Phase separation in mixtures of colloids and long ideal polymer coils

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Abstract

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.

By the addition of nonadsorbing polymer, colloidal suspensions can be made to separate into a dilute phase, a colloidal ‘vapour’, 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 colloidal particle is repulsive. The colloidal particles are spheres of diameter $\sigma$, and we can characterise 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 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 $R \approx \sigma + R_E$, 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 $R_E/\sigma$, it is known that the polymer creates an effective attraction between the colloidal particles but that this is not pairwise additive [4, 3]. 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 behaviour for large $R_E/\sigma$ is very different from that induced by a pairwise additive attraction. As $R_E \to \infty$ the colloidal density at the critical point tends to zero, whereas with a pairwise additive attraction, however long the range of the attraction $R$, 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

$$
  u_{CC}(r) = \begin{cases} 
  \infty & r < \sigma \\
  0 & r \geq \sigma 
  \end{cases},
$$

(1)

where $r$ is the distance between their centres. The polymer coils are taken to be ideal and so do not interact with each other, i.e., $u_{PP}(r) = 0$. For the interaction between a colloidal particle and a polymer coil, $u_{CP}$, we start from the Asakura-Oosawa model [2, 3]

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

(2)

where $\sigma_P$ 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 $R_E \ll \sigma$. 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 $R_E^3$ not $R_E^2$. 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 $\sigma$ [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 $\sigma$. This yields

$$n_B = \frac{R_E^2}{\sigma^2}, \quad n_B \geq 1. \quad (3)$$

So, we now have a polymer of $n_B$ blobs, each of which is $\sigma$ across. Each of these blobs is no larger than the colloidal particle so the Asakura-Oosawa interaction, Eq. (2), 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 $\sigma$, each of which interacts with a colloidal particle with an interaction potential given by Eq. (2) with $\sigma_p = \sigma$.

For ideal polymers, when calculating phase diagrams, it is simplest to work in a semigrand ensemble [13, 14]. 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 $z^* = z R_E^3$. We also define a reduced density of polymer, $\rho^* = \rho_F R_E^3$, where $\rho_F$ is the number density of polymer coils. The colloidal volume fraction is close to one half when the colloid (in the absence of polymer) crystallises, and $\rho^*$ 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 $\omega$ is [12, 13, 14]

$$\omega(\eta, z) = a_{HS}(\eta) - (z/\rho_C)\alpha(\eta; n_B), \quad (4)$$

where $a_{HS}$ is the Helmholtz free energy per particle of hard spheres, and $\alpha(\eta; n_B) = \exp\left[-\mu_{EX}(\eta; n_B)\right]$, 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 $\eta$. Equation (4) 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. 12, 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

$$\rho^* = z^*\alpha(\eta, n_B), \quad (5)$$

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 $\sigma$, as in the original Asakura-Oosawa model. Then $\mu_{EX}$ 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 [13], which he termed thermodynamic perturbation theory 1 (TPT1). Its prediction for $\mu_{EX}(\eta, n_B)$ is [16, 17]

$$\mu_{EX} = n_B \mu_{EX}^{(HS)} - (n_B - 1) \left[ \ln g_{HS} + \eta \left( \frac{dg_{HS}}{d\eta} \right) \right], \quad (6)$$

where $\mu_{EX}^{(HS)}$ and $g_{HS}$ are the excess chemical potential and pair distribution function at contact, respectively, of hard spheres. $\mu_{EX}$ is the work done in inserting a chain of $n_B$ spheres of diameter $\sigma$ 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. (6)) plus the work done in bringing the $n_B$ spheres together into a linear chain of spheres at contact (the second term) [13].

Equations (4) and (6) are all that is required to calculate the phase diagram in the $\eta - z^*$ plane. Then Eq. (6) can be used to calculate the polymer density from its activity and so these diagrams may be mapped onto the $\eta - \rho^*$ plane. The pressure and the
chemical potential of the colloid are both derivatives of $\Omega$, and so may be determined from Eq. (4), and then the conditions of equal chemical potential and pressure may be solved for phase coexistence. Results for $n_B = 5$ are shown in Fig. 3. This corresponds to $R_E = \sqrt[3]{5}\sigma$, the end-to-end separation of the polymer is a little over twice the diameter of the colloid. If the colloid is a globular protein molecule this corresponds to an $R_E$ of around 10nm.

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. (9). 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, crystallisation of the colloid takes place in the presence of almost no polymer and so occurs very close to its value for hard spheres, which is $\eta = 0.49$ (14), so is almost completely unaffected at these polymer activities. We do not show the crystallisation transition in Fig. 3 because it is at much higher densities than the vapour-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, $\eta_{CP}$, 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 $R \to \infty$, the volume fraction at the critical point tends to 0.13. The mixture phase separates into colloidal-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. (9) and (10). 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 vapour. Now, from Eq. (9) we see that this requires a $\mu_{EX}$ 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 [24] which finds that the reduction in entropy of the polymer molecule is of order one when the number density of obstacles of diameter $\sigma$ 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 [2]. 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 $\sigma$ 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 [8]. If the phase diagrams for colloid + short polymer [1,23], and for particles with a short-ranged pairwise-additive attraction [22] are compared they are seen to be qualitatively the same. In particular, 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 $R_E/\sigma$ 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 $\sigma$. For a globular protein with diameter of a few nms, this would mean a polymer molecule with an $R_E$ of 5nm or more. As with smaller polymer coils [3], the polymer induces a vapour-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 $R$, with that induced by a polymer of varying size, $R_E$. We find that for small $R$ or $R_E$ the variation of the critical density is similar in both cases. The critical density increases \([13, 22, 23]\) as $R$ or $R_E$ shrinks; if not preempted by crystallisation it tends to the random-close-packed density of hard spheres as $R$ or $R_E \rightarrow 0$ \([23]\). However, in the other limit, that of large $R$ 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 $R \rightarrow \infty$ 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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Figure 1: A schematic of the extended Asakura-Oosawa model. The black discs 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.

Figure 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 $\eta - z^*$ plane, and b) is it in the $\eta - \rho^*$ plane. The dashed lines are tie lines connecting coexisting phases and the circle in b) marks the critical point.

Figure 3: The volume fraction of colloidal particles at the fluid-fluid critical point, $\eta_{CP}$, as a function of the size of the polymer, measured by $n_B$. 