

# Demixing in Isotropic Binary Mixtures of Rodlike Macromolecules

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A binary mixture of long rigid rods of diameters  $D_i$  and lengths  $L_i$  ( $i = 1, 2$ ) may demix into two isotropic phases, and we give necessary conditions on the molecular size parameters for this transition to exist. These conditions imply that the two diameters must be sufficiently unequal,  $D_2/D_1 > (\frac{9}{7} + \frac{4}{7}\sqrt{2})^2$ , or  $D_2/D_1 < (\frac{9}{7} - \frac{4}{7}\sqrt{2})^2$ , while the length ratio is limited to an interval  $f_-(D_2/D_1) < L_2/L_1 < f_+(D_2/D_1)$ . The functions  $f_{\pm}$  are given explicitly.

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**KEY WORDS:** Colloids; phase transitions; binary mixtures; hard rods.

## 1. INTRODUCTION

For a monodisperse solution of thin hard rods, Onsager's theory,<sup>(1)</sup> exact in the limit of the diameter-to-length ratio going to zero, yields a first-order transition between an isotropic phase and a nematic phase. The generalization of Onsager's theory to binary mixtures shows that in addition to the isotropic-nematic transition,<sup>(2-3)</sup> demixing transitions both in the nematic phase<sup>(4-5)</sup> and in the isotropic phase<sup>(6-8)</sup> may appear, as well as associated three-phase equilibria. The existence of each of these demixing transitions depends on the diameter and length ratios,  $D_2/D_1$  and  $L_2/L_1$ , for the species. For the existence of the demixing transition in the nematic phase there exist explicit results (using gaussian parametrization of the orientational distribution functions) for arbitrary length and diameter ratios.<sup>(10)</sup> The present article deals with the demixing transition in the *isotropic* phase.

The demixing transition in the isotropic phase has been shown to exist only in three very special cases. The first<sup>(6)</sup> is in the limit when  $D_2/D_1 \rightarrow 0$ ,

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This work is dedicated to George Stell on the occasion of his 65th birthday.

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the second<sup>(7)</sup> is for a mixture in which  $L_1 D_1^2 = L_2 D_2^2$ , and the third<sup>(8-9)</sup> is for equal lengths,  $L_1 = L_2$ . Isotropic demixing is not seen in the much-studied case of rods with equal diameters ( $D_1 = D_2$ ). In the present article we study general diameter and length ratios, and determine by simple analytic means necessary conditions for the demixing transition to exist. In the concluding paragraph we compare our results to the special cases just mentioned.

## 2. FREE ENERGY FUNCTIONAL

We consider a bidisperse solution containing  $N_1$  hard rods of diameter  $D_1$  and length  $L_1$ , and  $N_2$  rods of diameter  $D_2$ , with aspect ratios  $L_i/D_i$  so large that Onsager's theory applies. We will also use the notation  $D_2/D_1 = d$  and  $L_2/L_1 = l$ . The distribution of directions  $\Omega$  of the rods of type  $i$  is described by a probability density  $f_i(\Omega)$ , normalized so that

$$\int f_i(\Omega) d\Omega = 1 \quad (1)$$

The basic equations for a multicomponent Onsager mixture are well known<sup>(5)</sup> so we just summarize them briefly. The Helmholtz free energy contains mixing entropy terms, orientational entropy terms, and excluded volume contributions. The difference  $\Delta F$  between the free energy of the solution and the solvent is given by

$$\frac{\Delta F}{(N_1 + N_2) k_B T} = \ln c + \sum_{i=1}^2 x_i \ln x_i + f_{ang} + f_{excl} \quad (2)$$

where  $c = (N_1 + N_2)/V$  is the number density,  $x_i$  is the mole fraction of species  $i$ , while  $k_B$ ,  $T$  and  $V$  have their usual meaning,

$$f_{ang} = \sum_{i=1}^2 x_i \int f_i(\vartheta) \ln[4\pi f_i(\vartheta)] d\Omega \quad (3)$$

measures the orientational entropy, while

$$f_{excl} = \frac{1}{2} c \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j \rho_{ij} L_i L_j (D_i + D_j) \quad (4)$$

is the contribution to the free energy due to excluded-volume effects. Here

$$\rho_{ij} = \iint |\sin \gamma| f_i(\vartheta) f_j(\vartheta') d\Omega d\Omega' \quad (5)$$

is the average of  $|\sin \gamma|$ ,  $\gamma(\Omega, \Omega')$  being the angle between a rod of type  $i$  and one of type  $j$ . An additive constant in (2) is omitted.

The minimalization of the free-energy functional (2) with respect to the orientational distribution functions  $f_i$  yields the following set of integral equations

$$c \sum_{j=1}^2 x_j L_i L_j (D_i + D_j) \int |\sin \gamma(\Omega, \Omega')| f_j(\vartheta) d\Omega' + \ln[4\pi f_i(\vartheta)] = \lambda_i \quad (6)$$

where the constants  $\lambda_i$  are fixed by the normalization conditions (1).

A priori one might consider the possibility that in one phase one component is isotropically distributed while the other is not. However, using in (6) the Legendre function expansion<sup>(11)</sup>

$$\begin{aligned} & \int_0^{2\pi} |\sin \gamma(\Omega, \Omega')| d\varphi \\ &= 2\pi \sum_{n=0}^{\infty} c_n P_{2n}(\cos \vartheta) P_{2n}(\cos \vartheta'), \quad \text{with } c_0 = \frac{1}{4}\pi; \quad (7) \\ & c_n = -\frac{(4n+1)[(2n-1)!!]^2}{2^{2n+2}(2n-1)n!(n+1)!} \pi \quad (n \geq 1) \end{aligned}$$

it is trivial to show that if one component is isotropically distributed ( $f(\vartheta) = 1/4\pi$ ), the other is also.

For sufficiently high densities an isotropic phase has a first-order transition to a nematic phase. For a one-component system the transition corresponds to coexisting dimensionless densities  $\hat{c} = \frac{1}{4}\pi L^2 Dc$  equal to  $\hat{c} \simeq 3.290$  and  $\hat{c} \simeq 4.191$ . For part of the discussion it will be convenient to introduce scaled densities

$$\hat{c}_i = \frac{1}{4}\pi L_i^2 D_i c x_i \quad (8)$$

so that in these variables the isotropic-nematic transitions for the pure components are identical in form.

### 3. CRITICAL POINT OF ISOTROPIC-ISOTROPIC TRANSITION

In isotropic phases the Helmholtz free energy (2) simplify since  $f_{ang} = 0$  and  $\rho = \pi/4$ . The corresponding chemical potentials

$$\mu_i = \left( \frac{\partial \Delta F}{\partial N_i} \right)_{T, V, N_j}$$

can be expressed as

$$\beta\mu_1 = \ln \hat{c}_1 + 2\hat{c}_1 + \hat{c}_2 l^{-1}(1+d^{-1}) \quad (9)$$

$$\beta\mu_2 = \ln \hat{c}_2 + 2\hat{c}_2 + \hat{c}_1 l(1+d), \quad (10)$$

apart from an unimportant additive constant.

We locate a possible critical point by equating to zero the first and second derivative of the chemical potential  $\mu_1$  with respect to the density  $\hat{c}_1$ , at constant chemical potential of the other species.

First we eliminate  $\hat{c}_2$  using (9):

$$\hat{c}_2 = \frac{ld}{1+d} (\beta\mu_1 - \ln \hat{c}_1 - 2\hat{c}_1) \quad (11)$$

Insertion into (10) and differentiation with respect to  $\hat{c}_1$  at constant  $\mu_2$  yields

$$\frac{\partial(\beta\mu_1)}{\partial\hat{c}_1} = \frac{1}{\hat{c}_1} + 2 - \frac{l(1+d)}{(\beta\mu_1 - \ln \hat{c}_1 - 2\hat{c}_1)^{-1} + 2dl/(1+d)} \quad (12)$$

A second differentiation yields

$$\begin{aligned} \frac{\partial^2(\beta\mu_1)}{\partial\hat{c}_1^2} &= -\frac{1}{\hat{c}_1^2} + \frac{l(1+d)}{[(\beta\mu_1 - \ln \hat{c}_1 - 2\hat{c}_1)^{-1} + 2dl/(1+d)]^2} \\ &\times \frac{(-\partial\beta\mu_1/\partial\hat{c}_1 + 2 + 1/\hat{c}_1)}{(\beta\mu_1 - \ln \hat{c}_1 - 2\hat{c}_1)^2} \end{aligned} \quad (13)$$

Equating the first and the second derivative, (12) and (13), to zero and eliminating  $\mu_1$ , we obtain

$$l = \frac{(1+d)^3 \hat{c}_1}{(1+2\hat{c}_1)[(1-d)^2 \hat{c}_1 - 2d]^2} \quad (14)$$

The value of  $\hat{c}_2$  follows from (11) and the critical value of  $\mu_1$  just determined through  $\partial\mu_1/\partial\hat{c}_1 = 0$ :

$$\hat{c}_2 = \frac{(1+2\hat{c}_1)d}{(1-d)^2 \hat{c}_1 - 2d} \quad (15)$$

Due to our scaling this relation is symmetric in  $\hat{c}_1$  and  $\hat{c}_2$ :

$$1 + 2\hat{c}_1 + 2\hat{c}_2 = (1-d)^2 d^{-1} \hat{c}_1 \hat{c}_2 \quad (16)$$

For a fixed  $d$  this is a hyperbola in the  $\hat{c}_1, \hat{c}_2$  plane, shown in Fig. 1. A point on the hyperbola corresponds to a definite length ratio  $l$ , given by (14).

#### 4. STABILITY OF ISOTROPIC PHASES

With increasing density the isotropic solution of the integral equations (6) will be unstable in the sense that a nonisotropic perturbation of the orientational distribution functions can lower the free energy. For the one-component system this first occurs<sup>(11)</sup> at  $\hat{c} = 4$ , a density in the transition region. At this density a second solution,  $f - 1/4\pi \propto P_2(\cos \vartheta)$  bifurcates from the isotropic solution. It is straightforward to generalize this procedure to the bidisperse situation, by finding the criterion for a non-isotropic integral equation solution

$$4\pi f_i(\vartheta) = 1 + \varepsilon \alpha_i P_2(\vartheta) \quad (17)$$

deviating infinitesimally from an isotropic solution, to exist. This criterion is useful since it provides an exact analytic bound for the presence of the isotropic phase. The bound also serves as an indication of the location of the isotropic-nematic transition.

Insertion of (17) into (6), linearizing, and using the Legendre function expansion (8) we obtain

$$\sum_j \left[ \delta_{ij} - \frac{1}{32} \pi c x_j L_i L_j (D_i + D_j) \right] \alpha_j = 0 \quad (18)$$

In terms of the dimensionless densities (8), the determinant of this set of homogeneous equations equals

$$\left| \delta_{ij} - \frac{1}{8} \hat{c}_j \frac{L_i}{L_j} \left( 1 + \frac{D_i}{D_j} \right) \right| = 0 \quad (19)$$

Written out for the bidisperse case, this takes the form

$$4 - \hat{c}_1 - \hat{c}_2 - \frac{1}{16} (d-1)^2 d^{-1} \hat{c}_1 \hat{c}_2 = 0 \quad (20)$$

For the monodisperse systems the value  $\hat{c}_i = 4$  is recovered, and for equal diameters ( $d=1$ ) the simple result  $\hat{c}_1 + \hat{c}_2 = 4$  agrees with Vroege and Lekkerkerker.<sup>(5)</sup> Note the important role of the diameter ratio, since for large  $d$ ,  $\hat{c}_1 + \hat{c}_2$  can be low as  $16/\sqrt{d}$ .

The relation (16) is a hyperbolic relation between the critical densities  $\hat{c}_1$  and  $\hat{c}_2$ . If this hyperbola is located wholly on the high-density side of the

bifurcation hyperbola (20), no isotropic-isotropic transition is present (see Fig. 1). The borderline case is when the hyperbolas touch, which by symmetry must occur at  $\hat{c}_1 = \hat{c}_2$ . The borderline case corresponds to  $\hat{c}_1 = \hat{c}_2 = \frac{7}{4}$  and  $(d-1)^2/d = 128/49$ . The two solutions of the equation for the borderline diameter are  $d_0$  and  $1/d_0$ , with

$$d_0 = \left(\frac{9}{7} + \frac{4}{7}\sqrt{2}\right)^2 = 4.38415 \quad (21)$$

Thus no isotropic-isotropic demixing occurs when

$$d \in \left(\left(\frac{9}{7} - \frac{4}{7}\sqrt{2}\right)^2, \left(\frac{9}{7} + \frac{4}{7}\sqrt{2}\right)^2\right) \simeq (0.228, 4.384) \quad (\text{no demixing}) \quad (22)$$

The corresponding length ratios follow from Eq. (14).  $d_0$  and  $1/d_0$  correspond to

$$l_0 = \frac{9}{7} - \frac{4}{7}\sqrt{2} \quad \text{or} \quad 1/l_0 = \frac{9}{7} + \frac{4}{7}\sqrt{2} \quad (23)$$

respectively. Note that  $d_0 l_0^2 = 1$ .

For  $d > d_0$  part of the critical point hyperbola (16) is outside the unstable high-density region. This part corresponds to

$$c_- < \hat{c}_1 < c_+, \quad \text{where} \quad c_{\pm} = \frac{1}{4}(7 \pm \sqrt{49 - 128d(d-1)^{-2}}) \quad (24)$$

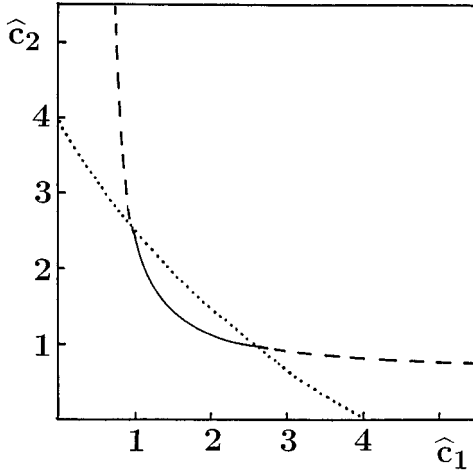


Fig. 1. Line of critical points in the density-density plane, fully drawn on the low-density side of the bifurcation line (dotted), dashed on the unstable high-density side of the bifurcation line. The  $\hat{c}_i$  are the scaled densities (8). The figure corresponds to  $D_2 = 5D_1$ .

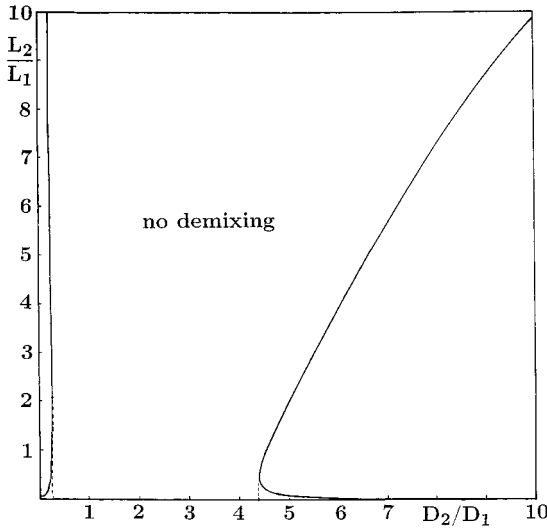


Fig. 2. Stability dependence on the diameter ratio  $D_2/D_1$  and length ratio  $L_2/L_1$ . In the central region no demixing can occur since the critical point is unstable. The upper boundary approach  $L_2/L_1 = 28$  for  $D_2/D_1 \rightarrow \infty$ . The dashed lines correspond to the borderline diameters (22).

Here  $c_- \leq \frac{7}{4} \leq c_+ \leq \frac{7}{2}$ . The density interval (24) corresponds via (14) to an interval of length ratios,

$$f_-(d) < l < f_+(d) \quad (25)$$

When  $d$  increases from  $d_0$  to infinity,  $f_-(d)$  decreases from  $l_0$  to zero, while  $f_+(d)$  increases from  $l_0$  to 28. For large  $d$

$$f_-(d) = \frac{1}{28} d^{-1} + \mathcal{O}(d^{-2}); \quad f_+(d) = 28 - \frac{1828}{7} d^{-1} + \mathcal{O}(d^{-2}) \quad (26)$$

Thus there can be no isotropic-isotropic demixing when  $l > f_+(d)$  or  $l < f_-(d)$ .

Figure 2 shows the set of molecular size parameters for which we now have demonstrated the absence of demixing. The figure is of course invariant under simultaneous inversion of both ratios (i.e.,  $d \rightarrow 1/d$ ,  $l \rightarrow 1/l$ ). For equal lengths ( $l=1$ ) no demixing occurs for diameter ratios in the interval (0.22079, 4.52921).

## 5. CONCLUDING REMARKS

We have derived necessary conditions for isotropic demixing to occur. In order to locate the necessary and sufficient conditions, i.e., to find

precisely where the isotropic-nematic phase transition preempts the isotropic demixing, numerical solutions of the coupled integral Eqs. (6) for the two orientational distribution functions must be performed, for different densities and compositions. This is not done here.

We can check how our results compare with the special cases that have been discussed in the literature. For  $d \rightarrow 0$  the critical condition (16) reduces to

$$l = \frac{1}{\hat{c}_1 + 2\hat{c}_1^2} \quad (27)$$

and the stability condition (20) to

$$4 = \hat{c}_1(1 + \frac{1}{16}\rho_2), \quad \rho_2 = \hat{c}_2/d \quad (28)$$

in agreement with Sear and Jackson (their Eqs. (14) and (31)).

Sear and Mulder<sup>(7)</sup> studied the symmetric-mixture case, defined by  $l^2d=1$ , and found that isotropic demixing first appears when their parameter  $\delta = 2/(l+l^{-1})$  is “slightly below 0.75.” This is consistent with our stability criterion for this case,  $\delta < 2(l_0 + l_0^{-1}) = \frac{7}{9} = 0.777$ . Evidently the transition appears fairly close to the stability threshold.

For  $L_1 = L_2$  our precise stability requirement is  $d > 4.52921$ . This is consistent with the conclusion of van Roij and Mulder<sup>(8)</sup> that “demixing sets in well before the orientational ordering if  $d$  is sufficiently large, at least larger than about  $d \approx 5$ .” Subsequently van Roij, Mulder and Dijkstra<sup>(9)</sup> found that for  $d=8$  isotropic-isotropic coexistence exists, while it is preempted by the isotropic-nematic transition for  $d=7$ .

A final remark is that it is not surprising that demixing requires the diameters of the two components to be sufficiently different. This is reminiscent of demixing in fluid hard-sphere mixtures which apparently requires the diameters of the two species to be sufficiently different, the necessary ratio estimated<sup>(12)</sup> to be of the order of 5. However, that the lengths of the two components must not be too different is unsuspected and remarkable.

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