Phase Separation in Mixtures of Colloids and Long Ideal Polymer Coils

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Colloidal suspensions with free polymer coils which are larger than the colloidal particles are considered. The polymer-colloid interaction is modeled by an extension of the Asakura-Oosawa model. Phase separation occurs into dilute and dense fluid phases of colloidal particles when polymer is added. The critical density of this transition tends to zero as the size of the polymer coils diverges.

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By the addition of nonadsorbing polymer, colloidal suspensions can be made to separate into a dilute phase, a colloidal "vapor," and a dense phase, a colloidal "liquid" [1]. Nonadsorbing polymer does not adsorb onto the surfaces of the particles; the interaction between a monomer and a colloidal particle is repulsive. The colloidal particles are spheres of diameter σ, and we can characterize the size of a polymer coil with its root-mean-square end-to-end separation, R_E. For polymer coils smaller than the particles, $R_E < \sigma$, the polymer-colloid interaction is, to a not unreasonable first approximation, a hard-sphere repulsion: the Asakura-Oosawa (AO) model [2,3]. For values of $R_E/\sigma = O(0.1)$, it has been found that to a good approximation the effect of the polymer is to create a short-ranged, range $\mathcal{R} \simeq \sigma + R_E$, pairwise additive attraction between the colloidal particles [4,5]. If this range is not too short, it induces a phase separation into dilute and dense fluid phases of the colloidal particles. In the other limit, that of large values of the ratio R_E/σ, it is known that the polymer creates an effective attraction between the colloidal particles but that this is not pairwise additive [4,6]. Here, we extend the Asakura-Oosawa model to deal with values of $R_E/\sigma > 1$, and then go on to show that the phase behavior for large R_E/σ is very different from that induced by a pairwise additive attraction. As $R_E \to \infty$ the colloid density at the critical point tends to zero, whereas with a pairwise additive attraction, however long the range of the attraction $\mathcal{R}$, the density at the critical point remains nonzero. A van der Waals fluid has a pairwise additive attraction of infinite range but a critical volume fraction of 0.13 [7]. The colloidal particles can be smaller than the polymer coils either because the particles are small, only a few nanometers across, the typical size of a globular protein [8], or the polymer coils are large, as they are for DNA [9].

The colloidal particles are modeled by hard spheres; there are no attractions between them. The interaction potential between two colloids, u_{CC}, is then that between a pair of hard spheres of diameter σ. The polymer coils are taken to be ideal and so do not interact with each other, i.e., $u_{PP}(r) = 0$, where r is the distance between their centers. For the interaction between a colloidal particle and a polymer coil, u_{CP}, we start from the Asakura-Oosawa

model [2,3],

$$u_{CP}(r) = \begin{cases} \infty & r < (\sigma + \sigma_P)/2 \\ 0 & r \geq (\sigma + \sigma_P)/2, \end{cases} \qquad (1)$$

where σ_P is an effective diameter of the polymer coil; it is close to R_E, the root-mean-square end-to-end separation of the polymer. The polymer does not adsorb onto the particles; the interaction between a monomer and the surface of a particle is repulsive. When the polymer is no larger than the colloid the Asakura-Oosawa model is reasonable. In the limit $\sigma \gg R_E$, the colloidal particle resembles a hard planar wall on the relevant length scale for the polymer, R_E, and a hard wall excludes a polymer from a slab of height of order R_E [10,11]. However, in the opposite limit, that of $R_E \gg \sigma$, the Asakura-Oosawa model is incorrect; it predicts that a particle excludes a polymer coil from a volume of R_E^3, whereas if R_E is much larger than the diameter of the colloid the colloid-polymer interaction must be extensive in the length of the polymer. For an ideal polymer $R_E = an^{1/2}$, where a is the monomer length and n is the number of monomers. The interaction must be extensive in n and so scales as R_E^2 not R_E^3 [10,11]. Thus, we cannot use the Asakura-Oosawa model for long polymers. We propose an extended Asakura–Oosawa model to deal with the case $R_E > \sigma$. Figure 1 is a schematic of the proposed model.

First, we rescale the monomer size to the colloid diameter σ [12]. As both R_E and the exponent of one-half remain constant when we rescale the monomer size, we have $R_E^2 = a^2 n = \sigma^2 n_B$, where n_B is the number of blobs: effective monomers of length σ. This yields

$$n_B = R_E^2/\sigma^2, \qquad n_B \geq 1. \qquad (2)$$

So, we now have a polymer of n_B blobs, each of which is σ across. Each of these blobs is no larger than the colloidal particle so the Asakura-Oosawa interaction, Eq. (1), is a reasonable (although not a quantitative) description of the interaction of a single blob with a colloid. Thus, our model for a long polymer is an ideal chain of blobs of diameter σ, each of which interacts with a colloidal particle with an interaction potential given by Eq. (1) with $\sigma_p = \sigma$.

For ideal polymers, when calculating phase diagrams, it is simplest to work in a semigrand ensemble [4,13,14].
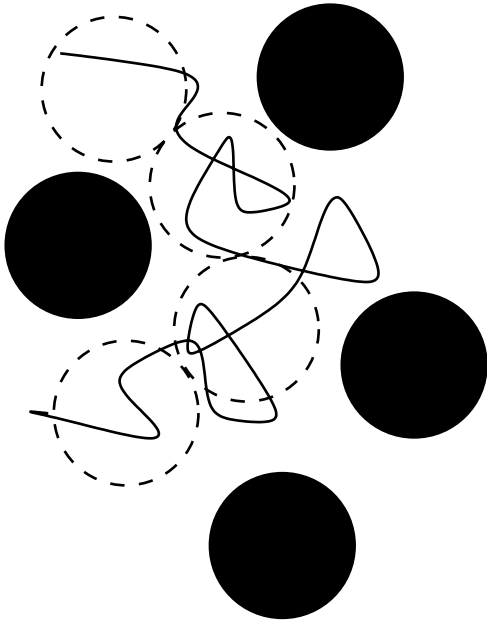
FIG. 1.   A schematic of the extended Asakura-Oosawa model. The black disks represent the colloids and the curve represents a polymer coil. The rescaled monomers used to estimate the polymer-colloid interaction are drawn as dashed circles.

This is an ensemble in which the variables are the volume, V, the number of colloidal particles, N_C, and the activity of the polymer, z. As all our interactions are athermal, the temperature T is a not a relevant variable. For simplicity we will use units such that the thermal energy $kT = 1$. The number density of the colloidal particles $\rho_C = N_C/V$. We use a reduced density for the colloidal particles, the volume fraction $\eta = (\pi/6)(N_C/V)\sigma^3$, and a reduced activity of the polymer $z^* = zR_E^3$. We also define a reduced density of polymer, $\rho^* = \rho_P R_E^3$, where ρ_P is the number density of polymer coils. The colloidal volume fraction is close to one-half when the colloid (in the absence of polymer) crystallizes, and ρ^* is close to one when the polymer coils start to overlap, and is less than one in the dilute regime [12].

The semigrand potential per colloidal particle ω is [1,4,5,13,14]

$$\omega(\eta, z) = a_{HS}(\eta) - (z/\rho_C)\alpha(\eta; n_B), \qquad (3)$$

where a_{HS} is the Helmholtz free energy per particle of hard spheres, and $\alpha(\eta; n_B) = \exp[-\mu_{EX}(\eta; n_B)]$, with $\mu_{EX}(\eta, n_B)$ the excess chemical potential of a chain of n_B blobs in a system of hard spheres at a volume fraction η. Equation (3) for the semigrand potential is approximate; it is essentially the semigrand potential expressed as the $z = 0$ limit (no polymer) plus a series expansion in powers of z, truncated after the first term. Thus, it becomes less accurate as the polymer activity increases. It can be derived in a couple of ways, see Refs. [1,4,5,13,14]. The Carnahan-Starling equation of state [15] is known to be

accurate so we will use thermodynamic functions and correlation functions derived from it. The density of polymer coils when its activity is z^* is

$$\rho^* = z^*\alpha(\eta, n_B), \qquad (4)$$

which is just the definition of the excess chemical potential, rearranged.

If $n_B = 1$, then the polymer-colloid interaction is modeled by just one hard sphere of diameter σ, as in the original Asakura-Oosawa model. Then μ_{EX} is just the excess chemical potential of hard spheres, which may be easily derived from the Carnahan-Starling equation of state. For $n_B > 1$ we require the excess chemical potential of a chain of blobs. Fortunately the problem of calculating this quantity has occurred in the treatment of dense liquids of oligomers, such as alkanes, and polymer melts. One of the best known theories is that of Wertheim [16], which he termed thermodynamic perturbation theory 1 (TPT1). Its prediction for $\mu_{EX}(\eta, n_B)$ is [16–18]

$$\mu_{EX} = n_B\mu_{EX}^{(HS)} - (n_B - 1)\left[\ln g_{HS} + \frac{\eta}{g_{HS}}\left(\frac{dg_{HS}}{d\eta}\right)\right], \qquad (5)$$

where $\mu_{EX}^{(HS)}$ and g_{HS} are the excess chemical potential and pair distribution function at contact, respectively, of hard spheres. μ_{EX} is the work done in inserting a chain of n_B spheres of diameter σ into the fluid of hard spheres, which is equal to the work done in inserting n_B widely separated spheres [the first term on the right-hand side of Eq. (5)] plus the work done in bringing the n_B spheres together into a linear chain of spheres at contact (the second term) [18]. The accuracy of the extended AO model plus TPT1 can be assessed by comparing its prediction for the virial coefficient of the interaction between a hard sphere and a polymer coil, with the exact field theory prediction, Eq. (3.11) of Ref. [10]. When $R_E = \sigma$ the AO model overpredicts by a factor of 1.4. For large R_E/σ the leading order term in our prediction is $(\pi/2)R_E^2\sigma$, whereas field theory yields a value which is two-thirds of this. The extended AO model + TPT1 overpredicts the interaction by 50% for large R_E.

Equations (3) and (5) are all that is required to calculate the phase diagram in the η-z^* plane. Then Eq. (4) can be used to calculate the polymer density from its activity and so these diagrams may be mapped onto the η-ρ^* plane. Phase diagrams for $n_B = 5$ are shown in Fig. 2. This corresponds to $R_E = \sqrt{5}\,\sigma$; the end-to-end separation of the polymer is a little over twice the diameter of the colloid.

The density of polymer coils decreases exponentially with increasing colloid volume fraction, with a coefficient in the exponential which is linear in n_B [Eq. (5)]. Thus for polymers which are several blobs long, the polymer density at a polymer activity $z^* = O(1)$ and at high colloid volume fractions, $\eta \gtrsim 0.3$, is extremely small. Thus, crystallization of the colloid takes place in the presence of
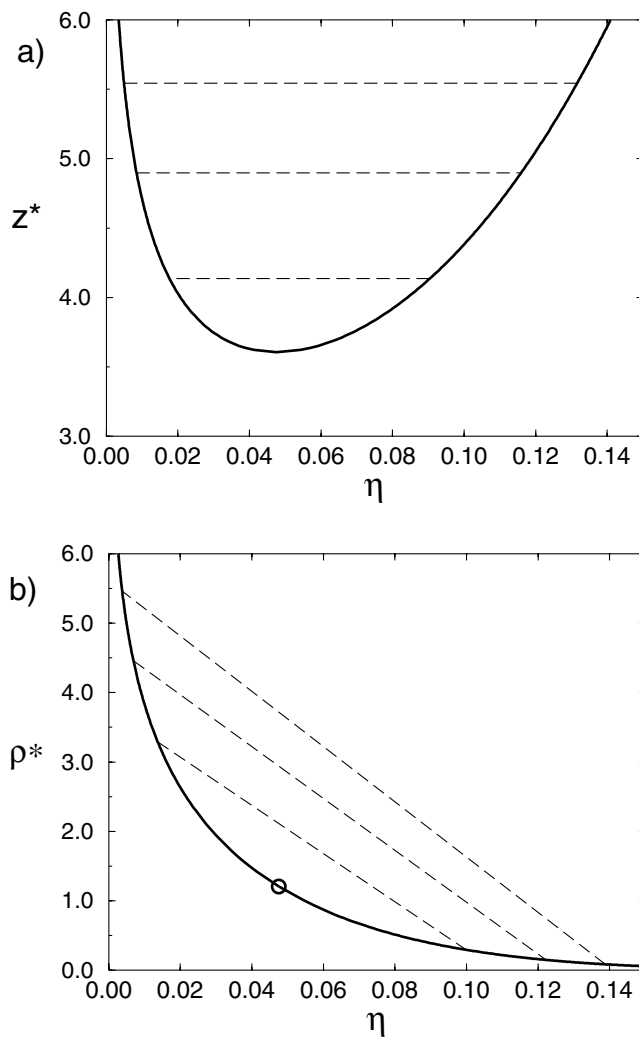
FIG. 2. The phase diagram of a colloid + polymer mixture, with a polymer of $n_B = 5$ blobs of diameter equal to that of the colloid. (a) is the diagram in the η-z^* plane, and (b) is it in the η-ρ^* plane. The dashed lines are tie lines connecting coexisting phases and the circle in (b) marks the critical point.

almost no polymer and so occurs very close to its value for hard spheres, which is $\eta = 0.49$ [19], so is almost completely unaffected at these polymer activities. We do not show the crystallization transition in Fig. 2 because it is at much higher densities than the vapor-liquid transition, but the density of the fluid phase which coexists with the crystalline phase is essentially a vertical line at a volume fraction of 0.49.

In Fig. 2 the volume fraction of the colloid at the critical point is very low. The density range of the colloidal liquid is very large, from the volume fraction at the critical point, 0.048, to 0.49. In Fig. 3 we have plotted the volume fraction of the colloid at the critical point, η_{CP}, as a function of polymer size, n_B. For large n_B, it decreases as n_B^{-1} (R_E^{-2}). Thus it tends to zero as $R_E \to \infty$, unlike the case for a pairwise additive attraction where as its range $\mathcal{R} \to \infty$, the volume fraction at the critical point tends to 0.13.

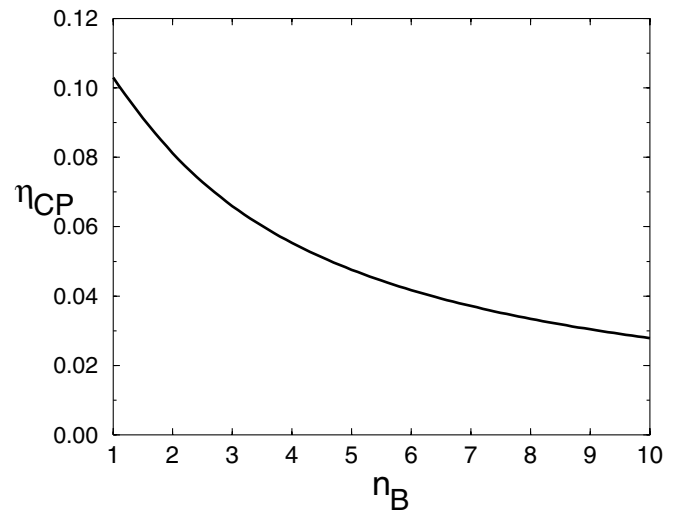FIG. 3. The volume fraction of colloidal particles at the fluid-fluid critical point, η_{CP}, as a function of the size of the polymer, measured by n_B.

The mixture phase separates into colloid-rich (polymer-poor) and colloid-poor (polymer-rich) phases at very low colloid concentrations when the polymer is larger than the colloid. The reason for the n_B^{-1} scaling is clear from Eqs. (4) and (5). The phase with the higher colloid density, the colloidal liquid, must have a sufficiently high density that at fixed z^* the polymer density is significantly below that in colloidal vapor. Now, from Eq. (4) we see that this requires a μ_{EX} which is at least of order unity (recall that $kT = 1$) in the liquid phase. At low colloid density $\mu_{EX} = (A + Bn_B)\eta + O(\eta^2)$, where A and B are constants. Thus, the colloidal volume fraction at which $\mu_{EX} = 1$ varies as $1/(A + Bn_B)$, which gives rise to a critical density with the same scaling. A critical volume fraction scaling as R_E^{-2} is consistent with work on a polymer molecule in the presence of a density of fixed obstacles [20] which finds that the reduction in entropy of the polymer molecule is of order 1 when the number density of obstacles of diameter σ is of order $1/(\sigma R_E^2)$.

A further point to note is that as the activity of the polymer is increased the density of the colloid-rich phase increases rather slowly [21]. In Fig. 2, even when the polymer activity is twice that at the critical point, the colloid volume fraction in the colloid-rich phase is only around 0.15. Ultimately, we expect that if the polymer activity is high enough there will be a triple point, where the dense fluid is sufficiently dense that it coexists not only with a dilute fluid phase but with a crystalline phase. However, this will be for much larger polymer activities than shown in Fig. 2. The polymer density in the colloid-poor, polymer-rich phase will be many times the overlap concentration, $\rho^* = 1$. Although simultaneous coexistence of dilute and dense fluid phases and a crystalline phase have been observed in experiment for colloid + polymer mixtures [1], this has been for values of R_E no larger than the

colloid diameter. Observing simultaneous coexistence of these three phases in experiment may be difficult if R_E is significantly greater than the colloid diameter.

In the limit of short polymers, R_E a few tenths of σ or less, the effect of polymer is to induce an attraction which is short ranged, $\mathcal{R} \approx \sigma + R_E$, and to a good approximation pairwise additive [5]. If the phase diagrams for colloid + short polymer [4,13], and for particles with a short-ranged pairwise additive attraction [22], are compared they are seen to be qualitatively the same. In both cases as R_E or $\mathcal{R}$ shrinks, fluid-fluid coexistence disappears from the equilibrium phase diagram. Thus, assuming that free polymer is equivalent in effect to a pair attraction between colloidal particles is a reasonable assumption for small values of R_E/σ but not for large values.

We have proposed an extended Asakura-Oosawa model to model the interaction between colloidal particles and ideal nonadsorbing polymer coils with end-to-end separations R_E larger than the diameter of the colloidal particle σ. For a globular protein with a diameter of a few nanometers, this would mean a polymer molecule with an R_E of 5 nm or more. As with smaller polymer coils [13], the polymer induces a vapor-liquid-like separation into two fluid phases: one rich in colloid (a colloidal liquid) but poor in polymer and one poor in colloid (a colloidal "gas") but rich in polymer. We showed that the critical point of this transition moves to lower and lower colloid densities as the polymer coils become larger. This is qualitatively different from what would be found if the effect of polymer was to induce a pairwise additive attraction between the colloidal particles. Let us compare the variation of the colloid density at a critical point induced by a pairwise additive attraction of varying range, $\mathcal{R}$, with that induced by a polymer of varying size, R_E. We find that for small $\mathcal{R}$ or R_E the variation of the critical density is similar in both cases. The critical density increases [13,22,23] as $\mathcal{R}$ or R_E shrinks; if not preempted by crystallization it tends to the random-close-packed density of hard spheres as $\mathcal{R}$ or $R_E \rightarrow 0$ [23]. However, in the other limit, that of large $\mathcal{R}$ or R_E, the variation in the critical density is very different in the two cases. With a pairwise additive potential it shrinks to 0.13 [7] as $\mathcal{R} \rightarrow \infty$ and then goes no lower, whereas with polymer coils, the present theory predicts that the critical density tends to zero as $R_E \rightarrow \infty$.

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