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Theory of the Isotropic-Liquid Crystal Phase Separation for a Solution of Bidisperse Rodlike Macromolecules

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An analytical theory is presented for the isotropic-liquid crystal phase separation in a solution of bidisperse rodlike polymers when either the bidispersity ratio is close to unity or the fraction of longer rods in the isotropic phase is relatively small. Gaussian trial functions are used that depend on adjustable parameters which are found by minimizing the free energy of the system. It is shown that in the nematic phase the longer rods are always more highly ordered than the shorter ones. The coexistence equations can be simplified significantly, so that they can be conveniently solved by only one iteration. From the solutions it is straightforward to understand the involved phase separation in qualitative terms as well as the physical mechanism of the generally strong fractionation. The theory is in good agreement with extensive numerical work.

Introduction

In his paper¹ on the nematic-isotropic phase transition in a solution of monodisperse rodlike particles, Onsager already hinted that an extension of his calculations to the case of polydisperse rods would prove to be interesting. Without giving a derivation he noted that the longer rods should prefer the anisotropic phase. This fractionation has been substantiated by experiments.²⁻⁷ A fair amount of numerical analysis has been devoted to the effect of polydispersity both within the original framework of distribution functions^{8,9} and in the lattice approximation.¹⁰⁻¹⁴ Nevertheless, in order to gain physical insight into the mechanism of the fractionation we present an analytical theory for a system of long, bidisperse rodlike macromolecules.

The distribution-function theory remains a well-founded way^{15,16} to elucidate the nematic-isotropic phase transition, especially in systems of long rods. In particular, the Onsager theory has been brought to a high level of perfection by Kayser and Raveché.¹⁷ Still, in practice there will be substantial deviations from these calculations because the rods are never ideally hard particles^{1,18} and they are always flexible, perhaps minutely but nonetheless significantly.¹⁹⁻²² Therefore, we take along only the leading order

terms from the asymptotic expansions of the Onsager theory¹ in studying the complicated influence of bidispersity, i.e., the fact that the solution contains rods of two different lengths. For this reason we cannot claim a very high degree of precision in all our results, but we stress that the physically important terms are retained. Since Onsager's leading order terms can be derived from a Gaussian-type distribution function, we may call our theory the Gaussian approximation.

Our analysis shows that the phase separation of bidisperse rodlike macromolecules is a very delicate phenomenon although it is quite amenable to interpretation. It turns out that the coupling between shorter and longer rods in the nematic phase acts very differently on the respective macromolecules so that the respective order parameters are highly asymmetric. The longer rods are always more highly ordered than the shorter ones but the precise factor depends markedly on the molar fraction. Furthermore, the coexistence equations simplify considerably in the Gaussian approximation so that they become soluble by iteration at least under certain circumstances. The theory agrees rather well with a lot of numerical work. Perhaps more importantly, the complex numerical results can now be given a physical interpretation.

The plan of the paper is as follows. We first minimize the free energy of the system of bidisperse particles with respect to the adjustable parameters α_1 and α_2 that occur in Gaussian trial functions which are assumed to approximate the orientation distribution functions of the respective macromolecules. The condition for the stability of the nematic phase is discussed. Next, the expressions for α_1 and α_2 are used to simplify the coexistence equations. These in turn are solved by iterating in two cases: (A) relatively small bidispersity ratio and (B) relatively low molar fractions in the isotropic phase. These solutions are compared with previously published numerical work as well as new work. Finally, we give a qualitative discussion of the analytical expressions and an outline of the resulting osmotic pressure-composition phase diagram for the case of a large bidispersity ratio.

Formalism

First we shall briefly summarize several of the starting equations that have been discussed in considerable detail before.^{1,9} Specifically, we will adhere to the notation of ref 9. Let us consider a solution of volume V that contains N_1 rods of length L_1 and N_2 rods of length L_2 , all rods having the same diameter D . The rods interact mutually like hard particles. They are relatively long, i.e., $L_1 \gg D$, $L_2 \gg D$. For the sake of being definite we take

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$L_2 > L_1$. The Helmholtz free energy of the solution in dialytic equilibrium with the solvent at temperature T is given by^{1,9}

$$\frac{\Delta F}{Nk_B T} = \frac{F(\text{solution}) - F(\text{solvent})}{Nk_B T} = \left[\frac{(1-x)\mu_1^\circ(T, \mu_0) + x\mu_2^\circ(T, \mu_0)}{k_B T} \right] - 1 + \ln c' + (1-x) \ln(1-x) + x \ln x + (1-x)\sigma_1 + x\sigma_2 + c\{ (1-x)^2 b_{11}\rho_{11} + 2x(1-x)b_{12}\rho_{12} + x^2 b_{22}\rho_{22} \} \quad (1)$$

Here, $\mu_j^\circ(T, \mu_0)$ signifies the standard chemical potential of the rods in the solvent of chemical potential μ_0 ($j = 1$ refers to the shorter rods, $j = 2$ to the longer), k_B is Boltzmann's constant, $N = N_1 + N_2$ is the total number of macromolecules, $c' = N/V$ is the number density, x is the molar fraction of the longer rods, and $b_{jk} = (\pi/4)L_j L_k D$ is the average volume excluded by a pair of rods of types j and k if they were randomly oriented. The one-particle-orientation-distribution functions $f_1(\Omega)$ and $f_2(\Omega)$ determine the parameters σ_j and ρ_{jk} .

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

$$\rho_{jk} = 4\pi^{-1} \int \int \sin \gamma(\Omega, \Omega') f_j(\Omega) f_k(\Omega') d\Omega d\Omega' \quad j, k = 1, 2 \quad (3)$$

where $\gamma(\Omega, \Omega')$ is the angle between rods j and k and the solid angles Ω and Ω' refer to the direction of these rods with respect to the director. Equation 1 is the second virial approximation accurate only whenever $L_1, L_2 \gg D$.

If the solution is not isotropic the negative (confinement) entropy terms σ_j are enhanced. Nevertheless, the translational entropy increases because the excluded volume decreases (see eq 3). Therefore it is entirely feasible that a nematic phase might form provided the b_{jk} terms are large enough.⁹ Evidently, if x is unequal to either zero or unity, the coupling term b_{12} ultimately causes large deviations from the behavior of typically monodisperse solutions. We elucidate the isotropic-nematic phase separation by finding convenient approximations to f_j and by subsequently solving the coexistence equations derivable from eq 1.

Minimization of the Free Energy

To proceed one can either minimize eq 1 with respect to f_1 and f_2 or, as Onsager did,¹ choose realistic trial functions and then minimize with respect to adjustable parameters. His choice was particularly convenient

$$f_j(\Omega) = f_j(\theta) = \frac{\alpha_j}{4\pi \sinh \alpha_j} \cosh(\alpha_j \cos \theta) \quad j = 1, 2 \quad (4)$$

with α_1 and α_2 adjustable parameters and with normalization conditions

$$\int f_j(\Omega) d\Omega = 1 \quad j = 1, 2 \quad (5)$$

For the nematic phase f_j depends on θ only where θ represents the angle between the rod and the director. We will assume α_1 and α_2 are significantly larger than unity in the anisotropic phase, a restriction that will not allow us an exhaustive analysis but which suffices for many purposes.

The entropy terms (eq 3) are calculated for these trial functions in the remarkable appendix to Onsager's paper.¹ As we mentioned before, we retain only the leading order terms of his asymptotic expansions for large α_j , although we will correct partially for this neglect later on.

$$\sigma_j(\alpha_j) \simeq \ln(\alpha_j) - 1 \quad (\alpha_j \gg 1) \quad j = 1, 2 \quad (6)$$

$$\rho_{jk} \simeq \frac{4(\alpha_j + \alpha_k)^{1/2}}{(2\pi)^{1/2} \alpha_j^{1/2} \alpha_k^{1/2}} \quad (\alpha_j, \alpha_k \gg 1) \quad j, k = 1, 2 \quad (7)$$

We call this the Gaussian approximation because eq 6 and 7 can be obtained from the high α_j limit of eq 4 which is a Gaussian

distribution in θ (see eq A1 of Appendix A). Onsager's derivation of the asymptotic expansions is rather complicated. Since the precise α_j, α_k dependence of ρ_{jk} is essential to understanding the mechanism of the fractionation, we give a simple alternative analysis of this leading order term in Appendix A. For convenience we introduce the following dimensionless parameters:⁹

$$q \equiv L_2/L_1 \quad (8)$$

$$b \equiv b_{11} = (\pi/4)L^2 D \quad (9)$$

$$b_{12} = qb$$

$$b_{22} = q^2 b$$

We call q the bidispersity ratio.

If we minimize eq 1 using eq 6 and 7, we obtain

$$\frac{1}{2} \pi^{1/2} (bc')^{-1} \alpha_1^{1/2} = (1-x) + 2^{1/2} x q h(Q) \quad (10)$$

$$\frac{1}{2} \pi^{1/2} (bc')^{-1} \alpha_2^{1/2} = 2^{1/2} (1-x) q g(Q) + x q^2 \quad (11)$$

with the help of the following definitions

$$Q \equiv \alpha_2/\alpha_1 \quad (12)$$

$$h(Q) \equiv \left(\frac{Q}{Q+1} \right)^{1/2} \quad (13)$$

$$g(Q) \equiv (1+Q)^{-1/2} \quad (14)$$

The scaled concentration $c \equiv bc'$ can immediately be eliminated from eq 10 and 11

$$Q^{1/2} = \frac{q[xq + 2^{1/2} g(Q)(1-x)]}{[2^{1/2} h(Q)xq + (1-x)]} \quad (15)$$

In Appendix B we prove that $Q \geq \frac{1}{2}(8q^2 + 1)^{1/2} - \frac{1}{2}$, i.e., the longer rods are always more highly ordered. Equation 15 simplifies in the following cases.

(i) *The Case $q \gg 1$.* Equation 15 shows at once that Q must likewise be large. Hence we approximate $g(Q)$ by $Q^{-1/2}$ and $h(Q)$ by $1 - (2Q)^{-1}$ in order to solve eq 15 explicitly.

$$Q^{1/2} = \frac{xq^2 + [x^2 q^4 + 4(2^{1/2} xq + (1-x))(2^{1/2} q - 2^{-1/2} qx)]^{1/2}}{2[2^{1/2} xq + (1-x)]} \quad (16)$$

Equation 16 has the following approximate limits

$$Q \simeq \frac{1}{2} q^2 \quad xq \gg 1 \quad (17)$$

$$Q^{1/2} \simeq 2^{1/4} q^{1/2} + \frac{1}{2} x q^2 - 2^{-1/4} q^{3/2} x \quad x^2 q^3 \ll 1 \quad (18)$$

(ii) *q Close to Unity.* If $Q - 1$ is small compared to unity, the approximation $2Q^{1/2} \simeq 1 + Q$ turns out to be very good, so that eq 15 simplifies

$$4Q = q^2 + q(q^2 + 8)^{1/2} \quad (19)$$

We have yet to investigate the stability of the nematic phase, but at this stage it is convenient to write the ρ_{jk} functions explicitly in terms of q, Q , and x . From eq 7, 10, and 11 we have

$$c\rho_{11} = \frac{2}{1-x + 2^{1/2} x q h(Q)} \quad (20)$$

$$c\rho_{12} = \frac{2^{1/2} h^{-1}(Q)}{1-x + 2^{1/2} x q h(Q)} \quad (21)$$

$$c\rho_{22} = \frac{2}{q[2^{1/2}(1-x)g(Q) + xq]} \quad (22)$$

Here c is the scaled concentration bc' . In eq 1 the term η occurs

$$\eta \equiv c[(1-x)^2 \rho_{11} + 2x(1-x)q\rho_{12} + x^2 q^2 \rho_{22}] \quad (23)$$

Very surprisingly this formidable-looking function reduces to a

pure number if one uses eq 13–15 a number of times after substituting eq 20–22 into eq 23.

$$\eta = 2 + 2^{3/2}x(1-x) \left\{ \left[\frac{q(h^{-1}-h)}{1-x+2^{1/2}xqh} \right] - \left[\frac{g}{2^{1/2}(1-x)g+xq} \right] \right\} = 2 \quad (24)$$

Now the distribution functions pertaining to the isotropic phase are also solutions to the integral equations obtained from eq 1 (see ref 9; eq A1 of Appendix A cannot, of course, yield the isotropic solution for it is meaningless for small values of α_j). Accordingly, we require that a completely nematic phase is to be more stable than a fully isotropic phase at some scaled concentration c_a and this implies

$$\Delta F_a(c_a, x_a) < \Delta F_i(c_a, x_a)$$

where the indices a and i will from now on refer to the anisotropic and isotropic phases, respectively. Hence, we derive the following condition from eq 1, 2, 23, and 24:

$$(1-x_a)\sigma_{1,a} + x_a\sigma_{2,a} + 2 < c_a(1-x_a+x_aq)^2$$

or

$$1 + \ln \alpha_1 + x_a \ln Q < c_a(1-x_a+x_aq)^2 \quad (25)$$

Equations 10 and 11 give values of α_1 and α_2 for which ΔF has an extremum. In order to ensure that the nematic phase is stable viz. that ΔF also attains its minimal value, we require $\partial^2 \Delta F / \partial \alpha_1^2 > 0$, $\partial^2 \Delta F / \partial \alpha_2^2 > 0$, and $(\partial^2 \Delta F / \partial \alpha_1^2)(\partial^2 \Delta F / \partial \alpha_2^2) - (\partial^2 \Delta F / \partial \alpha_1 \partial \alpha_2)^2 > 0$ for $0 \leq x \leq 1$ and $q \geq 1$. A straightforward but lengthy calculation bears out that this condition is fulfilled. When solving the coexistence equations we must check whether inequality (25) holds.

Coexistence Equations

If we assume there are two possible phases that may coexist—one of them isotropic, the other anisotropic, denoted hereafter by the indices i and a, respectively—we can find their composition and concentration from the equality of the osmotic pressure and the particle chemical potentials in the respective phases. In terms of the scaled concentrations $c_i \equiv bc'_i$ and $c_a \equiv bc'_a$, we then have the following coexistence equations^{1,9}

$$c_i(1 + c_i[(1-x_i)^2 + 2x_i(1-x_i)q + x_i^2q^2]) = c_a(1 + c_a[(1-x_a)^2\rho_{11} + 2x_a(1-x_a)q\rho_{12} + x_a^2q^2\rho_{22}]) \quad (26)$$

$$\ln c_i + \ln(1-x_i) + 2c_i[(1-x_i) + x_iq] = \ln c_a + \ln(1-x_a) + \sigma_1 + 2c_a[(1-x_a)\rho_{11} + x_aq\rho_{12}] \quad (27)$$

$$\ln c_i + \ln x_i + 2c_iq[(1-x_i) + x_iq] = \ln c_a + \ln x_a + \sigma_2 + 2c_aq[(1-x_a)\rho_{12} + x_aq\rho_{22}] \quad (28)$$

At first sight the set of eq 26–28 seems intractable. Fortunately, the right-hand sides of all three of them can be simplified considerably. We have already remarked that $\eta = 2$ (see eq 24). This means that, at least within the Gaussian approximation, the osmotic pressure in the nematic phase is completely independent of the bidispersity, at least in an explicit sense.

Part of the right-hand side of eq 27 is rearranged as follows

$$\ln c_a + \sigma_1 + 2c_a[(1-x_a)\rho_{11} + x_aq\rho_{12}] = 3 \ln c_a + \ln(4/\pi) + 3 + \xi \quad (29)$$

with

$$\xi \equiv 2 \ln(1-x_a + 2^{1/2}x_aqh) - \frac{2^{3/2}g(Q-1)x_a}{[2^{1/2}(1-x_a)g + x_aq]} \quad (30)$$

Here we have repeatedly applied eq 6, 7, and 13–15 just as in the simplification of eq 23. Note that $\xi = 0$ in the monodisperse case.

It turns out to be convenient to use eq 28 not directly but rather with eq 27 subtracted from it. In the same way as previously we

simplify the awkward terms that appear by aptly using eq 6, 7, and 13–15

$$\omega \equiv \sigma_2 - \sigma_1 + 2c_aq[(1-x_a)\rho_{12} + x_aq\rho_{22}] - 2c_a[(1-x_a)\rho_{11} + x_aq\rho_{12}] = \ln Q + \frac{2^{3/2}g(Q-1)}{[2^{1/2}(1-x_a)g + x_aq]} \quad (31)$$

Again $\omega = 0$ if we have rods of only one length.

If the bidispersity ratio q is not very large, it is not difficult to solve the set of eq 6, 7, 10–14, 19, and 26–28 analytically by perturbation theory. For arbitrary q , however, we can make headway only under certain circumstances, for instance if $x_iq \ll 1$.

(A) *The Case $q-1 \ll 1$.* We write $q-1 = \epsilon$ which we take to be a small perturbation parameter and we expand all expressions up to order ϵ . Equation 19 gives $Q = 1 + (4\epsilon/3)$. Hence, eq 10 and 11 reduce to

$$1/2\pi^{1/2}c_a^{-1}\alpha_1^{1/2} = 1 + 1/3x_a\epsilon + O(\epsilon^2) \quad (32)$$

$$1/2\pi^{1/2}c_a^{-1}\alpha_2^{1/2} = 1 + 1/3\epsilon + 1/3x_a\epsilon + O(\epsilon^2) \quad (33)$$

Equations 6, 7, 24, and 26–33 lead to the following expressions correct to order ϵ :

$$c_i[1 + c_i(1 + 2x_i\epsilon)] = 3c_a \quad (34)$$

$$\ln c_i + \ln(1-x_i) + 2c_i(1 + x_i\epsilon) = 3 \ln c_a + \ln(1-x_a) + \ln(4/\pi) + 3 \quad (35)$$

$$\ln c_i + \ln x_i + 2c_i(1 + \epsilon + x_i\epsilon) = 3 \ln c_a + \ln x_a + \ln(4/\pi) + 3 + 4\epsilon \quad (36)$$

Note that there are no terms of order $x_a\epsilon$. Furthermore, ϵ does not enter in the right-hand side of eq 35 implying that to order ϵ the chemical potential of the shorter rods in the anisotropic phase is explicitly independent of the bidispersity.

Equations 34–36 are readily solved by iteration. First we subtract eq 35 from eq 36

$$\ln \left[\frac{x_i(1-x_a)}{x_a(1-x_i)} \right] + (2c_i - 4)\epsilon = 0 \quad (37)$$

Next, we write $c_i = c_{i,0} + \epsilon c_{i,1}$ and $c_a = c_{a,0} + \epsilon c_{a,1}$, substitute these identities in eq 34, 35, and 37 and collect all terms of the same order in ϵ , keeping in mind that $\ln(1-x_i)(1-x_a)^{-1}$ is possibly also of order ϵ . The zero-order terms which correspond to a monodisperse solution are given by

$$c_{i,0} + c_{i,0}^2 = 3c_{a,0} \quad (38)$$

$$\ln c_{i,0} + 2c_{i,0} = 3 \ln c_{a,0} + \ln(4/\pi) + 3 \quad (39)$$

The terms of order ϵ are

$$c_{i,1}(2c_{i,0} + 1) + 2x_i c_{i,0}^2 = 3c_{a,1} \quad (40)$$

$$\ln \left(\frac{1-x_i}{1-x_a} \right) + \epsilon c_{i,1} c_{i,0}^{-1} + 2x_i \epsilon c_{i,0} + 2\epsilon c_{i,1} = 3\epsilon c_{a,1} c_{a,0}^{-1} \quad (41)$$

$$\ln \left[\frac{x_i(1-x_a)}{x_a(1-x_i)} \right] + (2c_{i,0} - 4)\epsilon = 0 \quad (42)$$

We can eliminate $c_{i,1}$ from eq 40 and 41

$$\ln \left(\frac{1-x_i}{1-x_a} \right) + 3\epsilon c_{a,1}(c_{i,0}^{-1} - c_{a,0}^{-1}) = 0 \quad (43)$$

The numerical solution of eq 38 and 39 is $c_{i,0} = 3.4516$ and $c_{a,0} = 5.1217$ which should be compared to Onsager's values¹ $c_{i,0}^0 = 3.3399$ and $c_{a,0}^0 = 4.4858$. The small but significant discrepancy between the respective anisotropic concentrations arises because we have used only the leading order terms of Onsager's asymptotic expansions.¹ One possible way of correcting for the neglect of the higher order terms in his series is to replace $c_{i,0}$ and $c_{a,0}$ in eq 40–43 by Onsager's values or those of others.^{9,14} For the sake

of complete consistency, however, we shall use our own values most of the time.

There is also a second solution to eq 38 and 39, viz. $c_{i,0}^* = 0.98347$ and $c_{a,0}^* = 0.65023$. This can be discarded for the moment not because it violates inequality 25 but because α_1 is much too small to be in the range of validity of the Gaussian approximation.

Equation 42 is rewritten as follows:

$$x_a = x_i + \epsilon(2c_{i,0} - 4)x_i(1 - x_i) \quad (44)$$

Equation 43 then yields

$$c_a = c_{a,0} - 2c_{a,0}\epsilon x_i \quad (45)$$

As x_i increases, the total concentration c_a of rods in the anisotropic phase decreases monotonically. Moreover, x_i is always smaller than x_a , i.e., the longer rods are preferentially absorbed into the anisotropic phase. For $x_i = 1$, c_a reduces to $c_{a,0} - 2\epsilon c_{a,0}$ as it should, for it must equal $q^{-2}c_{a,0}$ to order ϵ . The quantities α_1 and α_2 which are related to the order parameters by the relations $S_1 = 1 - 3\alpha_1^{-1}$ and $S_2 = 1 - 3\alpha_2^{-1}$ also decrease monotonically with increasing x_i for the scaled concentration c_a is lowered quite rapidly.

$$S_1 = S_0 - \frac{4\epsilon x_i}{3}(1 - S_0) \quad (46)$$

$$S_2 = S_0 + \frac{4\epsilon}{3}(1 - x_i)(1 - S_0) \quad (47)$$

Here S_0 is the order parameter for the nematic phase in the monodisperse case and it is equal to $1 - 3\alpha_0^{-1}$ with $\pi^{1/2}\alpha_0^{1/2} = 2c_{a,0}$ from eq 10. Equation 25 amounts to

$$2 \ln c_{a,0} + \ln(4/\pi) + 1 < c_{a,0}$$

a condition that is readily verified and in fact identical with that for the monodisperse case.

(B) *The Case $x_i q \ll 1$.* If we assume x_i is very much smaller than q^{-1} we can make significant progress in solving the coexistence equations analytically. Equations 24 and 26 now give us a simple relation between c_i and c_a .

$$c_i + c_i^2 = 3c_a \quad (48)$$

From eq 27, 29, and 30 we have

$$\ln c_i + 2c_i = 3 \ln c_a + \ln(4/\pi) + 3 + \ln(1 - x_a) + \xi \quad (49)$$

Likewise, eq 27, 28, and 31 reduce to

$$\ln(x_i/x_a) + 2c_i(q - 1) = \omega - \ln(1 - x_a) \quad (50)$$

With the help of eq 48 we can simply eliminate c_a from eq 49

$$j(c_i) \equiv 2c_i - 2 \ln c_i - 3 \ln(1 + c_i) + 3 \ln 3 - \ln(4/\pi) - 3 = \ln(1 - x_a) + \xi \equiv \xi' \quad (51)$$

From the structure of eq 50 and 51 one can easily discern a convenient way of solving them. The Gibbs phase rule tells us that there is one variable from the set (x_i, x_a, c_i, c_a) that can be freely chosen. Evidently x_a is very suitable as an independent quantity. A fast numerical scheme is the following. From eq 15 and given values of x_a and q we calculate Q by iteration. The concentration c_i is then obtained from eq 30 and 51. Then c_a is calculated from eq 48 and finally the composition of the isotropic phase can be derived from eq 31 and 50. Once one knows Q and c_a the parameters α_1 and α_2 can be calculated from eq 10 and 11.

There is one remaining problem. The function $j(c_i)$ attains a minimal value of -0.62786 for $c_{i,m} = 2$ which implies that the number of possible solutions is two, one, or zero.

The number of tenable solutions must be sorted out with the aid of the following restrictions: (i) $\alpha_1 \gg 1$; (ii) $x_i q \ll 1$; and (iii) inequality 25.

The variable $\xi' = \xi + \ln(1 - x_a)$ can easily be rather small compared to unity, for instance, when x_a is small but also in quite a few other cases. Accordingly, it is fruitful in analytical work to write $c_i = c_{i,0} + \delta c_i$ where δc_i is regarded as a perturbation and so expand eq 51 in δc_i . In this manner, we obtain

$$\delta c_i \left(2 - \frac{2}{c_{i,0}} - \frac{3}{1 + c_{i,0}} \right) = \xi'$$

or

$$c_i = c_{i,0} + 1.3393\xi' \quad (52a)$$

Earlier on we dismissed the solution $c_{i,0}^* = 0.98347$ for $x_a = 0$ (see the discussion after eq 43). However, if x_a and q are large enough, it becomes possible to satisfy inequality 25 again so we have to examine this solution too.

$$c_i = c_{i,0}^* - 0.64678\xi' \quad (x_a \text{ and } q \text{ large enough}) \quad (52b)$$

Equations 48, 50, 52a, and 52b constitute analytical solutions to the coexistence equations for a certain range of parameters. They will be compared to numerical work later on.

It is of interest to study these expressions in more detail for very small values of x_a . First, we expand eq 13-15

$$Q = Q_0 + x_a Q_1 + O(x_a^2) \quad (53)$$

with

$$Q_0(Q_0 + 1) \equiv 2q^2 \quad (54)$$

and

$$Q_1 \equiv \frac{2Q_0^{1/2}(Q_0 + 1)(q^2 - Q_0^{3/2})}{(2Q_0 + 1)} \quad (55)$$

$$h = h_0 + x_a h_1 + O(x_a^2) \quad (56)$$

with

$$h_0 \equiv Q_0^{1/2}(Q_0 + 1)^{-1/2} \quad (57)$$

and

$$h_1 \equiv \frac{1}{2}Q_1Q_0^{-1/2}(Q_0 + 1)^{-1/2} \quad (58)$$

$$g = g_0 + x_a g_1 + O(x_a^2) \quad (59)$$

with

$$g_0 \equiv (Q_0 + 1)^{-1/2} \quad (60)$$

$$g_1 \equiv -\frac{1}{2}Q_1(Q_0 + 1)^{-3/2} \quad (61)$$

Equations 53-61 can be used to expand ξ and ω .

$$\xi = (Q_0^2 - Q_0^{3/2} - Q_0^{1/2} + 1)x_a^2 + O(x_a^3) \quad (62)$$

$$\omega = \ln Q_0 + 2Q_0 - 2 - 2x_a(Q_0^{3/2} - 1)(Q_0^{1/2} - 1) + O(x_a^2) \quad (63)$$

These results are consistent with the ϵ expansions given earlier.

If x_a is very small, c_i is close to either $c_{i,0}$ or $c_{i,0}^*$ and therefore c_a is, analogously, almost equal to either $c_{a,0}$ or $c_{a,0}^*$. We are allowed to disregard the c^* type solution given by eq 52b because it does not satisfy inequality 25.

Equations 50, 52a, 62, 63 yield to order x_a

$$\ln(x_i/x_a) = -A - Bx_a \quad (64)$$

where

$$A = 2c_{i,0}(q - 1) - \ln Q_0 - 2Q_0 + 2$$

and

$$B = 2(Q_0^{3/2} - 1)(Q_0^{1/2} - 1) - 1 - 2.6786(q - 1)$$

As x_i tends to zero, x_a ultimately does the same as it should. However, for q somewhat larger than unity, x_i is very much smaller than x_a since we have $Q_0 < 2^{1/2}q$ and thus $A > 0$

$$(x_i/x_a)_{x_i \rightarrow 0} = e^{-A} \quad (65)$$

Equation 64 shows that a rapid enhancement of x_a as a function of x_i is expected when x_i reaches a certain value $x_{i,f}$. A variation of δx_i in x_i leads to a variation δx_a given by

$$\frac{\delta x_i}{x_i} - \frac{\delta x_a}{x_a} = -B\delta x_a$$

TABLE I: Values of Q and the Scaled Parameters $1/2\pi^{1/2}c_a^{-1}\alpha_j$ for the Extreme Limits of x_a As Calculated from Eq 10-14

scaled parameters	limiting values for	
	$x_a \rightarrow 0$	$x_a \rightarrow 1$
$1/2\pi^{1/2}c_a^{-1}\alpha_1^{1/2}$	1	$q^2Q^{-1/2}$
$1/2\pi^{1/2}c_a^{-1}\alpha_2^{1/2}$	$Q^{1/2}$	q^2
relation between q and Q	$Q^2 + Q = 2q^2$	$2Q^2 = q^2(Q + 1)$

Hence if x_a becomes so large that $x_a B$ approaches unity the molar fraction x_a must increase sharply when x_i is only slightly enhanced. This value x_i can be written as

$$x_{i,f} = \frac{1}{B} e^{-(A+1)} \quad (66)$$

Behavior of the Order Parameters

We know from previous numerical work⁹ that both order parameters exhibit a maximum as a function of x_i for $q = 2$ and $q = 5$, but for q close to unity we have shown this cannot be so. In order to assess the behavior of the order parameters S_j analytically, we note the following statements.

(1) For $\alpha_j \gg 1$, we have $S_j = 1 - 3\alpha_j^{-1}$ within the Gaussian approximation.

(2) $S_j(x_a=0) > S_j(x_a=1)$ for $q > 1$. This follows from (i) $c_a \rightarrow c_{a,0}$ as $x_a \rightarrow 0$ where $c_{a,0}$ is the anisotropic concentration for monodisperse rods of type 1 (In the Gaussian approximation). (ii) $c_a \rightarrow q^{-2}c_{a,0}$ as $x_a \rightarrow 1$, from the definition of the scaled concentration. (iii) Q is larger than $1/2(8q^2 + 1)^{1/2} - 1/2$ (see Appendix B). (iv) The limiting results for the parameters α_j (see Table I).

(3) We assume the order parameters S_j do not have a minimum as a function of x_a . As yet we have no proof of this conjecture.

From these statements we deduce that S_j will have a maximum if $\partial\alpha_j/\partial x_a \geq 0$ for $x_a = 0$, i.e., when $q > 1.51$ in the case of α_1 and $q > 1.47$ in the case of α_2 (see eq 10, 11, 48, 52a, 54, 57, and 62).

Comparison with Numerical Work

First, we compare our theory with numerical solutions of the relevant integral equations together with the coexistence equations. The method is expounded in ref 9 and one uses the expansion of the kernel $\sin \gamma$ in Legendre polynomials.¹⁷ With the help of Alain Stroobants (Vrije Universiteit Brussel) we have obtained numerical results (bearing the superscript num) for $q - 1 = \epsilon = 0.01$ and

$\epsilon = 0.1$ as outlined in Tables II and III. Also tabulated are the analytical calculations according to the following expressions:

$$\Delta x \equiv x_a - x_i = (2c_{i,0}^{\text{num}} - 1)\epsilon x_i(1 - x_i) \quad (67)$$

$$c_i = c_{i,0}^{\text{num}}(1 - 2\epsilon x_i) \quad (68)$$

$$c_a = c_{a,0}^{\text{num}}(1 - 2\epsilon x_i) \quad (69)$$

$$S_1 = S_0^{\text{num}} - \frac{1}{3}\epsilon x_i(1 - S_0^{\text{num}}) \quad (70)$$

$$S_2 = S_0^{\text{num}} + \frac{1}{3}\epsilon(1 - x_i)(1 - S_0^{\text{num}}) \quad (71)$$

Equations 67-71 are obtained from eq 38, 40, and 44-47 but with the analytical quantities $c_{i,0}$, $c_{a,0}$, and S_0 replaced by the numerical ones $c_{i,0}^{\text{num}} = 3.2904$, $c_{a,0}^{\text{num}} = 4.1910$, and $S_0^{\text{num}} = 0.7922$, respectively. The reason for this is that α_1 and α_2 are, of course, close to $\alpha_0 = 33.4$ when ϵ is small so that for these relatively low α 's the errors incurred are substantial but, as we stated before, they are diminished somewhat by the use of the "real" $c_{i,0}$, $c_{a,0}$, and S_0 .

Judging from Tables II and III we can see that the fractionation Δx^{num} follows closely a relationship of the form

$$\Delta x^{\text{num}} \simeq 0.71\Delta x \quad (72)$$

Thus the main functional dependence of Δx^{num} on x_i is correctly predicted by eq 67 although the theory overestimates the fractionation by about 40%. There is also a very slight asymmetry apparent in Table II: Δx^{num} is a bit underestimated for $x_i < 0.5$ but overestimated for $x_i > 0.5$. This asymmetry increases when $\epsilon = 0.1$ as can be seen from Table III. The other semianalytical eq 68-71 work remarkably well and need little comment.

Next, we compare the theory with several results for $q = 2$ and $q = 5$ from ref 9. Because $x_i q$ is never sufficiently small in Tables II and III of ref 9, we assess the theory by inserting the numerical values from those tables into our analytical expressions for the coexistence equations, viz. eq 26-28, but with the right-hand sides given by eq 23, 24, and 29-31. We should end up with identities and Table IV shows this is reasonably the case. The values of α_1 in Table IV are equal to about 30 or so and we have not checked other entries from ref 9 because α_1 is then much too small.

In Table V we have contrasted numerical results via Onsager trial functions (see eq 4) with those using the Gaussian approximation. When the values of the α 's are large, our theory works very well. We emphasize that for very high α 's the usual ex-

TABLE II: Theory for $q - 1 = \epsilon = 0.01$ Compared with Numerical Analysis of the Integral Equations Analogous to That Described in Ref 9^a

x_i	Δx	Δx^{num}	c_i	c_i^{num}	c_a	c_a^{num}	S_1	S_1^{num}	S_2	S_2^{num}
0.1	0.00232	0.00168	3.2838	3.2838	4.1826	4.1826	0.7919	0.7919	0.7947	0.7950
0.2	0.00413	0.00297	3.2772	3.2772	4.1742	4.1742	0.7916	0.7916	0.7944	0.7947
0.3	0.00542	0.00388	3.2707	3.2707	4.1658	4.1658	0.7914	0.7912	0.7941	0.7944
0.4	0.00619	0.00442	3.2641	3.2641	4.1575	4.1575	0.7911	0.7909	0.7938	0.7941
0.5	0.00645	0.00459	3.2576	3.2575	4.1491	4.1492	0.7908	0.7906	0.7936	0.7938
0.6	0.00619	0.00439	3.2509	3.2512	4.1407	4.1410	0.7905	0.7903	0.7933	0.7935
0.7	0.00542	0.00382	3.2443	3.2447	4.1323	4.1328	0.7902	0.7900	0.7930	0.7931
0.8	0.00413	0.00290	3.2378	3.2383	4.1240	4.1246	0.7900	0.7896	0.7927	0.7928
0.9	0.00232	0.00163	3.2312	3.2319	4.1156	4.1165	0.7897	0.7893	0.7925	0.7925
1.0	0	0	3.2246	3.2256	4.1072	4.1084	0.7894		0.7922	0.7922

^aThe numerical results are denoted by num. The theoretical values have been calculated from eq 67-71.

TABLE III: Theory for $q - 1 = \epsilon = 0.1$ ^a

x_i	Δx	Δx^{num}	c_i	c_i^{num}	c_a	c_a^{num}	S_1	S_1^{num}	S_2	S_2^{num}
0.1	0.0232	0.0183	3.2246	3.2209	4.1072	4.1009	0.7894	0.7897	0.8171	0.8183
0.2	0.0413	0.0313	3.1588	3.1547	4.0234	4.0155	0.7866	0.7870	0.8144	0.8159
0.3	0.0542	0.0396	3.0930	3.0917	3.9395	3.9344	0.7838	0.7840	0.8116	0.8133
0.4	0.0619	0.0436	3.0272	3.0316	3.8557	3.8573	0.7811	0.7809	0.8088	0.8106
0.5	0.0645	0.0437	2.9614	2.9740	3.7719	3.7839	0.7783	0.7776	0.8060	0.8077
0.6	0.0619	0.0406	2.8956	2.9189	3.6881	3.7139	0.7756	0.7742	0.8033	0.8048
0.7	0.0542	0.0343	2.8298	2.8660	3.6042	3.6471	0.7728	0.7707	0.8005	0.8017
0.8	0.0413	0.0253	2.7639	2.8152	3.5204	3.5832	0.7700	0.7671	0.7977	0.7985
0.9	0.0232	0.0138	2.6981	2.7664	3.4366	3.5221	0.7672	0.7635	0.7950	0.7954
1.0	0	0	2.6323	2.7193	3.3528	3.4636	0.7645		0.7922	0.7922

^aSee captions and footnotes to Table II.

TABLE IV: Theory Compared with Numerical Analysis of Integral Equations As Described in Ref 9^a

q	x_i^N	x_a^N	c_i^N	c_a^N	l_1	r_1	l_2	r_2	l_3	r_3
2	0.1	0.496	2.301	2.773	8.706	8.319	5.790	5.808	8.655	8.492
2	0.2	0.588	1.900	2.240	7.908	6.720	4.979	5.020	8.153	7.956
5	0.1	0.741	0.770	0.601	1.932	1.803	1.789	1.942	8.216	7.919

^aThe variables indexed N are taken from Tables II and III of ref 9. They are used to calculate l_1 = lhs of eq 26; r_1 = rhs of eq 26 with the use of eq 23 and 24; l_2 = lhs of eq 27; r_2 = rhs of eq 27 with the use of eq 29 and 30; l_3 = lhs of eq 28; r_3 = rhs of eq 28 calculated from eq 29–31.

TABLE V: Typical Values of the Composition, Concentration, and Ordering Derived from Theory for $x_i q \ll 1$ and from Numerical Calculations with the Use of Onsager Trial Functions^a

q	x_a	x_i^{num} (x_i^{num})	c_a^{num} (c_a^{num})	c_i^{num} (c_i^{num})	α_1^{num} (α_1^{num})	α_2^{num} (α_2^{num})	Q^{num} (Q^{num})
2	0.1481	0.645×10^{-2} (1.00×10^{-2})	4.66 (4.17)	3.27 (3.12)	40.2 (26.6)	98.8 (67.4)	2.46 (2.54)
2	0.5327	0.709×10^{-1} (1.00×10^{-1})	3.37 (2.86)	2.72 (2.32)	44.2 (27.5)	115 (74.8)	2.61 (2.72)
3	0.06848	0.467×10^{-4} (1.00×10^{-4})	4.95 (4.52)	3.39 (3.28)	44.3 (31.2)	177 (129)	4.01 (4.14)
3	0.6612	0.617×10^{-3} (1.00×10^{-3})	3.90 (3.63)	2.96 (2.84)	163 (139)	827 (713)	5.07 (5.13)
3	0.7513	0.243×10^{-2} (1.00×10^{-2})	3.30 (2.57)	2.68 (2.29)	139 (81.4)	716 (428)	5.15 (5.26)
5	0.6621	0.724×10^{-11} (1.00×10^{-11})	6.46 (6.34)	3.93 (3.89)	1247 (1199)	15724 (15138)	12.61 (12.62)
5	0.7761	0.930×10^{-10} (1.00×10^{-10})	5.65 (5.63)	3.65 (3.64)	1235 (1221)	15975 (15833)	12.94 (12.96)
5	0.8323	0.977×10^{-9} (1.00×10^{-9})	4.95 (4.94)	3.38 (3.38)	1064 (1056)	13918 (13846)	13.08 (13.11)
5	0.8671	0.804×10^{-8} (1.00×10^{-8})	4.34 (4.28)	3.14 (3.12)	876 (851)	11528 (11227)	13.16 (13.19)
5	0.8976	3.46×10^{-2} (1.00×10^{-2})	0.958 (1.13)	1.27 (1.37)	45.2 (60.5)	598 (827)	13.23 (13.66)

^aThe latter results are denoted by num. Equation 10–15, 30, 31, 50, and 52a have been used to calculate the analytical quantities except for the last entry where we have used eq 52b instead of eq 52a by way of illustration.

pansions in Legendre polynomials are very weakly convergent and may sometimes be useless.

Finally, we have also used the Onsager trial functions to analyze the phase separation for very low x_a for the case $q = 3.2$. The limiting value of $x_i^{\text{num}}/x_a^{\text{num}}$ can be approximately written as

$$\ln(x_i^{\text{num}}/x_a^{\text{num}}) = -6.25 - 20x_a$$

This result should be compared with

$$\ln(x_i/x_a) = -7.68 - 7.62x_a$$

obtained from eq 64 with $Q_0 = 4.053$. However, α_1 is not particularly large so that the use of the numerical values $Q_0^{\text{num}} = 4.32$ and $c_{i,0}^{\text{num}} = 3.3399$ may be expedient. In fact we then obtain

$$\ln(x_i/x_a) = -6.59 - 10.3x_a$$

which is in better agreement with the fully numerical result. As x_i^{num} increases from 0.2843×10^{-4} to 0.2844×10^{-4} the anisotropic molar fraction x_a^{num} increases extremely sharply from 0.021497 to 0.325785. From eq 66 we get $x_{i,f} = 0.36 \times 10^{-4}$ which is quite close to the numerical value.

Discussion

We present a qualitative discussion of the theory for large values of the bidispersity ratio q . It is fruitful to distinguish between several regions.

(I) For $x_a q^{3/2} \ll 1$, the q^2 term in eq 11 can be neglected so we have $\alpha_2 = O(c_a^2 q^2 Q^{-1})$, this term arising from the interaction of the longer rods with an excess of shorter ones. Because x_a is much smaller than unity we must have $c_a \approx c_{a,0}$ and we can write $\alpha_1 = O(c_{a,0}^2)$. Thus $\alpha_2/\alpha_1 = Q = O(q^2 Q^{-1})$ and so $Q = O(q)$. Finally, we have $\alpha_2 = O(c_{a,0}^2 q)$, i.e., the longer rods are quite highly ordered. We can understand this effect more deeply by looking closely at the excluded-volume terms. In eq A4 of Appendix A we have $\theta = O(\alpha_1^{-1/2})$ and $\theta' = O(\alpha_2^{-1/2})$ for typical values of the angles and we can profitably expand eq A3: $\gamma \approx \theta + O(\theta^2/\theta) + O(\theta' \cos \phi)$ in order to obtain $\rho_{12} = O(\alpha_1^{-1/2}) + O(\alpha_1^{1/2}/\alpha_2)$; $\rho_{11} = O(\alpha_1^{-1/2})$ and $\rho_{22} = O(\alpha_2^{-1/2})$. The coupling term in ρ_{12}

is $Q^{1/2}$ times smaller than ρ_{22} which together with the fact that the random excluded volume B_{12} is q times B_{11} , leads to expressions for α_2 just given. Now $c_{a,0}[(1-x_a)\rho_{12} + x_a q \rho_{22}] = O(1)$ and $\sigma_2 = O(\ln q)$ but it so happens that $c_{i,0}$ is large enough to dominate in eq 28 so that a strong fractionation occurs (see eq 64).

(II) Next we have the region $q^{-3/2} \ll x_a \ll q^{-1}$. Again, the fraction of longer rods is small so that $c_a \approx c_{a,0}$ and $\alpha_1 = O(c_{a,0}^2)$ but α_2 has increased markedly: $\alpha_2 = O(c_{a,0}^2 x_a^2 q^4)$ and $Q = O(x_a^2 q^4)$.

(III) When x_a is increased further we reach the very complex region $x_a \gg q^{-1}$. The usual solution based on $c_{i,0}$ is, however, simple to discuss. For instance, if $x_a = x_{a,0} \approx 1 - (e^2/2q^2)$, $\xi' = 0$ and from eq 51 $c_a = c_{a,0}$. Hence, $\alpha_2 = O(c_{a,0}^2 q^4)$ and $\alpha_1 = O(c_{a,0}^2 q^2)$ so that $Q = O(q^2)$. All the rods are highly oriented.

The c^* type solution is much more intricate.

(i) For large q , ξ' may be written as

$$\xi' \approx \ln[2x_a^2 q^2(1-x_a)] - 2 \quad (73)$$

See eq 30 and Table I. This has an upper bound equal to $\ln(8q^2/27) - 2$ for $x = 2/3$. From eq 51 we then have $c_i = O(q^{-1})$ and so $c_a = O(q^{-1})$. For large q , inequality 25 holds but the very small α_1 values ($= O(1)$) make this solution useless.

(ii) ξ' is zero for $x_{a,0} \approx 1 - (e^2/2q^2)$ and the solution to eq 51 is $c_{i,0}^*$. For large enough q , inequality 25 definitely holds and $\alpha_1 = O(c_{a,0}^2 x_{a,0}^2 q^2)$ is then surely large enough. Hence, we know two solutions exist for $x_a = x_{a,0}$.

(iii) ξ' equals $-0.62786\ldots$ for $x_{a,m} \approx 1 - (1.97/q^2)$. Equation 51 has only one solution, namely, $c_i = 2$, and thus $c_a = 2$ (α_1 is large enough if q is so).

(iv) For $x_a > x_{a,m}$, $\xi' < -0.62786\ldots$ and so eq 51 has no solutions at all. Of course this conclusion is valid only if $x_i q$ is indeed much smaller than unity. As x_i tends to unity, we must eventually come across solutions with x_a larger than $x_{a,m}$.

(v) For $x_a = x_{a,0}$, the right-hand side of eq 50 is easily shown to be $O(\ln q)$. Hence, if q is large, $x_i q$ is certainly much smaller than unity.

These results are conveniently plotted in a coexistence diagram of the osmotic pressure (π_p) vs. the molar fraction (x) as in Figure

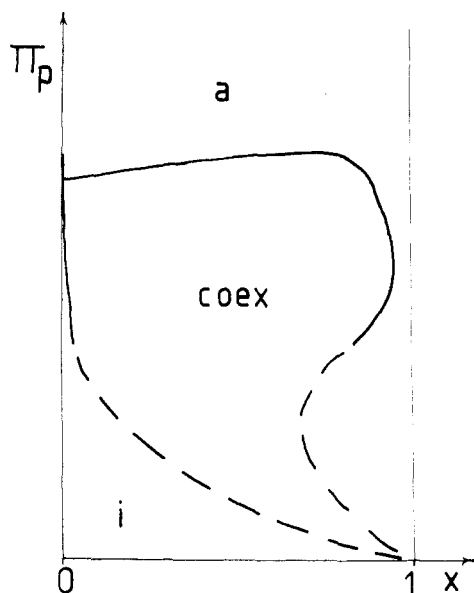


Figure 1. Qualitative features of the isotropic phase coexisting with the anisotropic phase as described by an osmotic pressure (Π)—molar fraction (x) diagram for large q . The full curves are drawn according to the Discussion whereas the dotted lines cannot be obtained from the present analytical expressions. A reentrant phase is evident.

1. Note that in view of eq 23 and 24, the osmotic pressure is just equal to $3k_B T c_a$. As can be seen from Figure 1, the theory provides evidence for the existence of a reentrant phase.

Concluding Remarks

Our theory which we have called the Gaussian approximation allows us to understand the physics behind the complicated phase separation occurring in solutions of bidisperse rodlike polymers. Although we cannot as yet fully comprehend those parts of the phase diagrams for which $x_i q$ is of order unity or larger, we find that the remaining parts are quite intricate although simply explainable. The comparison of the iteratively obtained equations with numerical work shows that the theory works quite well for both small and large bidispersity ratio. As a matter of fact, sometimes the predicted ordering is so high that we expect the analysis to be very reliable. We are thinking of extending the results in the near future.

Acknowledgment. We thank Alain Stroobants for providing us with the numerical results for the case of a small dispersity ratio and Jan Debruyne for carrying out the numerical calculations with the Onsager trial function.

Appendix A

If $\alpha_j \gg 1$, eq 4 can be approximated by

$$f_j(\theta) \simeq \left(\frac{\alpha_j}{4\pi} \right) \exp(-\frac{1}{2}\alpha_j \theta^2) \quad (0 \leq \theta \leq \frac{1}{2}\pi) \quad (\text{A1})$$

$$\simeq \left(\frac{\alpha_j}{4\pi} \right) \exp(-\frac{1}{2}\alpha_j(\pi - \theta)^2) \quad (\frac{1}{2}\pi \leq \theta \leq \pi)$$

In order to calculate γ we start from the well-known trigonometrical rule

$$\cos \gamma = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos \phi \quad (\text{A2})$$

Here ϕ is the angle between the rods when they are projected onto a plane perpendicular to the director. Because $\alpha_j \gg 1$, the angles θ , θ' , and γ are very small on the average so that we can expand eq A2

$$\gamma^2 \simeq \theta^2 + \theta'^2 - 2\theta\theta' \cos \phi \quad (\text{A3})$$

In spite of this simplification, the excluded volume term ρ_{jk} given by eq 3, A1, and A3 is still not trivial.

$$\rho_{jk} \simeq \frac{2\alpha_j \alpha_k}{\pi^2} \int_0^{2\pi} \int_0^{1/2\pi} \int_0^{1/2\pi} d\phi d\theta d\theta' \theta\theta' (\theta^2 + \theta'^2 - 2\theta\theta' \cos \phi)^{1/2} \exp(-\frac{1}{2}\alpha_j \theta^2 - \frac{1}{2}\alpha_k \theta'^2) \quad (\text{A4})$$

To make headway, we preaverage the cosine term, a procedure which should not lead to significant error.

$$\rho_{jk} \simeq \frac{\alpha_j \alpha_k}{\pi} \int_0^{1/2\pi} \int_0^{1/2\pi} d\theta^2 d\theta'^2 (\theta^2 + \theta'^2)^{1/2} \exp(-\frac{1}{2}\alpha_j \theta^2 - \frac{1}{2}\alpha_k \theta'^2) \quad (\text{A5})$$

If we switch to the new variables $t = \frac{1}{2}\alpha_j \theta^2$, $u = \frac{1}{2}\alpha_k \theta'^2$ and $\alpha_k/\alpha_j = P$ where we let $P \leq 1$ for convenience (otherwise $\alpha_j/\alpha_k = P$), we are able to integrate with respect to u .

$$\rho_{jk} \simeq 4.2^{1/2} \alpha_k^{-1/2} \pi^{-1} \int_0^\infty dt e^{t(P-1)} I(Pt) \quad (\text{A6})$$

with

$$I(z) \equiv \int_z^\infty dp p^{1/2} e^{-p}$$

Equation A6 is simplified by integrating by parts

$$\rho_{jk} \simeq 4(2\pi)^{-1/2} \frac{\alpha_j^{3/2} - \alpha_k^{3/2}}{(\alpha_j - \alpha_k) \alpha_j^{1/2} \alpha_k^{1/2}} \quad (\text{A7})$$

This expression is all but identical with eq 7. The small discrepancy of at most 6% when $\alpha_j = O(\alpha_k)$ is due to the preaveraging.

Appendix B

After straightforward but tedious algebra one finds

$$\frac{\partial Q^{1/2}}{\partial x} = \frac{q^2(1+Q)^{3/2}(1-2hg)}{(2^{1/2}hxq + 1-x)[(1+Q)^{3/2}(2^{1/2}hxq + 1-x) + 2^{1/2}Q^{1/2}q]} \quad (\text{B.1})$$

From this expression it follows that $\partial Q^{1/2}/\partial x \geq 0$. The equality holds for $Q = 1$. For $x = 0$ one finds

$$Q = Q_0 = \frac{1}{2}(8q^2 + 1)^{1/2} - \frac{1}{2} \quad (\text{B.2})$$

Thus for $q > 1$ one finds $Q_0 > q > 1$ and this means that, for $q > 1$, Q is a monotonically increasing function of x that lies between

$$\frac{1}{2}(8q^2 + 1)^{1/2} - \frac{1}{2} \quad (\text{for } x = 0)$$

and

$$\frac{q^2}{4} + \frac{q^2}{4} \left(1 + \frac{8}{q^2} \right)^{1/2} \quad (\text{for } x = 1)$$