0922	0.774	4.334
0.8000	0.8351	0.1259	0.1369	0.412	0.567	0.0869	0.135	4.156
0.9000	0.9181	0.1228	0.1334	0.401	0.564	0.0823	-0.768	3.995
1.0000	1.0000	0.1201	0.1303	-	0.554	0.0783	-	3.850

Table Ib.

x^{iso}	x^{an}	ϕ^{iso}	ϕ^{an}	$\langle P_2 \rangle_1$	$\langle P_2 \rangle_2$	$\pi D^3 \beta \Pi$	$\beta (\mu_1 - \mu_{0,1})$	$\beta (\mu_2 - \mu_{0,2})$
0.00000	0.00000	0.1824	0.1965	0.545	-	0.1856	5.176	-
0.00001	0.05248	0.1793	0.2186	0.719	0.950	0.1800	5.013	24.314
0.00010	0.20249	0.1620	0.2266	0.770	0.958	0.1500	4.105	22.504
0.00102	0.30905	0.1362	0.1993	0.738	0.953	0.1100	2.717	19.018
0.00748	0.35960	0.1107	0.1624	0.662	0.941	0.0760	1.281	15.211
0.01003	0.36251	0.1066	0.1558	0.644	0.938	0.0710	1.039	14.561
0.10286	0.27620	0.0671	0.0813	0.287	0.833	0.0290	-1.703	7.370
0.20313	0.30496	0.0534	0.0601	0.176	0.715	0.0180	-2.951	4.529
0.30000	0.38650	0.0469	0.0520	0.149	0.658	0.0135	-3.705	3.181
0.50000	0.56974	0.0407	0.0447	0.129	0.607	0.0096	-4.789	1.858
0.75000	0.79177	0.0372	0.0408	0.121	0.580	0.0076	-6.021	1.124
1.00000	1.00000	0.0353	0.0388	-	0.567	0.0065	-	0.7356

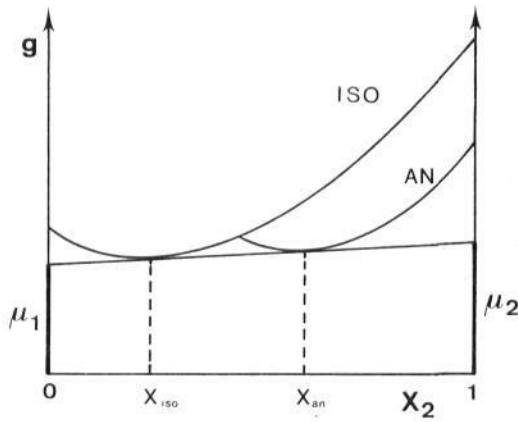


Fig. 1. — Schematic representation of the double tangent construction to locate the coexisting phases.

We performed calculations for systems with short rods with a constant L/D ratio equal to 20 and several kinds of long rods with L/D ratios equal to 30, 50, 100, 200. The results for the compositions, volume fractions, osmotic pressure and chemical potentials of the coexisting phases and the order parameter of both components in the anisotropic phase are displayed in figures 2, 3 and 4 and/or listed in table I. The most remarkable result is the considerable enrichment in long rods in the anisotropic phase (up to 0.35) for very low concentrations of long rods in the isotropic phase. We further see that Onsager's prediction about the long rods being more perfectly ordered is borne out by the present work.

The extension of the Onsager theory presented here provides an explanation of the weight fractionation between the isotropic and anisotropic phase that has

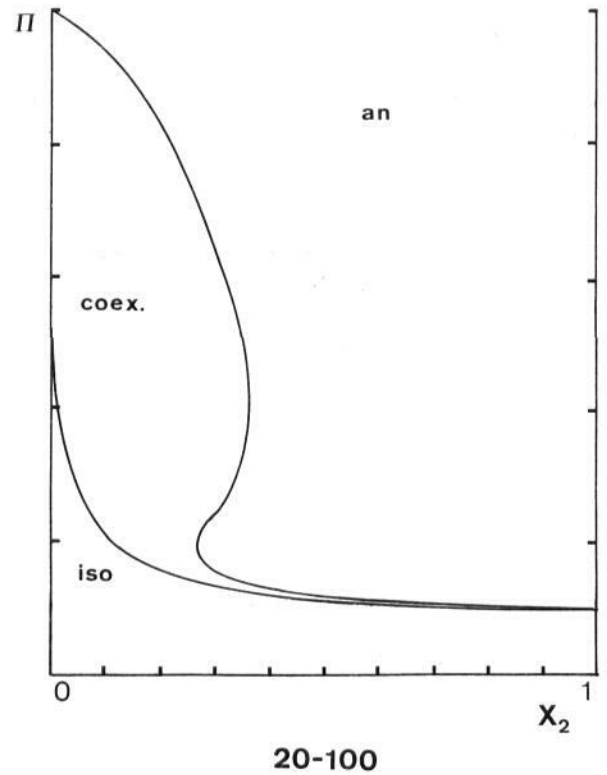
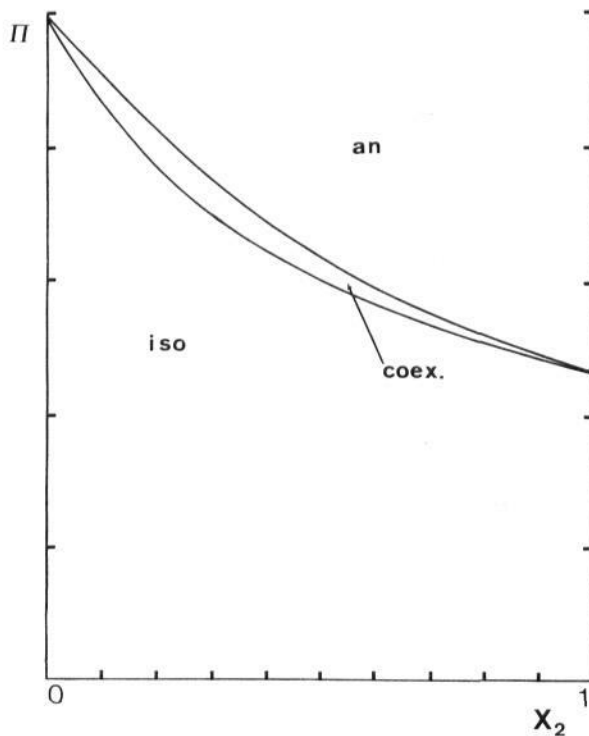


FIG. 2. b

Fig. 2. — Π - x diagram for the coexisting phase. (a) $(L/D)_1 = 20$, $(L/D)_2 = 30$; (b) $(L/D)_1 = 20$, $(L/D)_2 = 100$.



20-30
FIG. 2. a

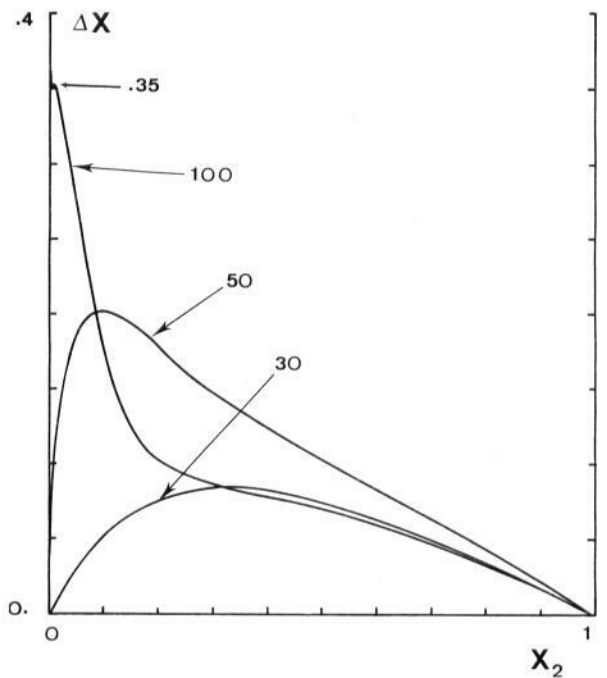
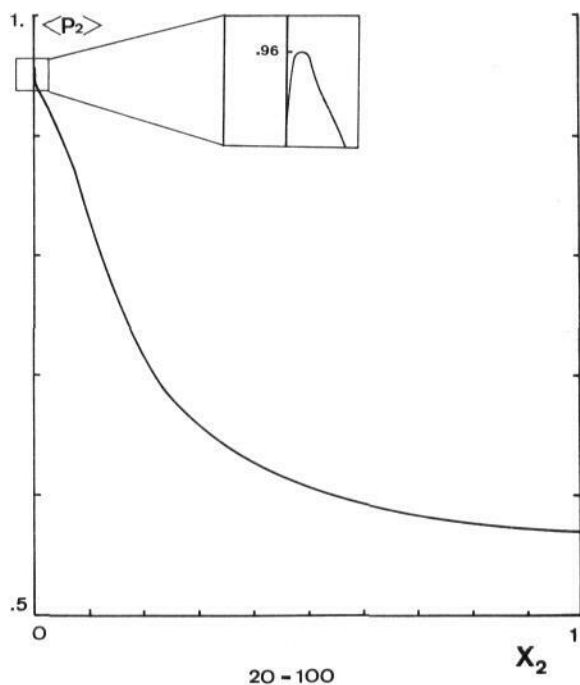


Fig. 3. — Enrichment of the long rods $\Delta x = x_2^{an} - x_2^{iso}$ in the anisotropic phase as function of the molefraction of these particles in the isotropic phase.



been observed in polydisperse solutions of Tobacco Mosaic Virus [7], polybenzamides [8] and polyphenyleneterephthalamides [9]. It would be of interest to try to observe the enhanced orientational order of the long rods in the anisotropic phase as well.

Acknowledgments. — We thank Mr. J. De Bruyne, for his competent assistance in the numerical calculations and Dr. D. Van Dijk for his helpful advice concerning the algorithm of the double tangent construction.

Fig. 4. — Order of the long rods in the anisotropic phase as function of the molefraction of these particles in the isotropic phase.

References

- [1] BERNAL, J. D. and FANKUCHEN, I., *J. Gen. Physiol.* **25** (1941) 111.
- [2] ONSAGER, L., *Phys. Rev.* **62** (1942) 558. *Ann. N.Y. Acad. Sci.* **51** (1949) 627.
- [3] STRALEY, J. P., *Mol. Cryst. Liq. Cryst.* **24** (1973) 7.
- [4] ISIHARA, A., *J. Chem. Phys.* **19** (1951) 1142.
- [5] COTTER, M. A., *J. Chem. Phys.* **66** (1977) 1098.
- [6] PRIGOGINE, I. and DEFAY, R., *Chemical Thermodynamics* (Longmans, London) 1954, Ch. 16.7.
- [7] OSTER, G., *J. Gen. Physiol.* **33** (1950) 445.
- [8] KOWLEK, S. L., U.S. Patent 3 671 542 (1972).
- [9] BAIR, T., MORGAN, P. W. and KILLIAN, F. L., *Macromolecules* **10** (1977) 1396.