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PRELIMINARY COMMUNICATIONS

Osmotic pressure of a nematic solution of polydisperse rod-like macromolecules

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For a nematic solution of polydisperse rigid rods the osmotic pressure is proved to be independent of the length distribution and proportional simply to the total number density. This rule holds in the gaussian approximation to the Onsager theory. Its accuracy is demonstrated for bidisperse systems.

The degree of orientational order in a nematic solution of slender, hard rods is quite high. Therefore, a physically plausible zero-order approximation to the orientational distribution function for a single rod is one that is gaussian in the angle which the rod makes with respect to the director. The leading terms in Onsager's theory [1] of monodisperse rods are precisely those obtained in this so-called gaussian approximation [2]. For instance, Onsager's result for the osmotic pressure, π_a, of a nematic solution of slender rod-like macromolecules of length L, diameter D and number density c'_a (the subscript a denotes the anisotropic phase) can be written as

$$\pi_a/kT = 3c'_a(1 + \mathcal{O}(c_a^{-2})). \tag{1}$$

Here, T signifies the temperature and k is the Boltzmann constant. In the order term we have introduced the scaled concentration $c_a = bc'_a$ with $b = (\pi/4)L^2D$ which is the average volume excluded by a pair of rods if they are randomly oriented. The gaussian approximation to equation (1) is simply

$$\pi_a/kT = 3c'_a. \tag{2}$$

For monodisperse rods equation (2) improves in accuracy as the scaled number density increases. Incidentally, we note that Monte Carlo results for hard platelets is also asymptotic towards equation (2) in spite of the fact that several higher order virial coefficients come into play in that case [3].

Previously, it was shown that in the gaussian approximation equation (2) holds even for bidisperse rods provided c'_a is now the total number of particles per unit volume [2]. The terms correcting equation (2) are in general substantially smaller than those entering equation (1) because of the enhanced ordering in bidisperse systems [2, 4]. This is demonstrated later. It is now a small step towards surmising the correctness of equation (2) for polydisperse rods, i.e. it holds irrespective of composition. In this Preliminary Communication we show this straightforwardly. It is to be emphasized that the validity of equation (2) depends not only on the gaussian approximation, but also on the neglect of virial coefficients higher than the second and the neglect of end effects in the second virial coefficient itself. This implies that the rods must be sufficiently slender.

We first demonstrate the effectiveness of equation (2) in describing the osmotic pressure for systems of bidisperse rods. The longer rods are q times as long as the shorter ones ($L_2 = qL_1$) and whenever convenient the concentrations c' will be scaled with respect to $b_1 = (\pi/4)L_1^2D$, thus $c = c'b_1$. Because the rods are very slender the osmotic pressure, π_i, in the isotropic phase (denoted by the subscript i is given by

$$\pi_i/kT = c'_i(1 + c_i[1 + (q - 1)x_i]^2). \tag{3}$$

This expression does depend on the mole fraction x_i of longer rods. When the isotropic and nematic phases co-exist we should have the approximate rule on combining equations (2) and (3)

$$\begin{aligned} p &= \frac{c_i + c_i[1 + (q - 1)x_i]^2}{3c_a} \\ &= 1. \end{aligned} \tag{4}$$

In the table the prediction expressed by equation (4) is tested against the numerical solution [4] of Onsager-type integral equations for $q = 2$ and 5. For a relatively small length ratio ($q = 2$) the average value of p with the attendant standard deviation is $1·084 \pm 0·023$ but the gaussian theory [2] improves for $q = 5$, viz. $p = 1·040 \pm 0·033$. Hence, equation (2) is practically useful for bidisperse systems which gives us good reason for also proving the same equation for polydisperse systems.

Values of p calculated via equation (4) using values from tables II and III of [4]. In the gaussian approximation p equals unity.

x_i	$q = 2$	$q = 5$
0	1·123	1·123
0·1	1·047	1·072
0·2	1·056	1·027
0·3	1·067	0·997
0·4	1·076	1·000
0·5	1·086	1·011
0·6	1·093	1·029
0·7	1·102	1·058
0·8	1·109	1·074
0·9	1·116	1·092

The Helmholtz free energy of a solution of N polydisperse rods of total number density c' can be written in the second virial approximation as [1, 2, 4]

$$\begin{aligned} \Delta F/NkT = {} & \sum_i (x_i\mu_i^0/kT) - 1 + \ln c' + \sum_i x_i \ln x_i + \sum_i \sigma_i x_i \\ & + c' \sum_i \sum_j x_i x_j q_i q_j b \varrho_{ij}. \end{aligned} \tag{5}$$

Here the indices i and j refer to the different species, μ_i^0 is the standard chemical potential of rods i, x_i is the mole fraction of rods i, $q_i = L_i/L_1$ where L_1 is the length of the shortest rods, again the excluded volume $b_1 = (\pi/4)L_1^2D$ with D the diameter which is the same for all rods ($D \ll L_1$), $b_{ij} = q_i q_j b_1$ is the isotropic excluded volume between rods of types i and j. In the nematic phase, the negative of the orientational entropy σ_i and the dimensionless excluded volume ϱ_{ij} are given by

$$\sigma_i = \ln \alpha_i - 1, \tag{6}$$

$$\varrho_{ij} = \frac{4(\alpha_i + \alpha_j)^{1/2}}{(2\pi)^{1/2}\alpha_i^{1/2}\alpha_j^{1/2}}. \tag{7}$$

These quantities have been calculated in the gaussian approximation [2], i.e. they are just the leading order terms from Onsager's theory [1]. The parameters α_i are to be determined variationally; the maximization of ΔF with respect to α_i yields

$$\tfrac{1}{2}\pi^{1/2}c_a^{-1}\alpha_i^{1/2} = 2^{1/2}\sum_j x_j q_j q_i g(Q_{ij}), \tag{8}$$

with

$$g(z) = (1 + z)^{-1/2}, \tag{9}$$

and

$$\left.\begin{aligned} Q_{ij} &= \alpha_i/\alpha_j \\ c_a &= c_a' b_1. \end{aligned}\right\} \tag{10}$$

There are as many equations (8) as there are different species of rods and these equations are all interdependent. In spite of this complication, we can make significant progress in deducing π_a by following the analysis of [2].

Firstly, we find from equation (5) that

$$\pi_a/kT = c_a'(1 + \eta), \tag{11}$$

with

$$\eta = c_a\sum_i\sum_j x_i x_j q_i q_j \varrho_{ij}. \tag{12}$$

We rewrite equation (7) as follows, using equations (8)–(10),

$$c_a\varrho_{ij} = \frac{g^{-1}(Q_{ij})}{\sum_l x_l q_l q_i g(Q_{il})}. \tag{13}$$

Hence equation (12) can be written as

$$\eta = \sum_i\left(\frac{\sum_j x_i x_j q_i q_j g^{-1}(Q_{ij})}{\sum_l x_l q_l q_i g(Q_{il})}\right). \tag{14}$$

At this stage it is natural to express g^{-1} as

$$g^{-1}(Q_{ij}) = g(Q_{ij}) + Q_{ij}g(Q_{ij}). \tag{15}$$

Since by definition we have

$$\sum_i x_i = 1$$

η is reduced to

$$\eta = 1 + \sum_i\left(\frac{\sum_j x_i x_j q_i q_j Q_{ij} g(Q_{ij})}{\sum_m x_m q_m q_i g(Q_{im})}\right). \tag{16}$$

It is now expedient to eliminate c_a from equation (8)

$$Q_{ij}^{1/2} = \frac{\sum_k x_k q_k q_i g(Q_{ik})}{\sum_m x_m q_m q_j g(Q_{jm})}, \tag{17}$$

whence

$$\eta = 1 + \sum_j \left(\frac{\sum_i x_i x_j q_i q_j Q_{ij}^{1/2} g(Q_{ij})}{\sum_l x_l q_l q_j g(Q_{jl})} \right). \tag{18}$$

The use of the equality $Q_{ij}^{1/2} g(Q_{ij}) = g(Q_{ji})$ finally establishes the fact that $\eta = 2$; accordingly, equation (2) also holds for polydisperse rods.

We stress that in this Preliminary Communication we simply assume that the nematic phase is stable. To prove that equation (3) can be written as a positive definite form is not straightforward and we have not yet been able to do this. None the less it is easy to prove for the bidisperse case [2]. On physical grounds alone it would seem rather unlikely that a nematic phase would not form at high concentrations just because of polydispersity.

On the experimental side we remark that several groups of workers have started serious work on the characterization of anisotropic phases of stiff polymers such as TMV [5–6], polybenzylglutamate [7] and schizophyllan [8–10]. However, one severe difficulty in testing rigid-rod theories in practice is the influence of semiflexibility. Its effect has been shown to be very significant even for quite short wormlike chains [11–15].

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