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Phase Behaviour of Athermal Mixtures of Rigid-Rod and Flexible Polymers

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Abstract. — Lyotropic mixtures of rodlike and flexible polymers are studied. The rodlike polymer is modelled by a hard rod and the flexible polymer by a self-avoiding walk. The interaction between rodlike and flexible polymers is studied and a tendency for this interaction to force demixing is found. Diameters of the rod which are much larger than the diameter of the segments of the flexible polymer but much smaller than its radius of gyration are considered because of their relevance to mixtures of helical biopolymers and flexible polymers.

1. Introduction

The term polymer covers a very wide range of molecules which have little in common except that they are spaghetti-like, they are very long and thin [1]. The diameter of a polymer molecule is always much less than its length but it varies widely between different polymers; it is only $\sim 0.2 \text{ nm}$ for a flexible polymer such as polyethylene oxide but is estimated to be $\sim 4 \text{ nm}$ for poly($\gamma$-stearyl $\alpha$,L-glutamate) helices [2] and is $\sim 2 \text{ nm}$ for the DNA double helix [3, 4]. Another feature of polymers which varies widely from polymer to polymer is the flexibility of the polymer chain, as measured by its persistence length. The persistence length [4, 5] measures the flexibility of the polymer; the polymer molecule only bends significantly over distances of the persistence length or greater. The polymers with the largest diameters are helices and these helices tend to be very rigid; for example, DNA has a persistence length $\sim 50 \text{ nm}$ [3]. So, at one extreme we have polymers whose diameters and persistence lengths are both a few tenths of nanometers and at the other are polymers with diameters of several nanometers and persistence lengths of perhaps 100 nm. Here, we study a mixture of two polymers, one from each extreme. Such mixtures occur in the study of biological systems [6], in protein partitioning [7], and they form the basis of molecular composites [8].

Our mixtures are lyotropic, the two polymers are in solution. Indeed we consider only the case where the fraction of the solution's volume occupied by the two polymers is small. This solvent is good for the flexible polymer which is therefore swollen [1]. The interactions between the rigid polymer molecules are taken to be just those between hard rods [5, 9]; there are no attractive interactions. Any flexibility in the rodlike polymer is also neglected. The interaction between the rigid and flexible polymers is taken to be a simple excluded volume interaction.

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Each rod excludes the segments of the flexible polymer from a volume a little bigger than the volume it occupies \([10]\). Thus, our theory cannot describe all rigid-polymer–flexible-polymer mixtures. However, the requirement that there be no attractive interactions between the rigid rods is required in order that the solution be stable \([11, 12]\) and the effect of small amounts of flexibility is not too dramatic, although it certainly moves the isotropic–nematic transition to higher densities \([5, 13, 14]\). The absence of attractive interactions between the two polymers means that we are unable to describe systems in which the flexible polymer adsorbs on the rodlike polymer \([15]\) but the athermal system we can describe may provide a useful reference system.

In the following section we derive the scaling form for the interaction between a large diameter rigid polymer and a small diameter flexible polymer. The diameter of the rigid polymer is always much smaller than the radius of gyration of the flexible polymer. The case where the two diameters are the same has been considered by Joanny \([16]\). We then combine this with existing expressions for the interactions between rods \([9]\) and between polymer coils \([1]\), to give a free energy for the mixture. Using this, we discuss the effect on the phase behaviour, in particular on the isotropic–nematic transition, of adding a dilute solution of coils to a solution of the rigid polymer. In fact, we limit our discussion to mixtures in which the small polymer is dilute. The case of mixtures in which the small polymer is semidilute is also interesting but requires a different theoretical approach from that presented here.

### 2. The Rod-Coil Interaction

Here we consider the interaction between a polymer coil, modelled as a self-avoiding walk \([1]\) and a rigid, hard rod \([5]\), see Figure 1. First we consider the interaction when the centres of mass of both are fixed and then we go on to calculate the second virial coefficient of the interaction. We will be mainly dealing with the case of \(D\), the diameter of the rigid rod, much larger than the Kuhn length of the polymer \(a\). The regime where \(D \gg a\) is both relevant and very little studied. Rigid polymers and in particular rigid biopolymers such as DNA have quite large diameters of a few nanometers whereas the Kuhn length of many flexible polymers is a few tenths of nanometers, \(e.g.\) that of polyethylene oxide (PEO) is given as 0.3 nm \([17]\).
The large diameter and the rigidity are connected: DNA’s rigidity and large diameter are both due to the fact that DNA exists as a helix. We only determine the virial coefficient up to a dimensionless constant of order unity, that is we only determine the scaling of the coefficient with the three relevant length scales: \( D, L \) and \( R_G \).

We start by considering not a long rod but a sphere of diameter \( D \gg a \) and determine its interaction with a polymer coil of size \( R_G \gg D \). The polymer coil is swollen due to self-interactions \([1]\) and so \( R_G \) is related to the Kuhn length \( a \) and the number of segments \( N \) by \( R_G = aN^{3/5} \). The polymer segments are (mostly) found within a volume of \( \sim R_G^3 \) but the polymer segments actually occupy only a small, \( \sim N^{-4/5} \), fraction of this volume. Indeed, due to the fractal nature of the polymer there are spaces within the volume “occupied” by the coil of all sizes up to a fraction of \( R_G \) across. Thus, if we attempt to insert a particle of size \( D \ll R_G \) into a polymer coil we will almost certainly succeed — the particle will almost certainly not overlap with any part of the polymer.

If \( D \approx a \) then calculating the free volume, \( i.e. \), the volume accessible to the particle, and hence its chemical potential is straightforward. The fraction of the free volume is simply \( Na^3/R_G^3 = N^{-4/5} \). The chemical potential difference \( w \) between a particle in pure solvent and one inside a polymer coil is simply minus the logarithm of the free volume fraction inside a coil, \( i.e. \),

\[
\frac{w}{T} = -\ln(1 - N^{-4/5}) \sim N^{-4/5} = \left( \frac{a}{R_G} \right)^{4/3}
\]

(1)

We use energy units for the temperature \( T \). However, when \( D \gg a \) we must account for the fact that the positions of the polymer segments are correlated, that they form chains. To do this we recognize that if the particle interacts with the chain it interacts not with one segment but with a piece of the polymer of length \( D \). We rescale the segment length of the polymer to be \( D \) \([7]\); as the radius of gyration of the polymer must be left unchanged by this rescaling we must then have \( N_D \) segments of length \( D \), where \( N_D \) is given by

\[
R_G = aN^{3/5} = DN_D^{3/5}
\]

(2)

Now, as our particle is only big enough to interact with one of these segments we may consider them uncorrelated and the free volume is \( 1 - N_D D^3/R_G^3 \), giving a chemical potential difference \( w \) between a pure solvent and within a coil of

\[
\frac{w}{T} \sim \left( \frac{D}{R_G} \right)^{4/3}
\]

(3)

the expression derived by de Gennes \([7,18,19]\). The interaction between the particle and the polymer coil \( (3) \) does not depend on \( a \). This is because the interaction between the rod and the particle takes place at a length scale \( D \), and \( D \) is much greater than \( a \).

The derivation of the free volume of a long rod follows directly from that for a particle, again the interaction is with a polymer of \( N_D \) segments of Kuhn length \( D \). If the rod interacts only once with the polymer, \( i.e. \), if we neglect configurations of the polymer in which two widely separated parts of the coil overlap with the rod then the effective volume fraction denied to the rod by the coil is one minus the probability of a rod-polymer segment overlap. This probability is just \( L/D \) times that denied to a particle, for \( L < R_G \), and \( R_G/D \) times that for a particle if \( L > R_G \). Thus, for a rod

\[
\frac{w}{T} \sim \begin{cases} \\
\frac{D^{1/3} L}{R_G^{4/3}} & L < R_G \\
\left( \frac{D}{R_G} \right)^{1/3} & L > R_G
\end{cases}
\]

(4)
The upper expression is valid only when the rod is wholly within the polymer coil. \((w/T)\) is much less than unity, justifying \(a \text{ posteriori} \) our assumption that the rod overlaps with at most one part of the coil. The probability that it overlaps with two parts of the coil is of order \((w/T)^2\) and so is very small. Note that for \(L > R_G\), \((w/T)\) is only much less than unity if the coil is swollen, if the coil is ideal and \(R_G\) scales as \(N^{1/2}\) then it is of order unity \([10,16]\). As \((w/T) \ll 1\), a rigid rod and a polymer coil interpenetrate for \(D \ll R_G\). If \(D \sim R_G\) then the rod cannot penetrate the coil and the rod and coil interact as a hard rod of length \(L\) and diameter \(D\), and a hard sphere of diameter \(\sim R_G^3\) \([20,21]\). Mixtures of this type have been studied by Warren \([22]\) and by Lekkerkerker and Stroobants \([23]\).

The second virial coefficient of the rod–coil interaction \(B_{rc}\), is obtained by integrating over the potential of mean force \(u(r)\) between the rod and the coil

\[
B_{rc} \sim \int dr \left(1 - \exp \left[\frac{-u(r)}{T} \right]\right),
\]

(5)

\(u(r)\) is taken to be a function of the separation of the centres of mass of the rod and coil; the configurations of the coil being already integrated out and the orientation of the rod disregarded as irrelevant. The potential of mean force is just of order \(w\) if the rod penetrates the coil and zero otherwise. As \(w/T\) is small, we may linearize the exponential in equation (5). We then integrate over the volume of overlap of the coil and the rod, which is \(\sim LR_G^2\) for \(L \gg R_G\), to give

\[
B_{rc} \sim LD^{1/3}R_G^{5/3}
\]

(6)

Equation (6) agrees with that given by Eisenriegler \textit{et al.} \([10]\) but note that neither their nor our derivation is rigorous. For \(L \ll R_G\), the volume of overlap of the rod and coil is \(R_G^3\) and using equation (5) we again get equation (6) for the second virial coefficient. For \(L \sim R_G\), we should take account of relative positions of the rod and coil in which the rod is only partially within the coil. We would then obtain an interpolation formula between the two regimes \(L \ll R_G\) and \(L \gg R_G\). However, as all our calculations are only accurate to an order of magnitude we simply use equation (6) for all values of the ratio \(L/R_G\). The virial coefficient scales as \(L\) and as \(R_G^{5/3}\) and so is extensive in the lengths of both the rod and the flexible polymer.

In the limit \(D \rightarrow a\), equation (6) gives the correct form for the second virial coefficient between a coil and a rod of diameter \(a\) which interacts with a segment of the polymer coil by excluding it from a volume \(\sim L a^2\). Equation (6) then agrees with that derived by Joanny \([16]\). We may therefore hope that equation (6) is reasonable for all values of \(D\) which satisfy \(a \leq D \ll R_G\).

As an aside, we can utilize the rescaling of the Kuhn segment of the polymer coil from \(a\) to \(D\) together with the calculation of Joanny \([16]\) to calculate the second virial coefficient between an ideal coil and a rigid rod \(B_{rc}^{\text{id}}\). As before we scale the monomer size to \(D\), then we have \(N_D\) monomers of size \(D\), where \(N_D = (R_G/D)^2\). The calculation performed by Joanny for the case where the \(D = a\) may then be carried over to the case where \(D \gg a\), yielding \([16]\)

\[
B_{rc}^{\text{id}} \sim \frac{LR_G^2}{\ln(R_G/D)}.
\]

(7)

This expression for the interaction between a flexible and a rigid-rod polymer is appropriate if the solvent is a theta solvent for the flexible polymer.

Also required are the second virial coefficients for the interaction between a pair of rods, \(B_r\) and between a pair of coils, \(B_c\). For rods \(B_r\) is given by the expression of Onsager \([5,9]\)

\[
B_r \sim L^2 D.
\]

(8)
In dilute solution, when the volume per coil is much greater than $R_G^3$, the coils interact almost as hard spheres [1, 4]. Then

$$B_c \sim R_G^3.$$  
(9)

Now that we know all three second virial coefficients we know the free energy $A$ of a mixture of rigid-rod and flexible polymers up to second order in density. In an isotropic fluid phase it is

$$\frac{A}{VT} = c_r(\ln c_r V_r - 1) + c_c(\ln c_c V_c - 1) + B_r c_r^2 + B_c c_c^2 + B_{rc} c_r c_c,$$  
(10)

where $V$ is the volume, and $c_r$ and $c_c$ are the number densities of rigid and flexible polymers, respectively. $V_r$ and $V_c$ are thermal volumes. It is important to define the limits of validity of equation (10) for the free energy; it is a low density expansion which neglects terms of cubic and higher order in the density. The limit of validity of the second virial coefficient approximation for a pure fluid of hard rods has been extensively studied, see the review [5]. If $L \gg D$, which is the case here, it is a good approximation for all concentrations such that $c_r LD^2 \ll 1$, i.e., as long as the volume fraction occupied by the rods is much less than unity. The second virial coefficient approximation is valid only for a dilute solution of polymer coils, when $c_c R_G^3 \ll 1$ and the coils are far apart [1]. In the mixture there is a further limit set by rod–rod interactions which are present if two rods are both within the same polymer coil. These interactions are related to the so-called critical Casimir forces found in a suspension of colloidal particles in a solvent which is near a critical point [24]. They are attractive and just as the second virial coefficient terms, they act to segregate the rods from the coils; as such their neglect will not affect the qualitative behaviour. The fraction of rods which fall inside a coil is $\sim c_c L R_G^3$ and if this is small then the number of pairs will be of the order of this number squared and so be even smaller. So, here we will keep $c_c L R_G^3$ small, leaving the case of rods inside a semidilute solution of a flexible polymer for later work.

The pressure $p$ and chemical potentials of the rods $\mu_r$ and of the coils $\mu_c$ may be derived from the free energy (10). They are,

$$\frac{p}{T} = c_r + c_c + B_r c_r^2 + B_c c_c^2 + B_{rc} c_r c_c,$$  
(11)

$$\frac{\mu_r}{T} = \ln c_r V_r + 2B_r c_r + B_{rc} c_c,$$  
(12)

and $\mu_c$ is simply equation (12) but with the subscripts $r$ and $c$ interchanged.

Long rigid rods form a nematic phase, as first shown by Onsager [5, 9]. Later, we will be studying the isotropic–nematic transition of long rods in the presence of polymer coils. Thus we require the free energy of our mixture in the nematic phase. As neither the coil–coil nor the coil–rod interaction is angle dependent the coil–coil and coil–rod interactions are not directly affected by the presence of nematic ordering of the rods (in the second virial approximation). So, we can simply replace the ideal and $B_r$ terms in equation (10) with the ideal and $B_r$ terms in a nematic phase of pure hard rods. These are well-known, see references [5, 13]. Although exact results for both these terms have been calculated we restrict ourselves to the simple but crude Gaussian approximation of Odijk [13]. Within this approximation the free energy in the nematic phase is

$$\frac{A}{VT} = c_r(\ln c_r V_r \alpha - 2) + c_c(\ln c_c V_c - 1) + B_r \frac{4}{(\pi \alpha)^{1/2}} c_r^2 + B_c c_c^2 + B_{rc} c_r c_c,$$  
(13)

where $\alpha$ is a parameter [9, 13] related to the nematic ordering. The conventional nematic order parameter [3], the average of the second Legendre polynomial, is $\sim 1 - 3/\alpha$. The equilibrium
free energy of the nematic phase is equation (13) at its minimum with respect to variations in $\alpha$. So, we take the derivative of equation (13) with respect to $\alpha$ and equate it to zero to obtain an equation for the equilibrium value of $\alpha$. This is

$$\alpha = \frac{(2c_rB_r)^2}{\pi}$$

(14)

Substituting equation (14) back into equation (13) we obtain

$$\frac{A}{VT} = c_r \ln \left( \frac{4B_r^2c_r^3V_r}{\pi} \right) + c_c(\ln c_c V_c - 1) + B_c c_c^2 + B_L c_r c_c.$$  

(15)

The pressure is now

$$\frac{p}{T} = 3c_r + c_c + B_c c_c^2 + B_r c_r c_c,$$  

(16)

and the chemical potential of the rods is

$$\frac{\mu_r}{T} = \ln \left( \frac{4B_r^2c_r^3V_r}{\pi} \right) + B_L c_c.$$  

(17)

The chemical potential of the coils is given by the same expression in the nematic phase as in the isotropic.

3. Phase Behaviour

We consider only the rod-rich side of the phase diagram, as our expressions for the free energy are only reliable there. The phase diagram for $D/R_G = 0.1$ and $L/R_G = 2$ is shown in Figure 2; these parameter values were chosen as they are similar to the values in the experimental work of Jamil et al. [2]. As shown by Onsager [9] hard rods undergo a transition from the isotropic fluid phase to the nematic phase as they are compressed. The transition is, as we would expect, at densities of order $1/B_r$. Along the x-axis the system is a one component fluid of rods and the first-order isotropic–nematic transition is clearly seen. Also clear is that on adding polymer coils, the width of the density gap between the coexisting isotropic and nematic phases widens. Notice that the widening is due to the coexisting isotropic density decreasing and the coexisting nematic density increasing. These two trends in the coexisting isotropic and nematic densities are characteristic of a second component (the polymer coils) which has a tendency to demix from the first and does not order. If we add not coils to the rods but another species of rod [25,26], then as these rods too tend to form a nematic phase the density of the original species of rods in the coexisting nematic phase decreases.

The widening of the density gap is due to partitioning; as can be seen by the negative slope of the tie lines the density of polymer coils is much lower in the nematic phase than in the isotropic phase. Fractionation of the polymer coils between the two coexisting phases forces the rod densities in the two phases to move apart as polymer coils are added. As the density of coils is higher in the isotropic phase than in the nematic phase, adding coils tends to increase the pressure of the isotropic phase to a value greater than in the nematic phase. In order to keep the phases at the same pressure the density of rods decreases in the isotropic phase and increases in the nematic phase.

We can look at the partitioning of the polymer coils more closely if we consider the limit of the density of coils being much less than the density of rods. Then we can neglect the interactions between coils, this simplifies our expression for $\mu_c$ to

$$\beta \mu_c = \ln c_c V_c + B_c c_r.$$  

(18)
Thus if the density of rods in the coexisting isotropic phase is \( c^i_c \) we have for the density of coils \( c^i_r \) in this phase
\[
c^i_c = \exp (\beta \mu_c - B_{cr} c^i_r). \tag{19}
\]
There is an analogous equation relating the densities in the nematic phase, \( c^n_c \) and \( c^n_r \). At equilibrium the chemical potential of the coils is the same in each coexisting phase. So, dividing equation (19) by its equivalent in the nematic phase
\[
\frac{c^i_c}{c^n_c} = \exp \left( B_{cr} (c^n_c - c^i_c) \right). \tag{20}
\]
The rod densities at coexistence differ by of order \( 1/B_{cr} \) [5]. Then, for the fractionation in the limit of the coil density tending to zero, we have
\[
\frac{c^i_c}{c^n_c} \sim \exp \left( \frac{B_{cr}}{B_r} \right) \sim \exp \left( \frac{R_G^{5/3}}{LD^{2/3}} \right), \tag{21}
\]
using equations (6) and (8). We see that the fractionation is largest for rods which are not much longer than \( R_G \) and have small diameters. If the rods have a diameter \( D \approx a \), then equation (21) still holds and the fractionation is very large if the polymer coils are large. Note that the ratio of the densities \( c^i_c/c^n_c \) is given by the exponential of a combination of the relevant length scales. Thus, the ratio is very sensitive to relatively small changes in these length scales. A change of one of these length scales by a factor of only two can change it by more than order of magnitude. Because of this sensitivity, our estimates of this partitioning using our scaling forms for the virial coefficients are highly approximate.

The widening of the isotropic–nematic coexistence region is indicative of a tendency to demix. As well as the existing isotropic–nematic transition there is the possibility of phase separation into two coexisting isotropic phases. In order to examine this possibility we look at the local stability of the free energy (10) [27]. If there is demixing there will be a demixing spinodal, where the local stability is lost. We now search for the conditions under which there is such a spinodal in our simple free energy. The condition for local stability is that the determinant \( D \) formed from the second derivatives of equation (10) be positive
\[
D = \left| \frac{\partial^2 A/(VT)}{\partial c_i \partial c_j} \right| > 0, \quad i, j = c, r. \tag{22}
\]
Substituting equation (10) in equation (22),
\[
1 + 2c_t B_r + 2c_c B_c + c_t c_c (4B_r B_c - B_{cr}) > 0. \tag{23}
\]
Local stability is lost and the mixture will demix if the inequality (23) is violated. This can only happen if the term in parentheses is negative. Using equations (6), (8) and (9) we may rewrite this term and formulate the condition for demixing as
\[
L^2 DR_G^3 \left( 4k_t k_c - k_{rc} \left( \frac{R_G}{D} \right)^{1/3} \right) < 0, \tag{24}
\]
where \( k_{rc}, k_t \) and \( k_c \) are the proportionality constants in equations (6), (8) and (9), respectively. Although \( k_t \) is known to be \( \pi/4 \) and we have a good estimate for \( k_c \) [28], the constant \( k_{rc} \) is unknown. Depending on the ratio \( k_{rc}/(4k_t k_c) \) there are two possibilities. If the ratio is near unity then there is always a limit to the density at which the isotropic phase is stable, although
this limit may lie above the transition to the nematic phase. However, if the ratio is $\mathcal{O}(10)$ then there is a small range of $D/R_G$ values for which the isotropic mixture is always stable. In the nematic phase the excluded volume interactions between the rods are reduced, but not those between rods and coils. Therefore, the mixture is highly immiscible in the nematic phase; as we saw in Figure 2, the density of coils in the nematic phase is low.

If equation (24) is satisfied demixing in the isotropic phase is possible. However, the demixing may be preempted by the isotropic–nematic transition, resulting in just a very broad isotropic–nematic coexistence region. For demixing to occur the term in parentheses in equation (23) must be sufficiently large. As we only know $B_{nc}$ to within a numerical factor of order unity we cannot tell how large the ratio $R_G/D$ has to be in order to observe isotropic–isotropic coexistence. All what our theory tells us, is that it is this ratio that determines whether or not there is coexistence and that, as $R_G/D$ is raised to the low power of $1/3$ in equation (24), it may be that very large values are required in order to see coexistence.

4. Light Scattering

In addition to studying their bulk phase behaviour, mixtures can be studied via light scattering [29]. In particular, by contrast matching one polymer [2,29] of a binary mixture of polymers, the partial structure factor of the second polymer can be obtained. Contrast matching is achieved when the refractive index of one polymer is the same as that of the solvent; then light scattering, which is sensitive to fluctuations in the refractive index, only detects the other polymer. Then, the partial structure factor [30] of the visible polymer may be obtained. A partial structure factor of a component is essentially the Fourier transform of the pair distribution function of that component [30]. As such it is a function of wavevector; in the limit of this wavevector going to zero the structure factor may be related to thermodynamic quantities. Experimentally what is obtained [29] is the inverse of the partial structure factor. The zero wavevector limit of the

Fig. 2. — A partial phase diagram for a mixture of polymer coils and thick, rigid rod polymers. With our present theory we look only at the part of the diagram in which the density of flexible polymer is low. The thick curves separate the coexistence region from the isotropic phase (labelled with an I) and the nematic phase (unlabelled, it is the region below the righthand solid curve). The dashed lines are tie lines. The parameters are: $L/R_G = 2$ and $D/R_G = 0.1$; the densities are made dimensionless by multiplying with $R_G^3$. 

![Diagram showing phase diagram with coexistence regions and tie lines]

- $c R_G^3$ vs. $c R_G$
- The graph shows the transition from the isotropic phase to the nematic phase, with the coexistence region marked by thick curves. The dashed lines indicate the tie lines between the isotropic and nematic phases.
partial structure factor of the polymer coils $S_{cc}(0)$ is, in the second virial approximation [29],

\[
\frac{1}{cS_{cc}(0)} = 1 + 2c_{c} \left[ B_{c} - \frac{c_{r}B_{r}^{2}}{2(1 + 2c_{r}B_{r})} \right],
\]

(25)

where $c$ is the total number density, $c = c_{r} + c_{c}$. $S_{cc}(0)$ may be determined if the rods are contrast matched. If $1/[cS_{cc}(0)]$ is obtained at a number of values of $c_{c}$ then the slope of the $1/[cS_{cc}(0)] - c_{c}$ line gives the term in square brackets in equation (25). This term, sometimes referred to as the apparent second virial coefficient, is accessible experimentally and is directly related to the phase behaviour. Consider the behaviour of the apparent second virial coefficient as a function of $c_{r}$. The negative second term in the apparent coefficient increases as $c_{r}$ increases, until when $c_{r}B_{r} \gg 1$ we may neglect the first term in its denominator. Then the apparent second virial coefficient is $B_{c} - B_{cc} / (4B_{r})$, which is just the term in parentheses in equation (23) divided by $4B_{r}$. Thus, within the second virial approximation, the isotropic phase has an upper limit to the density at which it is stable if and only if the apparent second virial coefficient of one component can be made negative by adding the other component. So, as the apparent second virial coefficient of the coils was observed to become negative in the experiments of Jamil et al. [2], their mixture’s isotropic phase will become unstable at high densities. However, this instability may be preempted by a transition to a nematic phase.

5. Conclusion

We have studied a mixture of polymer coils and rigid rods where the diameter of the rods is much less than the radius of gyration of the coils. We studied the rod-rich part of the phase diagram as there the second virial coefficient approximation is expected to be reasonable. The most noticeable feature of this part of the phase diagram is the partitioning of the polymer coils between the coexisting isotropic and nematic phases (see Eq. (21)). The partitioning of the polymer coils, so that most coils are in the phase with the lower density of rods is suggestive of a tendency of the rods and coils to demix. Indeed there is such a tendency to demix; equation (24) shows that, especially for thin rods, there is a driving force for demixing to form two coexisting isotropic phases. This is in agreement with experimental results which show such coexistence [31] but contradicts the theoretical results of Flory [32]. It appears that the absence of any isotropic–isotropic coexistence in Flory’s calculations is an artifact of his lattice theory. All the above applies to coils in a good solvent; coils in a theta solvent do not interact ($B_{c} = 0$) and so, of course, they will phase separate from a solution of rods.

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