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Flory-Huggins theory for athermal mixtures of hard spheres and larger flexible polymers

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A simple analytic theory for mixtures of hard spheres and larger polymers with excluded volume interactions is developed. The mixture is shown to exhibit extensive immiscibility. For large polymers with strong excluded volume interactions, the density of monomers at the critical point for demixing decreases as one over the square root of the length of the polymer, while the density of spheres tends to a constant. This is very different from the behavior of mixtures of hard spheres and ideal polymers, these mixtures, although even less miscible than those with polymers with excluded volume interactions, have a much higher polymer density at the critical point of demixing. The theory applies to the complete range of mixtures of spheres with flexible polymers, from those with strong excluded volume interactions to ideal polymers.

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I. INTRODUCTION

Athermal mixtures are remarkable because the only energy they possess is thermal energy; their behavior including their phase behavior is determined solely by entropy. But this does not mean that this phase behavior is uninteresting, entropy alone can drive phase transitions such as freezing and, in mixtures, demixing into coexisting fluid phases. This demixing is found almost whenever the two components of the mixture are very different, such as the athermal polymer and hard spheres considered here. We look at mixtures of hard spheres and an athermal polymer where the polymer is as large or larger than the spheres: the mean-square end-to-end separation of the polymer greater than or equal to the diameter of the spheres. This complements earlier work on mixtures where the polymer is smaller. As might be expected we find extensive immiscibility between the polymer and the spheres. We calculate phase boundaries and determine their scaling with the sizes of the components, for example, the density of monomers at the critical point is found to scale as one over the square root of the number of monomers in a polymer, just as does the critical point for demixing of a polymer and a poor solvent.

We are most interested in the limit where the size of the polymer, R_E, is much greater than that of the colloid, σ. R_E is the root-mean-square end-to-end distance of the polymer, and σ is the hard-sphere diameter. Our theory is motivated by the idea that for $R_E \gg \sigma$ the effect of the colloids is a small length-scale effect in the sense that if the colloid degrees of freedom of the mixture are integrated out we are left with polymers which at length-scales large in comparison to σ behave qualitatively just like a polymer in structureless solvent. The colloids effect the quality of this effective structureless solvent but do not introduce any new physics on length-scales large with respect to σ. If this is correct then the long length-scale behavior and the phase behavior of colloid-polymer mixtures may be mapped onto the well-understood long length-scale and phase behavior of a polymer plus solvent system. The phase separation of polymer and much smaller colloidal spheres will be qualitatively identical to that of a long polymer and a poor solvent. This phase separation has been extensively studied and is quite well understood [1–4]. The approximate theory we will develop is essentially a Flory-Huggins polymer-plus-solvent free energy with an effective solvent quality which depends on the concentration of the colloid. It is known that a Flory-Huggins free energy describes rather well the qualitative features of the phase separation of a long polymer and a poor solvent; see the comparison with computer simulation data in Refs. [2–4]. It is also known that purely entropic effects can result in the polymer effectively being in a poor solvent [5].

The literature on mixtures of colloidal particles and non-adsorbing polymers is extensive because colloid-polymer mixtures are common, and the limit we consider where all interactions are purely repulsive is a rather fundamental limit of these mixtures. Mixtures in which the polymer molecules are both larger than the particles and flexible (as opposed to semiflexible) are formed when the particles are small, a few nm across. Nanoparticles are colloidal particles of this size as are proteins. Protein-polymer mixtures are common, for example, polymers are mixed with proteins in order to induce the proteins to crystallize [6,7]. Although in practice it is unlikely that the monomer-protein interaction is ever purely repulsive over all the surfaces of a protein, however, the limit we study here provides a basis for incorporating the effects of weak adsorption of the polymer onto a protein molecule. The limit in which all three interactions, sphere-sphere, monomer-monomer, and sphere-monomer, are purely repulsive is an important and fundamental limit. It is fundamental in the sense that as we are assuming the monomers to be much smaller than the spheres, then the details of the monomer-sphere interaction are irrelevant as long as it is purely repulsive; the details of the monomer-monomer interaction only effect the behavior by altering a single parameter, the monomer-monomer second virial coefficient, and any sharply repulsive sphere-sphere interaction will behave almost like hard spheres. Thus many of the details of the mixture are irrelevant.

The interactions between colloidal spheres and polymer molecules have been studied theoretically via a number of techniques: scaling approaches [8–10], field theory [11–14],

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*Electronic address: r.sear@surrey.ac.uk computer simulation [15,16], integral equations [17,18], and other approaches [19–22]. The phase behavior has been studied via computer simulation [15], scaling theory [23], and perturbation theory [24,25], where Refs. [15,24] are for ideal polymers. Reference [18] is a review of recent work on colloid-polymer mixtures, focusing mainly on the structure and on the results of integral equations, but also discussing other approaches and the phase behavior. Earlier work by the author [23] assumed that the phase separation would occur when the polymer was semidilute. The more careful and better founded work here finds that this is not correct, the phase separation occurs at the boundary between the dilute and semidilute regimes where the free energy expression assumed in Ref. [23] is not valid. Therefore in particular the findings of Ref. [23] for the polymer density where phase separation occurs are incorrect and should be discounted. The opposite limit to that of interest here, i.e., where the polymer molecules are smaller than the colloidal spheres, has been considered extensively, see Refs. [26–28,15,29] and references therein. In this limit the polymer (with or without monomer-monomer excluded volume interactions) induces crystallization of the spheres, there is no equilibrium separation into coexisting fluids.

II. MODEL AND PHYSICAL PICTURE

Our colloidal particles are modeled by hard spheres of diameter σ and our polymers are modeled by flexible chains of N monomers, each of length a. We characterize the interaction between a pair of monomers of the polymer with a second virial coefficient for this interaction, B_M. We start with a polymer in a good solvent far from the theta temperature where $B_M = O(a^3)$ and the polymer behaves as a self-avoiding walk (SAW). The interaction between a pair of hard spheres is similarly characterized by its second virial coefficient $B_S = (2/3)\pi\sigma^3$. The interaction between a sphere and a monomer is taken to be purely repulsive and short range, a monomer cannot overlap with a sphere but otherwise does not interact with it. The polymers do not adsorb onto the surface of the spheres. The monomer size a is much smaller than the diameter of the spheres, and here we are considering particles which are smaller than the polymers so our three length-scales satisfy $a \ll \sigma < R_E$.

A mixture of spheres and polymer is difficult to deal with because of the sphere-polymer interaction. Pure hard spheres and pure polymers have both been studied extensively and the equilibrium behavior of both is well understood. The sphere-polymer interaction is hard to deal with because of the large difference between the size of a sphere and that of a monomer and because of the connectivity of the polymers; if the interaction of a sphere and a monomer was independent of the interaction of the sphere with the next monomer along the polymer, then the sphere-polymer interaction could be estimated easily. However, when the monomers are much smaller than the sphere this is very far from being true. The problem of the disparity in sizes can be solved by rescaling the monomer size from a to σ, i.e., by viewing the polymer not as being composed of N monomers of size a but of n_B monomers of size σ. This rescaling is quite common, see the book of de Gennes [1]. It has already been applied to mixtures of ideal large polymers and spheres [24], where it was referred to as the extended Asakura-Oosawa model. We call the rescaled monomers of size σ, blobs. In principle this rescaling can be done exactly, i.e., it can be done leaving the free energy etc., exact, but here we view it as part of a physically motivated approximation scheme. See Fig. 1 for a schematic of our sphere-polymer mixture showing the polymer composed of a chain of blobs of size σ. If there are N_B monomers of size a in one blob of size σ then n_B is related to N by $n_B = N/N_B$. So, relating the number of blobs to the number of monomers requires estimating N_B, we defer this to Sec. IV. Until then we specify the polymer size by specifying n_B and do not concern ourselves with how n_B is found for a given polymer. The approximate free energy we will obtain depends on the polymer length only through n_B.

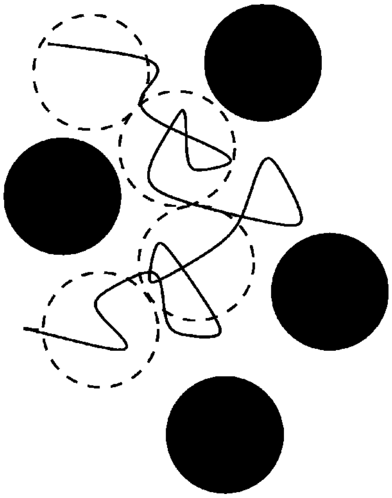

FIG. 1. A schematic of our mixture of large polymer molecules and colloidal spheres. The black disks represent the colloids and the curve represents a polymer coil. The rescaled monomers used to estimate the polymer-colloid interaction are drawn as dashed circles.

Having performed the rescaling we approximate the interaction between a sphere and a polymer as being n_B independent sphere-blob interactions. This is quite a reasonable approximation as the blobs and spheres are of the same size. Applying this approximation before rescaling, i.e., approximating the sphere-polymer interaction by N sphere-monomer interaction is qualitatively wrong because the monomers are so much smaller than the sphere so the sphere interacts with many monomers at a time. We rescaled the monomers just so we could apply this simplifying approximation. The blob-blob and sphere-blob interactions are characterized by their second virial coefficients, B_B and B_{SB}, respectively. The second virial coefficient for the interaction between a sphere and a blob is of order that for the interaction between two hard spheres of diameter σ but is a little smaller. We defer its estimation to Sec. IV. Returning to our assumption that the interaction between a polymer and a sphere consists of n_B independent blob-sphere interactions, this implies that the second virial coefficient for the sphere-polymer interactions is $n_B B_{SB}$. Finally, we remark that after rescaling, our mixture of polymers of blobs and spheres resembles the athermal polymer + solvent mixture considered by Frenkel and Louis [5]. The phase separation in both cases is driven by unfavorable excluded volume interactions.

III. FLORY-HUGGINS-TYPE THEORY

We start with the basic Flory-Huggins theory for a polymer of monomers which interact only via excluded volume interactions, see, for example, the book of de Gennes, pages 113–115. This is often referred to as an athermal polymer solution. For our ''monomers'' we take the blobs not the original monomers of length *a*. Thus the ''monomer'' density in the theory is actually the density of blobs which is equal to $\rho_P n_B$; ρ_P is the number density of polymer molecules. As usual we use a reduced ''monomer'' density, ϕ, which we obtain by multiplying the blob number density by the volume one blob excludes to another, $2B_B$, $\phi=\rho_P n_B(2B_B)$. The Flory-Huggins Helmholtz free energy F then has the usual form

$$\frac{F(2B_B)}{V}=f=\frac{\phi}{n_B}\ln\phi+(1-\phi)\ln(1-\phi), \tag{1}$$

which defines the reduced Helmholtz free energy per unit volume *f*. Throughout, we use units such that the thermal energy $kT=1$. This is for a polymer solution, no colloidal spheres present. We add on the contribution of the colloidal spheres using a virial expansion,

$$f=\frac{\phi}{n_B}\ln\phi+(1-\phi)\ln(1-\phi)+(2B_B)\{\rho_C[\ln\rho_C-1]+\rho_C^2B_S+\rho_C\rho_P n_B B_{SB}\}, \tag{2}$$

where we have truncated the expansion after the second virial coefficient terms. We have dropped cubic and higher order terms, which is only valid at low colloid densities. The last term within the braces is the second virial coefficient term for the polymer-sphere interaction: within our approximation it is just n_B independent sphere-blob excluded volume interactions, each with an excluded volume B_{SB}. In order to obtain a simple analytic theory we will neglect not only all terms for the sphere-polymer interaction beyond the leading order, second virial coefficient term, but all the terms from sphere-sphere interactions, including the leading order $\rho_C^2B_S$ term shown in Eq. (2). This latter approximation is quite severe but we do this in the expectation that the sphere-sphere interactions will not be very large when the colloidal spheres and polymer demix and that the sphere-sphere interactions, unlike the blob-blob interactions, are not essential to understanding the basic physics of this demixing.

Making these two approximations and defining a reduced density of spheres $\phi_C=\rho_C(2B_B)$, Eq. (2) becomes

$$f=\frac{\phi}{n_B}\ln\phi+(1-\phi)\ln(1-\phi)+\phi_C[\ln\phi_C-1]+\phi_C\phi b, \tag{3}$$

where we have changed the $\ln\rho_C$ term to the $\ln\phi_C$ term which we can do as the difference between the two is a constant, $\ln(2B_B)$, which has no effect on the phase behavior. The quantity b is the ratio between the excluded volumes of the sphere-blob and blob-blob interactions, $b=B_{SB}/(2B_B)$.

Apart from a somewhat more complex dependence on ϕ, Eq. (2) is of the same form as the free energy of Eq. (1) of Ref. [30]. Although in that work the mixture was of a mixture of thick and thin hard rods and the free energy was exact. Below, we will transform Eq. (3) following the same approach as used in Ref. [30]. The free energy Eq. (3) is linear in the density of spheres, ϕ_C. This makes it easy to analytically transform from fixed ρ_P and ρ_C to fixed ρ_P and μ_C, where μ_C is the chemical potential of the colloidal spheres. This transformation is useful as then we have a thermodynamic potential, called the semigrand potential, which depends on one density variable, ρ_P or ϕ, and on one field variable, μ_C. This is completely analogous to the Helmholtz free energy of a single component system in which temperature is important; that free energy also depends on a density variable (the number density) and a field variable (the temperature). As such once we have the semigrand potential calculating phase equilibria is just as easy as for a single component system.

So, at fixed ϕ and μ_C the relevant thermodynamic function is the semigrand potential Ω. In fact it is slightly more convenient to work with the activity of the colloid $z_C=\exp(\mu_C)$, not the chemical potential. We need the semigrand potential Ω which is a Legendre transform of the Helmholtz free energy

$$\frac{\Omega(2B_B)}{V}=\omega=f-\phi_C\mu_C, \tag{4}$$

which defines the reduced semigrand potential per unit volume ω [31]. The chemical potential μ_C is just the ϕ_C derivative of *f*, so, taking this derivative of Eq. (3),

$$\mu_C=\ln\phi_C+\phi b=\ln z_C, \tag{5}$$

which can be rearranged to obtain an equation for ϕ_C in terms of z_C

$$\phi_C=z_C\exp(-\phi b). \tag{6}$$

Using Eq. (3) to substitute for *f* and Eq. (5) to substitute for μ_C, in Eq. (4),

$$\omega=\frac{\phi}{n_B}\ln\phi+(1-\phi)\ln(1-\phi)-\phi_C, \tag{7}$$

but we want it in terms of the relevant variables which are ϕ and μ_C so we use Eq. (6) to substitute for ϕ_C

$$\omega=\frac{\phi}{n_B}\ln\phi+(1-\phi)\ln(1-\phi)-z_C\exp(-\phi b). \tag{8}$$

This equation completely describes the thermodynamics of the mixture.

A. The critical point

We begin the determination of the phase behavior by finding the critical point for demixing. First we need the chemical potential μ of the polymer, which is just the ϕ derivative of Eq. (8),

$$\mu=\frac{\ln\phi}{n_B}+n_B^{-1}-1-\ln(1-\phi)+z_C b\exp(-\phi b). \tag{9}$$

Now, the critical point is the point where the first and second ϕ derivatives of the chemical potential are equal to zero. The derivatives are

$$\frac{\partial\mu}{\partial\phi}=\frac{1}{n_B\phi}+\frac{1}{1-\phi}-z_C b^2\exp(-\phi b), \tag{10}$$

$$\frac{\partial^2\mu}{\partial\phi^2}=-\frac{1}{n_B\phi^2}+\frac{1}{(1-\phi)^2}+z_C b^3\exp(-\phi b). \tag{11}$$

Setting them to zero results in two simultaneous equations for the polymer blob density ϕ^{cp} and the sphere activity z_C^{cp} at the critical point. Note that we could have obtained the critical point directly from the Helmholtz free energy Eq. (3) but transforming to the semigrand potential ω is rather simpler as then we only have one density variable. In contrast, the Helmholtz free energy depends on two density variables and so determining the critical point from it requires analyzing determinants. Both routes yield the same critical point as Eqs. (3) and (8) are exact Legendre transforms of each other and so yield identical behavior. Combining these two equations yields an equation solely in terms of ϕ^{cp},

$$\begin{aligned}-(1-\phi^{cp})^2+n_B(\phi^{cp})^2+b\phi^{cp}(1-\phi^{cp})^2\\+bn_B(\phi^{cp})^2(1-\phi^{cp})=0,\end{aligned} \tag{12}$$

and also one for z_C^{cp}

$$z_C^{cp}=b^{-2}\left[\frac{1}{n_B\phi^{cp}}+\frac{1}{1-\phi^{cp}}\right]\exp(\phi^{cp}b). \tag{13}$$

Equation (12) may be solved numerically for ϕ^{cp} and then z_C^{cp} obtained from Eq. (13).

For large n_B the equations simplify and we can solve the equations explicitly. For large n_B we look for a solution with ϕ^{cp} small. Equations (12) and (13) then yield

$$\phi^{cp}=\frac{n_B^{-1/2}}{\sqrt{(1+b)}},\quad z_C^{cp}=\frac{1}{b^2}(1+n_B^{-1/2}2\sqrt{1+b}),\quad n_B\gg 1. \tag{14}$$

For large polymers, $n_B\gg 1$, at the critical point the density of polymer blobs scales as $n_B^{-1/2}$ while the sphere activity tends to a constant as n_B increases. The reduced density of spheres ϕ_C tends to b^{-2} for n_B large, from Eqs. (6) and (14).

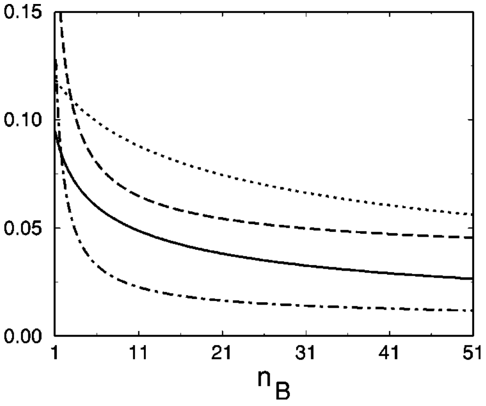

FIG. 2. The variation of the volume fractions of polymer blobs and colloidal spheres at the critical demixing point, as a function of polymer length n_B. The solid and long-dashed curves are for polymer in a good solvent, $b=3.9$; the solid curve is the volume fraction of polymer blobs, η_B^{cp}, and the long-dashed curve is that of the spheres, η^{cp}. The dotted and dot-dashed curves are for a polymer in a quite poor solvent, $b=20$; the dotted curve is η_B^{cp} and the dot-dashed curve is η^{cp}.

In order to estimate the magnitude of the sphere-sphere interactions we require the volume fraction η of the spheres, $\eta=\rho_C(\pi/6)\sigma^3=\rho_C(B_{SB}/8)$. At the critical point the volume fraction of the spheres is

$$\eta^{cp}=\frac{1}{8b}\left(1+n_B^{-1/2}\frac{2+b}{\sqrt{1+b}}\right)n_B\gg 1. \tag{15}$$

For large polymers the volume fraction η of spheres at the critical point is close to $1/8b$. For our neglect of the sphere-sphere interactions to be valid η must be small. We estimate b in the next section and find it to be generally around 4 or larger, so the volume fraction of spheres at the critical point is roughly 0.03 or less and our neglect of sphere-sphere interactions is not unreasonable. Having defined the volume fraction of spheres we can also define an effective volume fraction of the blobs. If we regard each blob as filling a spherical volume of diameter σ then the "volume fraction" of blobs equals $\phi(b/8)$ and so at the critical point we have a blob volume fraction at the critical point

$$\eta_B^{cp}=\frac{n_B^{-1/2}b}{8\sqrt{(1+b)}}n_B\gg 1. \tag{16}$$

In order to illustrate the trends in the demixing behavior with polymer length, measured by n_B, we have calculated [using Eqs. (12) and (13)] the volume fractions of spheres and of blobs at the critical demixing point, η^{cp} and η_B^{cp}, respectively. The results are shown in Fig. 2 where the solid curve is the volume fraction of blobs, and the long-dashed curve is the sphere volume fraction. For large n_B, we see that while the sphere volume fraction is tending towards a plateau, that of the polymer blobs is continuing to decrease, which is just what we expect from Eqs. (15) and (16). For the calculations we have set $b=3.9$ which is approximately its value in the $a/\sigma\rightarrow 0$, $B_M\neq 0$ limit. We will discuss the

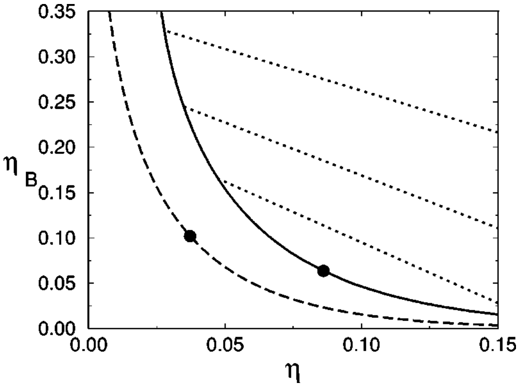

FIG. 3. The phase diagrams of two colloid-polymer mixtures in the η-η_B plane; the x and y axes are the volume fractions of the colloidal particles and blobs, respectively. The curves denote the coexisting densities and the black circles denote the critical points. Both curves are for $n_B=5$ blobs. The solid curve is for a good solvent $b=3.9$ while the long-dashed curve is for a rather poor solvent, $b=20$. The dotted lines are tie lines, lines connecting two coexisting phases.

estimation of b and its variation with solvent quality in Sec. IV. The phase diagram in the plane of the volume fractions of colloidal spheres and blobs, for spheres and polymers with $n_B=5$ blobs, is plotted in Fig. 3. Note the large region of fluid-fluid coexistence.

B. Virial expansion

We can expand out our semigrand potential Eq. (8) as a virial or density expansion,

$$\omega=\frac{\phi}{n_B}\ln\phi-z_C-\phi+zb\phi+\frac{1}{2}(1-z_Cb^2)\phi^2+\frac{1}{6}(1+z_Cb^3)\phi^3+\frac{1}{12}\left(1-\frac{1}{2}z_Cb^4\right)\phi^4+\cdots. \tag{17}$$

So, the second B_2 and third B_3 virial coefficients for the monomer-monomer interactions in the presence of the colloidal spheres are

$$B_2=\frac{1}{2}(1-z_Cb^2)(2B_B),\quad B_3=\frac{1}{6}(1+z_Cb^3)(2B_B)^2. \tag{18}$$

Using Eq. (14) for the activity of spheres at the critical point in the above equation for the virial coefficients, we find that the critical point occurs when the second virial coefficient in the expansions is negative and small, of order $B_Bn_B^{-1/2}\sim\sigma^3n_B^{-1/2}$, when n_B is large. This holds for B_B of order σ^3 which is correct when the excluded volume interactions within a blob are strong, see the next section for a discussion of this point. The third virial coefficient is of order σ^6 at the critical point, again assuming the intrablob excluded volume interactions are strong. This is just as in the standard Flory-Huggins free energy for a polymer in a poor solvent [1].

Thus, within our simple mean-field theory, adding small colloidal particles, $\sigma\ll R_E$, to large polymer molecules in a good solvent is essentially equivalent to altering, worsening, the solvent quality. As more and more spheres are added the rescaled monomers, the blobs, start to attract each other and so the polymer and spheres demix just as the polymer and a poor solvent demix. If this picture is correct then at length-scales large in comparison to the blob size σ the polymers will behave just as a normal polymer in a good, theta, or poor solvent, depending on the concentration of spheres. The behavior of polymers as the solvent quality is worsened and phase separation occurs has been well-studied and is now well understood; see the results of recent computer simulations [2–4]. These simulations have found that the mean-field theory prediction of $n_B^{-1/2}$ scaling of the density of a polymer at the critical point and the size of the second virial coefficient B_2 are almost correct, there are only logarithmic corrections.

IV. SOLVENT QUALITY

The phase behavior depends on only two parameters: the number of blobs of size σ in the polymer, n_B, and the ratio of the blob-sphere to blob-blob excluded volume, b. The blob-blob excluded volume, $2B_B$, is needed to convert from our reduced densities to number densities, but only the ratio $b=B_{SB}/(2B_B)$ affects the nature of the phase behavior.

First, let us consider polymers in which the excluded volume interactions are strong, we are far from the theta temperature, and the particles are not too small. This is the ‘‘excellent’’ solvent regime of Odijk [21]. Note that whether or not a solvent is excellent in this sense depends not only on the properties of the solvent but on the size of the particles. There is a parameter which describes how strong the excluded volume interactions are [1,32], it is often denoted by ζ. For a single blob we have ζ_B which is [1,32]

$$\zeta_B=\frac{B_M}{a^3}N_B^{1/2}. \tag{19}$$

When $\zeta_B\ll1$ then an individual blob is close to being a random walk, the excluded volume interactions within a single blob are negligible. In the other limit, $\zeta_B\gg1$; the excluded volume interactions within a single blob are strong.

The $\zeta_B\to\infty$ limit is the limit of a large SAW, as $N_B\to\infty$, $\zeta_B\to\infty$, Eq. (19). This is the scaling regime of a SAW, which is widely studied and employed, it is the limit in which R_E scales as a power law of N with the Flory exponent ν which is close to 3/5. Calculations on SAWs [32,33] give the second virial coefficient between two SAWs with radii of gyration R_G as $B_B=5.5R_G^3$ in the large ζ_B limit. They also find $R_E=2.5R_G$, so $B_B=0.35\sigma^3$ between two SAWs with mean end-to-end separations of σ. Hanke *et al.* [12] have applied field theory to obtain the result that $B_{SB}=2.7\sigma^3$ [34]. This result is not exact but is more than accurate enough for the purposes of the present theory. This result is obtained in the scaling limit of strong excluded volume interactions. For comparison, for ideal polymers $B_{SB}=3.0\sigma^3$. A swollen blob is more open than one which is ideal so B_{SB} is correspondingly smaller for polymers with the same R_E. So, with strong excluded volume interactions even within blobs the ratio $b=3.9$. In this limit the blob-blob interaction is strong and the chain as a whole will be swollen, so if the radius R_E of the chain is known, then n_B may be estimated from $n_B \sim (R_E/\sigma)^{5/3}$. Alternatively, if the number of monomers N_B in a chain with $R_E=\sigma$ is known then the number of blobs may be found from $n_B=N/N_B$.

So far we have considered only polymer-colloid mixtures in which the solvent for the polymer is sufficiently good and the colloidal particle sufficiently large that $\zeta_B \gg 1$ and even pieces of the polymer as small as σ are strongly swollen. Then we can use the value of the blob-blob and blob-sphere second virial coefficients, B_B and B_{SB}, in the $\zeta_B \to \infty$ limit. But what if the solvent quality is less good and the particles not too large? As the solvent quality decreases the monomer-monomer interaction, B_M decreases from its value in a good solvent which is of order a^3. This will decrease the blob-blob interaction, measured by B_B, while leaving the blob-sphere second virial coefficient B_{SB} still at around σ^3. The second virial coefficient for the interaction between an ideal chain, $R_E=\sigma$, and a hard sphere, of diameter σ, is known exactly [11] and is close to $3\sigma^3$. Thus, when ζ_B is no longer much larger than one, the ratio between the sphere-blob and blob-blob excluded volumes, b, will increase as ζ_B decreases. It is divergent for ideal polymers as then the blob-blob excluded volume is zero.

We expect that as the solvent quality for the polymer worsens and the polymer-polymer interactions weaken that phase separation will be enhanced, the polymer and colloid will be less miscible. With this in mind we return to the equation for the density of polymer at the critical point, Eq. (12). We assume that the critical density will be very low but make no further assumptions, Eq. (12) then simplifies to

$$-1+n_B(\phi^{cp})^2+b\phi^{cp}+bn_B(\phi^{cp})^2=0, \tag{20}$$

which is a quadratic solution with a physical root,

$$\phi^{cp}=\frac{-1+\sqrt{1+4(n_B/b)(1+1/b)}}{2n_B(1+1/b)}. \tag{21}$$

For n_B/b large, i.e., long polymers with blob-blob interactions which are not too weak, this equation simplifies to Eq. (14), for very long polymers even weak monomer-monomer and hence blob-blob excluded volume interactions are sufficient to obtain the standard scaling of the critical density as $n_B^{-1/2}$. The other limit in Eq. (21) is when n_B/b is small, i.e., the blob-blob interactions are weak and the polymer is not too long. In this limit, Eq. (21) simplifies to

$$\phi^{cp}=b^{-1}, \quad n_B/b \ll 1, \tag{22}$$

or

$$\eta_B^{cp}=1/8, \quad n_B/b \ll 1. \tag{23}$$

The density of blobs at the critical point is independent of the length of the polymer. Recalling that ϕ is the number density of blobs times $2B_B$, we rewrite Eq. (22) as

$$\rho_P^{cp}=\frac{1}{n_B B_{SB}}; \quad n_B/b \ll 1, \tag{24}$$

where ρ_P^{cp} is the number density of polymer molecules at the critical point, which is of order $1/(n_B\sigma^3)$. This scaling has been derived before for mixtures of colloidal hard spheres and ideal polymers [24]. Our present theory for polymers with excluded volume interactions, although rather different in a number of ways from the theory of Ref. [24] predicts the same critical density of a polymer when these excluded volume interactions are turned off, giving us confidence in both theories. We can easily obtain the density of spheres at the critical point in the $n_B/b \ll 1$ limit. The reduced activity is $z_C^{cp}=e/(n_B b)$, from Eq. (13), and hence the reduced density at the critical point $\phi_C^{cp}=1/(n_B b)$ and finally the volume fraction

$$\eta^{cp}=\frac{1}{8n_B}, \quad n_B/b \ll 1, \tag{25}$$

which again is the same scaling as found previously [24]. For weak interactions between the blobs the density of spheres at the demixing critical point is dramatically below its value when there are strong interactions between the blobs, Eq. (15). Also, note that the ζ parameter for the whole chain is $\zeta_P=N^{1/2}B_M/a^3 \simeq n_B^{1/2}B_B/\sigma^3$. We can rewrite this in terms of b, $\zeta_P \simeq n_B^{1/2}/b$, ignoring a numerical prefactor. When $n_B/b \ll 1$, then substituting for b, $\zeta_P \ll n_B^{-1/2}$ and so as n_B is larger than one $\zeta_P \ll 1$, an individual polymer molecule in dilute solution and before the colloidal spheres are added is ideal, its $R_E=aN^{1/2}$. Equations (22)–(25) are for demixing of a polymer which is effectively ideal, its monomer-monomer excluded-volume interactions are negligible.

Returning to Fig. 2, we can compare the densities at the demixing critical point for polymers in a good solvent (solid and long-dashed curves) with those in a rather poor solvent, $b=20$ (dotted and dot-dashed curves). We see that as the solvent quality worsens the volume fraction of polymer blobs increases (compare the solid and dotted curves) and the volume fraction of spheres decreases (compare the long-dashed and dot-dashed curves). Also, for $b=20$ and for not-too-large n_B the density of blobs at the critical point for demixing is relatively insensitive to n_B, which is what we expect from Eq. (23). Note that for the polymer in a good solvent the effective volume fraction of polymer blobs is lower than that of the spheres at the critical point whereas for a poor solvent, $b=20$, the opposite is true.

In Fig. 4 we have plotted the variation of the densities at the critical point for fixed n_B and varying solvent quality b. For a small polymer, $n_B=3$, the volume fractions of blobs and spheres are plotted as the solid and long-dashed curves, respectively, while the dotted and dot-dashed curves are the volume fractions of blobs and spheres, respectively, for a much longer polymer, $n_B=30$. The mixture of the longer polymer and the spheres demixes at lower densities than the

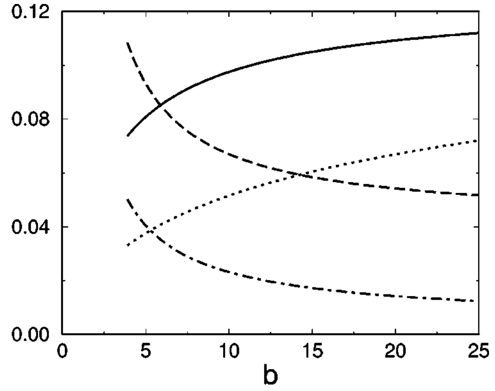

FIG. 4. The variation of the volume fractions of polymer blobs and colloidal spheres at the critical demixing point, as a function of solvent quality, measured by *b*. The solid and long-dashed curves are for a polymer of length $n_B=3$; the solid curve is the volume fraction of polymer blobs, η_B^{cp}, and the long-dashed curve curve is that of the spheres, η^{cp}. The dotted and dot-dashed curves are for a polymer of length $n_B=30$; the dotted curve is η_B^{cp} and the dot-dashed curve is η^{cp}.

mixture of the shorter polymer and spheres of course, and as the solvent quality decreases the volume fraction of polymer increases while that of the spheres decreases. In Fig. 3 we have plotted the phase diagrams in the plane of the two volume fractions for polymers of length $n_B=5$ for a good solvent, $b=3.9$ and a rather poor solvent, $b=20$. The coexistence curve for the poorer solvent lies outside that for the good solvent: reducing the solvent quality increases the extent of the immiscibility.

The larger density of polymer at the critical point comes from the fact that, near their critical points, the third virial coefficient is relatively much larger for ideal polymers than for polymers with excluded volume interactions. The values of the virial coefficients are obtained by inserting the activity of colloidal spheres at the critical point, z_C^{cp}, into Eq. (18). For polymers with excluded volume interactions near the critical point $B_3=O(\sigma^6)$. While for ideal polymers near their critical point $B_3=O(\sigma^6/n_B)$. Small B_3's lead to high critical densities, see the Appendix for details.

A. Comparison with computer simulation

Finally in this section, we compare with the results of recent computer simulations of colloidal particles and hard spherical particles by Meijer *et al.* [35]. They studied colloidal particles + SAWs with $R_E/\sigma=4.8$, 7.0, and 9.9. In the simulations the size of the colloidal particle not that of the polymer was varied but for the moment we will assume that in each case $\zeta_B \gg 1$ so that in the simulations the blob-blob and blob-sphere interactions are both in the good solvent scaling regime and our parameter $b=3.9$. This leaves us with the problem of estimating the values of our parameter n_B for the simulated systems. For large polymers we must have that $n_B \sim (R_E/\sigma)^{1/\nu}$ as n_B is extensive in the contour length of the polymer. In order to obtain an estimate for n_B we set the unknown numerical prefactor in this scaling relation to 1, and $\nu=0.6$, and so obtain $n_B=14$, 26, and 46 for the three simulated systems.

For these three systems we predict critical points at polymer blob volume fractions $\eta_B^{cp}=0.045$, 0.035, and 0.028, respectively. Preliminary simulation results for the critical densities are $\rho_P^{cp}/\rho_P^*=2.04$, 3.19, and 4.65, where $\rho_P^*=1/[(4\pi/3)R_G^3]$. Using the theoretical result $R_E=2.5R_G$ in the good solvent regime and converting from R_E/σ to n_B as above we have that $\rho_P=3.7/n_B^{1.8}$. Converting our theoretical predictions to values of the ratio ρ_P^{cp}/ρ_P^*, we have $\rho_P^{cp}/\rho_P^*=0.19$, 0.25, and 0.31. The theoretical predictions are about an order of magnitude too small, although the trend with increasing R_E/σ is correct. Part of the discrepancy may come from our crude estimation of the relationship between the size of the polymer, R_E/σ, and the number of blobs, n_B, but it seems very likely that the theory is also underpredicting the density of the polymer when it demixes from the spheres. Preliminary results for the volume fraction of spheres at the critical demixing point, η^{cp}, are around 0.2–0.25 whereas we find 0.03–0.05 for this range of values of R_E/σ. Again the theory overestimates the extent of the immiscibility. It should be noted that, in simulation, for the largest value of R_E/σ, the colloidal spheres have a diameter only about ten times that of the monomer. If the blobs are too small to be in the good solvent regime, the requirement $\zeta_B \gg 1$ will be violated, and our parameter *b* will be >3.9. Then the weaker blob-blob interactions in simulation will increase the polymer density at demixing with respect to that given by the theoretical prediction for the good-solvent scaling regime. The simple theory derived here is clearly not quantitative but this is perhaps no surprise, it is really only capable of giving rough estimates and the qualitative nature of trends. The precise nature of the trends for $R_E/\sigma \gg 1$ will be those for a long polymer in a poor solvent; see the simulation results of Refs. [2–4].

B. Solutions of two different polymers

Our semigrand potential for the mixture, Eq. (8), only includes the hard-sphere nature of the colloidal particle through the parameter *b*: the ratio of the excluded volume of the particle-blob interaction to that of the blob-blob interaction. Thus it is trivial to generalize our theory to describe mixtures in which the smaller species is something other than a hard sphere, providing that the assumptions which underly Eq. (8) remain valid. These assumptions are essentially that the interaction between the small species and the large polymer is well described by a simple excluded volume and that the neglect of interactions between the small species is reasonable. So, if the hard spheres are replaced by small polymer molecules with root-mean-square end-to-end distance σ, and strong repulsive interactions with the large polymer but not too strong interactions with other small polymer molecules, the theory developed here will continue to apply.

It will apply if the small polymer molecules can be treated as particles which they can if they are dilute, i.e., at concentrations below their overlap concentration. Also, the neglect of interactions between small polymer molecules will be a good approximation if the solvent is a near-theta solvent for the small polymer molecules. For such mixtures of small and large, chemically distinct and incompatible, polymers our theory can be used to calculate the phase behavior once the parameter b is known. But even without calculating b we know that the scaling of, for example, the critical density, with the length of the larger polymer will be as described in this and the preceding section. From Fig. 4 we see that as either the length of the larger polymer is increased, or the excluded volume interactions between blobs of the larger polymer are decreased (i.e., if the quality of the solvent for the large polymer is decreased), the density of the larger polymer at the critical point decreases.

Finally, note that although the functional form of our Eq. (3) is rather similar to that of a standard Flory-Huggins theory for a system of polymer plus polymer plus solvent, see, for example, Sec. IV 4 of Ref. [1], our ϕ is a volume fraction of blobs not a volume fraction of a polymer. We have rescaled the monomer size, which is appropriate when both polymers are dilute enough that the correlation length is larger than the size of the smaller polymer, and so coils of the smaller polymer do not interpenetrate with the blobs of the larger polymer. Thus in this limit our theory is correct and a standard Flory-Huggins theory is incorrect because the latter ignores correlations between the monomers. However, in the limit where the polymers are compatible enough that they only demix when the solution is quite concentrated, then the standard Flory-Huggins theory is essentially correct as the correlations will be screened.

V. CONCLUSION

Mixtures of hard spheres and larger, flexible polymers which do not absorb onto the surface of the spheres exhibit extensive immiscibility. The cross excluded volume interactions in these mixtures, i.e., the excluded volume interactions between the sphere and the polymer, are large. So, the spheres and polymers "get in each others way" so reducing each others entropy and driving them apart into separate phases [5]. The tendency to demix increases as the polymers become larger and larger because the excluded volume interactions scale linearly with the length of the polymer while the translational entropy gained by mixing solutions of spheres and polymers does not vary with polymer length. Here we derived a simple analytic theory for these mixtures and found that when the excluded volume interactions were so strong that even blobs of size equal to that of the spheres were swollen, a mixture of polymer and much smaller spheres behaves much as a polymer in a poor solvent does. By contrast, as we showed in earlier work, a mixture of spheres and ideal polymers behaves rather differently. There the effective third virial coefficient of the polymer is very small, which pushes up the polymer density at the critical point for demixing.

Our results are of relevance to mixtures of globular proteins and polymers, as in these mixtures it is easily possible to have polymers larger than the protein. However, our assumption of a purely repulsive interaction between the polymer and the spheres is rather unrealistic for proteins which have rather complex surfaces. Some part of this complex surface may well attract the monomers. A clean comparison with experiment could be done with experiments on either small synthetic colloidal particles or nanoparticles. Another possibility is to instead of making the colloidal particles smaller, make the polymer bigger by employing DNA [36]. There, however, the colloidal particles would have to be reasonably large as the effective monomer length of DNA is about $a=100$ nm and our theory assumes that $a\ll\sigma$. An objective for future work could be to relax this restriction to account more accurately for mixtures of spheres with semiflexible polymers such as DNA.

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APPENDIX: VIRIAL EXPANSIONS AND CRITICAL DENSITIES

Here we explore how the critical density varies with the size of the third virial coefficient. Consider the simplest possible virial expansion that has a critical point, an expansion truncated after the third virial coefficient. For the chemical potential μ as a function of density ρ this is

$$\mu=\ln\rho+2B_2\rho+3B_3\rho^2,$$

where B_2 and B_3 are the second and third virial coefficients, respectively. Assuming that B_3 is fixed and that B_2 varies linearly with some temperature-like variable t, we have $B_2=B(1-t)$, and

$$\mu=\ln\rho+2B(1-t)\rho+3B_3\rho^2.$$

The critical point occurs when the first and second derivatives of the chemical potential are zero, giving two equations for the critical value of t, t^{cp}, and the critical density ρ^{cp}:

$$\frac{1}{\rho^{cp}}+2B(1-t^{cp})+6B_3\rho^{cp}=0,$$

$$-\frac{1}{(\rho^{cp})^2}+6B_3=0.$$

The second equation gives the density at the critical point straightaway, $\rho^{cp}=1/\sqrt{6B_3}$: the critical density does not depend on the value of the second virial coefficient but on that of the third virial coefficient. For our mixtures of ideal polymers and spheres, as the polymers are ideal their blobs do not repel each other, they only interact with each other via the spheres. Thus the third virial coefficient of the polymer blobs (at constant sphere chemical potential) is very small and the density at the critical point of demixing correspondingly high.

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[31] Note that our semigrand potential is a function of the density of polymer and the chemical potential of spheres, whereas the semigrand potential of mixtures of spheres with small polymer molecules of Ref. [28] and the body of work which has followed this reference, is a function of the chemical potential of the polymer and the density of spheres. In principle of course it is possible to develop exact theories for both semigrand potentials. However, in practice the component whose density is specified is the one whose interactions cannot be neglected. When the spheres are larger than the polymer molecules, the sphere-sphere interactions are important as demixing tends to occur at high sphere volume fractions. When the polymer molecules are larger the blob-blob interactions are important as we show in Sec. IV.
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