Notes

On the Flory–Ronca Theory of Systems of Rodlike Particles

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Introduction

Lattice theory for mixtures of rodlike particles with spherical solvent molecules was introduced by Flory[1] in 1956 and refined later by Flory and Ronca.[2-3] The theory proposed by these authors[1-3] is especially appealing since the orientation of the rodlike molecule on the lattice is allowed to be continuous, whereas most other lattice theories[4-7] allow only for the discrete number of orientations of the molecule.

A cubic lattice divides the space into cubic cells of dimension equal to the diameter of the particles. For simplicity, it is assumed that the diameters of solvent molecules and rodlike particles are equal. Each rod has length x in lattice units, i.e., x is the length-to-width ratio for the rods. The lattice consists of $n_0 = n_1 + xn_2$ sites, with n_1 of them occupied by solvent and xn_2 occupied by n_2 rodlike molecules. The volume fraction of solvent is $v_1 = n_1/n_0$, and the volume fraction of rodlike molecules is $v_2 = xn_2/n_0$. According to the theory[1,2] a rod oriented at angle ψ with respect to the preferred axis of a given domain might be represented by y sequences of x/y segments, as shown in Figure 1 of ref 2. In the refined theory by Flory and Ronca[2] the number of y_k sequences for a rod oriented in the kth direction (ψ_k, ϕ_k) is

$$y_k = x \sin \psi_k[|\sin \phi_k| + |\cos \phi_k|] \tag{1}$$

as might be seen from Figure 2 of ref 2 which shows the cross section of the cubic lattice in the transverse directions. It has been assumed that there is a finite number of directions with the kth direction confined within the solid angle $\omega_k = \sin \psi_k \, d\psi_k \, d\phi_k$. In the continuous limit, summation over directions is replaced by proper integrals over solid angles. The lattice assumption enables the calculation of the combinatory Z_{comb} and orientational Z_{orient} factors of the configuration partition function $Z_M = Z_{comb}Z_{orient}$. The equilibrium orientational distribution of rods is obtained by minimizing the system's free energy $F = -k_BT \ln Z_M$. The result is[2]

$$\frac{n_{2,k}}{n_2} = \frac{1}{f_1}\omega_k \exp(-ay_k) \tag{2}$$

where $n_{2,k}$ is the number of rodlike molecules with orientations within the solid angle ω_k and $n_2 = \sum_k n_{2,k}$. Here

$$a = -\ln [1 - v_2(1 - \bar{y}/x)] \tag{3}$$

where

$$\bar{y} = \frac{1}{n_2}\sum_k y_k n_{2,k} \tag{4}$$

and

$$f_1 = \sum_k \omega_k \exp(-ay_k) \tag{5}$$

The calculation of chemical potentials for the solvent and for rodlike molecules (eqs 19 and 20 of ref 2) enabled Flory and Ronca to carry out the calculation of biphasic equilibrium.

The dependence of the number of sequences y representing a rod oriented in direction (ψ, ϕ) is given by eq 1. Instead of using this expression for y, Flory and Ronca used the value of y preaveraged over the angle ϕ

$$y_{FR} = \frac{1}{2\pi}\int_0^{2\pi} d\phi \, x \sin \psi[|\sin \phi| + |\cos \phi|] = \frac{4}{\pi}x \sin \psi \tag{6}$$

This unweighted averaging, although it is not rigorous, simplifies the problem, leading to equations for biphasic equilibrium with single integrals, while the more proper treatment of the problem involves double integrals, which makes the numerical calculation of biphasic equilibrium in the system more time-consuming.

In the following we will show the solution of the problem without the simplifying preaveraging over the angle ϕ and compare the results with the Flory–Ronca results. The average value of the number of sequences $\bar{y}$ (given by eq 4) for rodlike molecules is an inverse measure of the orientational order for the system and is therefore referred to as the disorientation parameter. For all rods perfectly aligned in one direction, $\bar{y} = 1$, while in the isotropic phase, $\bar{y} = x$. Actually, since eqs 1 and 6 have been derived from the projection of a *line* of length x onto the perpendicular plane of the nematic director, they predict $y = 0$ instead of $y = 1$ when $\psi = 0$. The Flory–Ronca theory has been corrected by Warner[8] in this regard, however, by representing a mesogenic molecule on a lattice by a spherocylinder instead of a line, which leads to

$$y = \frac{4}{\pi}(x - 1) \sin \psi + 1 \tag{7}$$

Using eqs 2 and 4 and replacing summation over directions by integrals the expression for $\bar{y}$ becomes

$$\frac{\bar{y}}{x} = [\int_0^{2\pi} d\phi \int_0^{\pi} d\psi \sin^2 \psi[|\cos \psi| + |\sin \phi|] \times \exp\{-ax \sin \psi[|\cos \phi| + |\sin \phi|]\}]/[\int_0^{2\pi} d\phi \int_0^{\pi} d\psi \sin \psi \times \exp\{-ax \sin \psi[|\cos \phi| + |\sin \phi|]\}] \tag{8}$$

while the Flory–Ronca ϕ-preaveraged result is

$$\left(\frac{\bar{y}}{x}\right)_{FR} = \frac{4}{\pi}\frac{\int_0^{\pi} d\psi \sin^2 \psi \exp\left(-\frac{4}{\pi}ax \sin \psi\right)}{\int_0^{\pi} d\psi \sin \psi \exp\left(-\frac{4}{\pi}ax \sin \psi\right)} \tag{9}$$

with a in both cases given by eq 3. It should be noted that

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the present treatment improves only one of many approximations of the Flory–Ronca theory. Other approximations of the theory have not been improved in the present treatment. These include (1) the neglect of the translational and orientational short-range order; (2) the approximation of the expected number $\nu_j(y_j)$ of ways of adding the jth rod consisting of y_j subrods in calculation of the combinational part Z_{comb} of the partition function by $\nu_j(\bar{y})$, where $\bar{y}$ is the ensemble average of y; (3) the assumption that the partition function Z_M may be factored into combinatorial and orientational parts $Z_M = Z_{comb}Z_{orient}$; and (4) the derivation of eq 1 for only a *line* of length x.

Numerical Results

Figure 1 shows plots of $\bar{y}/x$ vs x calculated from eqs 8 (solid lines) and 9 (dashed lines) for neat liquid ($v_2 = 1$, $v_1 = 0$) and for an equivolume mixture of rodlike particles with solvent ($v_1 = v_2 = 0.5$). The horizontal line $(\bar{y}/x) = 1$ corresponds to the isotropic solutions for eqs 8 and 9. For large x the difference between the present solution and the Flory–Ronca result becomes very small, and since biphasic equilibrium solutions correspond to this part of the curve, we may expect that the present results for biphasic equilibrium will be very close to those obtained by Flory and Ronca. For very large values of $\alpha = (4/\pi)ax$ an asymptotic expansion for eq 8 might be derived similarly as has been done by Flory and Ronca. Since for large values of α

$$\int_0^{\pi/2}d\phi\int_0^{\pi}d\psi\,\sin^2\psi(\cos\phi+\sin\phi)\times \exp\left\{-\frac{\pi}{4}\alpha\sin\psi(\cos\phi+\sin\phi)\right\}\approx\frac{2}{\left(\frac{\pi}{4}\alpha\right)^3}b_1+\frac{12}{\left(\frac{\pi}{4}\alpha\right)^5}b_2 \quad (10)$$

and

$$\int_0^{\pi/2}d\phi\int_0^{\pi}d\psi\,\sin\psi\exp\left\{-\frac{\pi}{4}\alpha\sin\psi(\cos\phi+\sin\phi)\right\}\approx \frac{1}{\left(\frac{\pi}{4}\alpha\right)^2}b_1+\frac{3}{\left(\frac{\pi}{4}\alpha\right)^4}b_2 \quad (11)$$

with

$$b_1=\int_0^{\pi/2}\frac{1}{1+2\cos\phi\sin\phi}\,d\phi=1 \quad (12)$$

and

$$b_2=\int_0^{\pi/2}\frac{1}{(1+2\cos\phi\sin\phi)^2}\,d\phi=\frac{2}{3} \quad (13)$$

we obtain

$$\frac{\bar{y}}{x}\approx\frac{2}{\frac{\pi}{4}\alpha}+\frac{6}{\left(\frac{\pi}{4}\alpha\right)^3}\frac{b_2}{b_1}=\frac{8}{\pi}\left(\frac{1}{\alpha}+\frac{32}{\pi^2\alpha^3}\right) \quad (14)$$

The asymptotic expansion for the Flory–Ronca ϕ-preaveraged theory[2] is

$$\left(\frac{\bar{y}}{x}\right)_{FR}\approx\frac{8}{\pi}\left(\frac{1}{\alpha}+\frac{3}{\alpha^3}\right) \quad (15)$$

and since $32/\pi^2 \approx 3.242$ is close to 3, the difference between the second terms of eqs 14 and 15 is not very large. The main difference between the present results and the results of the Flory–Ronca theory with preaveraged y is the bifurcation value x_b of the axial ratio, as seen in Figure 1. The bifurcation value x_b is the value of x for which the anisotropic solution ($y/x \neq 1$) of the nonlinear equation

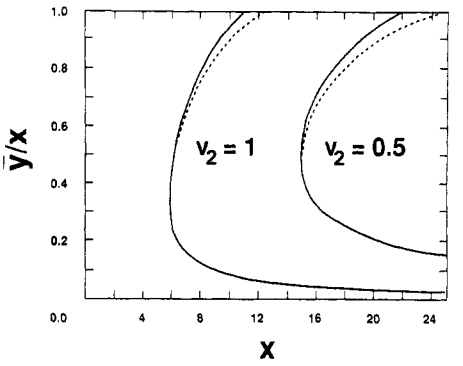

Figure 1. $\bar{y}/x$ vs x according to the present treatment (solid lines) and the Flory–Ronca approximation (dashed lines) for two values of the volume fraction v_2.

Table I
Comparison of Flory–Ronca Results with Present Results

	Flory–Ronca	present
	Neat Liquids	
x_{crit}	6.4166	6.3476
$\bar{y}_{crit}$	1.24445	1.2817
$(\bar{y}/x)_{crit}$	0.19394	0.2019
$^3/_2\langle\cos^2\theta\rangle - {}^1/_2$	0.9473	0.9379
	Athermal Solutions	
v_2^{iso} for $x = 20$	0.36417	0.3604
v_2^{nem} for $x = 20$	0.49784	0.4864
$\bar{y}$ for $x = 20$	4.0397	4.2646
$\bar{y}/x$ for $x = 20$	0.20198	0.2132
$\bar{y}/x$ for $x = \infty$	0.23242	0.2484
xv_2^{iso} for $x = \infty$	7.8937	7.7947
xv_2^{nem} for $x = \infty$	11.5668	11.1458

(eq 8 or 9) for the disorientation parameter $\bar{y}$ branches off the isotropic solution ($\bar{y}/x = 1$). For values of x larger than x_b, the isotropic phase is unstable.[9,10]

The bifurcation parameter x_b may be easily obtained by linearizing eq 8 or 9 around $\bar{y}/x = 1$. The bifurcation value in the present theory (eq 8) is

$$v_2x_b=\frac{3}{4/\pi-1}\approx 10.98 \quad (16)$$

while the bifurcation value in the Flory–Ronca ϕ-preaveraged theory (eq 9) is

$$(v_2x_b)_{FR}=\frac{1}{32/3\pi^2-1}\approx 12.38 \quad (17)$$

The calculation of the biphasic equilibrium requires the solution of the equations $\mu_2^{iso} = \mu_2^{nem}$ and $\mu_1^{iso} = \mu_1^{nem}$, where μ_2 and μ_1 are given by eqs 19 and 20 of ref 2 together with the equation for $\bar{y}/x$ (eq 8 or 9 in the Flory–Ronca theory). The comparison between the present results for biphasic equilibrium and the results obtained by Flory and Ronca by using the ϕ-preaveraged expression for y is shown in Table I. The first four rows of Table I show the critical values of parameters corresponding to coexistence of two phases for the neat liquid, without solvent ($v_2 = 1$, $v_1 = 0$). The present treatment gives a slightly smaller value of the axial ratio $x_{crit} = 6.3476$ in comparison with the Flory–Ronca result $x_{crit}^{FR} = 6.4166$, while the present value of $\bar{y}_{crit}$ (1.2817) is slightly larger than $\bar{y}_{crit}$ obtained by Flory and Ronca (1.24445). The results obtained by Warner[8] based on eq 7 are $x_{crit} = 8.7536$ and $\bar{y}_{crit} = 2.8287$. The remaining rows in Table I compare athermal solutions for both models for $x = 20$ and $x = \infty$. In the limit $x \to \infty$ eq 3 becomes

$$\lim_{x\to\infty} a = (1-\bar{y}/x)(xv_2^{nem}) \quad (18)$$

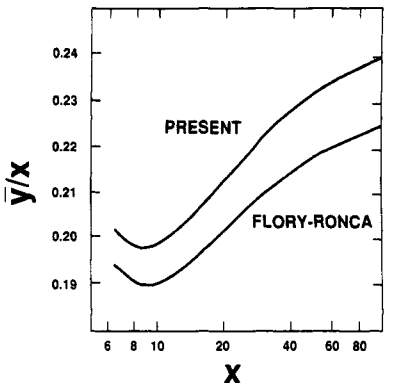

Figure 2. Values of $\bar{y}/x$ at biphasic equilibrium as a function of x for the present theory and the Flory–Ronca approximation.

and the biphasic equilibrium is determined by the equations

$$-{}^1/_2[(xv_2^{nem})^2 - (xv_2^{iso})^2] = xv_2^{nem} - xv_2^{iso} - {}^1/_2(xv_2^{nem})^2(1 - \bar{y}/x)^2 \quad (19)$$

$$\ln \frac{v_2^{nem}}{v_2^{iso}} = xv_2^{iso} - \left(\frac{\bar{y}}{x}\right)(xv_2^{nem}) + \ln f_1 \quad (20)$$

and eq 8 (present calculations) or 9 (Flory–Ronca calculations), which give $\bar{y}/x$, xv_2^{iso} and xv_2^{nem}. Here v_2^{iso} is the volume fraction of rodlike molecules in the isotropic phase, v_2^{nem} is the volume fraction of rodlike molecules in the nematic phase, and

$$f_1 = \int_0^{\pi/2} \sin\psi e^{-\alpha \sin\psi}\, d\psi \quad \text{Flory–Ronca} \quad (21)$$

$$f_1 = \frac{1}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi} d\psi \sin\psi \times \exp\{-ax \sin\psi[|\cos\phi| + |\sin\phi|]\} \quad \text{present} \quad (22)$$

The difference between the volume fraction of rodlike molecules v_2 in both phases given by the present solution and the Flory–Ronca solution is very small, so that Figure 4 in the Flory–Ronca paper[2] remains practically unchanged. For given axial ratio x the volume fractions v_2^{nem} and v_2^{iso} for the present solution are always slightly smaller than the corresponding volume fraction obtained by Flory and Ronca. The difference between both solutions decreases from 3.6% for v_2^{nem} and 1.3% for v_2^{iso} for $x = 100$ to 0.5% for v_2^{nem} and 0.9% for v_2^{iso} for $x = 6.5$.

The difference between $\bar{y}/x$ at biphasic equilibrium for the present solution and the Flory–Ronca solution is more substantial as seen in Figure 2. The values of $\bar{y}/x$ are always larger than those obtained by Flory and Ronca irrespective of the axial ratio x. It is interesting to note that the present solution of the model gives slightly better agreement with the Onsager results[11] than does the Flory–Ronca solution. Onsager used the virial expansion method for hard spherocylinders terminated at the second virial coefficient. Table I shows that for $x \to \infty$, the present results are slightly closer to the Onsager estimate ($v_2^{nem}/v_2^{iso} = 1.343$, $xv_2^{iso} = 3.34$, $xv_2^{nem} = 4.486$) than are the Flory–Ronca results.

Generally, the Flory and Ronca approximation based on the ϕ-angle preaveraging of y gives results very close to the present results (except in the bifurcation region as seen in Figure 1, which does not influence calculations of biphasic equilibrium). The Flory and Ronca approximation enables reduction of double integrals to single integrals, which simplifies the numerical calculations of the biphasic equilibrium and is fully justified according to our analysis. This approximation, however, should not be used to study the stability of isotropic phases determined by the bifurcation value of x.

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