

Interfacial tension and nucleation in mixtures of colloids and long ideal polymer coils

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Mixtures of ideal polymers with hard spheres whose diameters are smaller than the radius of gyration of the polymer, exhibit extensive immiscibility. The interfacial tension between demixed phases of these mixtures is estimated, as is the barrier to nucleation. The barrier is found to scale linearly with the radius of the polymer, causing it to become large for large polymers. Thus for large polymers nucleation is suppressed and phase separation proceeds via spinodal decomposition, as it does in polymer blends.

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I. INTRODUCTION

In earlier work [1] immiscibility in mixtures of colloidal hard spheres and long ideal polymer molecules was studied. Long means that the root-mean-square end-to-end separation of the polymer molecules, R_E , is larger than the diameter σ of the hard spheres. A mixture of spheres and long polymers was found to demix at comparable number densities of polymer molecules and spheres, both densities scale with R_E as $1/R_E^2\sigma$, for $R_E > \sigma$. This scaling comes directly from the leading order term in the second virial coefficient for the sphere-polymer interaction. The interaction and hence the virial coefficient must be extensive in the number of monomers for large R_E and hence must scale as R_E^2 for our ideal polymers. The requirement that it has the dimensions of a volume then imposes the scaling $R_E^2\sigma$ as σ is the only other relevant length in the problem: the monomer size is assumed to be much less than σ and so is irrelevant. Once the mixture has demixed we have two coexisting phases: one with a high density of colloidal particles and a low density of polymer molecules, and one with a high density of polymer molecules and a low density of colloidal particles. There is an interface between these two coexisting phases. Here we determine the scaling of the interfacial tension γ of this interface, and use it to show that when a mixed sample of polymer and colloid is prepared and quenched into the two-phase region, the dynamics of the separation into two phases starts off with spinodal decomposition not nucleation. The fact that the phase separation starts off with spinodal decomposition makes mixtures of the long polymers like polymer blends but unlike simple mixtures, e.g., mixtures of oil and water. Thus, we can apply much of what we have learned of spinodal decomposition in systems like polymer blends, to mixtures of colloidal spheres and much larger polymer molecules.

The colloid-polymer interactions in, and bulk thermodynamics of, mixtures of colloids and large ideal polymers have both been studied, see Refs. [1–7]. 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. [2,8–10] for work on the bulk phase behavior and Refs. [11–13] for work on interfaces. The

following two sections deal with the interfacial tension, and with nucleation. Throughout, the objective will be to determine the scaling of the behavior with the ratio of the size of the polymer to that of the sphere. Also note that here the polymers are always ideal, mixtures of polymers with strong excluded volume interactions and spheres, are very different [14–17].

II. INTERFACIAL TENSION BETWEEN THE DEMIXED PHASES

The interfacial tension between the demixed phases, one colloid rich, the other polymer rich, can be estimated by just using dimensional analysis. The tension γ is an energy per unit area. It is obtained by multiplying the free energy per unit volume, which is $kT/(R_E^2\sigma)$ [1], by the width of the interface. This width will be of the order of the polymer size R_E . Thus, $\gamma \sim kT/R_E\sigma$. Note that the energy scale has to be the thermal energy kT as there are no other relevant energy scales in the problem. The mixture is athermal, there are no attractive interactions or soft repulsions to provide another energy scale. The free-energy density is then of order kT times the number density, which is of order $1/R_E^2\sigma$ for both the polymer molecules and the colloidal spheres when they demix. This is just a simple scaling argument so we confirm it by determining the scaling of γ within a standard square-gradient or Cahn-Hilliard theory for the interface [18–22].

We apply this theory to the system in the semigrand ensemble of Ref. [1] where the characteristic thermodynamic potential is the semigrand potential ω , which is a function of the number density of colloidal particles, ρ_C , and the activity z of the polymer molecules. As we are specifying the activity not the density of the polymer our system is equivalent to a single component system whose thermodynamic state depends on the density and on the activity of the polymer z ; $\ln z$ acts as an inverse temperature in the sense that the larger it is the stronger is the effect of the attractions. Thus we can apply the standard square-gradient expression for the interfacial tension of a single component system, which is [12,18,19,21,22]

$$\gamma = \int dx \left[\Psi + \kappa \left(\frac{d\rho_C}{dx} \right)^2 \right], \quad (1)$$

where

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$$\Psi = \omega[\rho_C(x)] - \omega^{(b)} - \mu_C[\rho_C(x) - \rho_C^{(b)}], \quad (2)$$

is the excess grand potential at a point. $\omega^{(b)}$ and $\rho_C^{(\alpha)}$ are the semigrand potential and density in either one of the coexisting phases. The superscript $\alpha = C, P$ for the colloid-rich and polymer-rich phases, respectively. μ_C is the chemical potential of the colloid. The interface is normal to the x axis. The coefficient κ of the gradient term is assumed to be density independent. The equilibrium profile is obtained by minimizing Eq. (1). Then standard manipulations enable a simpler expression for the equilibrium interfacial tension to be derived [21]:

$$\gamma = 2 \int_{\rho_C^{(P)}}^{\rho_C^{(C)}} d\rho_C [\kappa \Psi]^{1/2}. \quad (3)$$

If we require that the functional Eq. (1) be consistent with linear response theory [22] we obtain an expression for the coefficient κ of the gradient term,

$$\kappa = \frac{kT}{12} \int d\mathbf{r} r^2 c_2(r; \rho_C, z), \quad (4)$$

where $c_2(r; \rho_C, z)$ is the direct correlation function of the fluid of colloidal hard spheres in the presence of polymer. For our systems the most basic assumption is to use the low density approximation to the direct correlation function. This replaces c with the Mayer f function for the effective sphere-sphere interaction in the presence of the polymer [22]. For two spheres with centers separated by less than σ , the interaction energy is infinite and the Mayer f function equals -1 . For separations larger than σ the only interaction is that due to the polymer. This interaction is known [4], and is long range and weak thus we linearize the Mayer f function. Adding this altogether we obtain

$$c(r; \rho_C, z) \sim \begin{cases} -1, & r < \sigma \\ zR_E^2 \sigma(\sigma/r), & \sigma < r \leq R_E \\ 0, & r \gg R_E, \end{cases} \quad (5)$$

the ideal polymer induces an attraction that decays as $1/r$ for separations less than the radius of the polymer and roughly exponentially beyond this. Putting our approximate c into Eq. (4), we obtain an estimate of this coefficient:

$$\kappa \sim kT z R_E^2 \sigma^2 \int_0^{R_E} dr r^3 \quad (6)$$

$$\sim kT z \sigma^2 R_E^6. \quad (7)$$

We now return to Eq. (3) for the interfacial tension and determine its scaling with R_E . We note that the density difference $\rho_C^{(C)} - \rho_C^{(P)} \sim 1/R_E^2 \sigma$, κ scales as given by Eq. (7), $\Psi \sim kT/R_E^2 \sigma$ and the polymer activity is of order the polymer number density $z \sim 1/R_E^2 \sigma$. Putting this all together we see that we recover the scaling $\gamma \sim kT/R_E \sigma$ obtained earlier by dimensional analysis. Also, from Eq. (1) we see that the characteristic length scale for the interface must be

$(\kappa/\Psi)^{1/2} \rho_C^{(\alpha)} \sim R_E$, as we assumed earlier. Earlier work by Vrij [11], and by Brader and Evans [12] on the interfacial tension between demixed colloid-rich and polymer-rich phases when the colloid and polymer were of comparable sizes, $R_E \sim \sigma$, found that, as expected, $\gamma \sim kT/\sigma^2 \sim kT/R_E^2$. This is consistent with experimental findings [23].

The interfacial tension γ will be of order $kT/R_E \sigma$ only if we are not too close to the critical point of the polymer-colloid demixing. In general, we have $\gamma = (kT/R_E \sigma) s(z/z_c - 1)$, where s is a scaling function and z_c is the polymer activity at the critical point. We have been assuming that we are not very close to the critical point, i.e., that $z/z_c - 1 = O(1)$, and for these values of its argument $s = O(1)$ and we return to γ being of order $kT/R_E \sigma$. However, as the critical point is approached, $z/z_c - 1 \ll 1$, we have that the scaling function $s(x) = s_0 x^\mu$ for $x \ll 1$, where s_0 is a dimensionless constant and μ is the (positive) critical exponent of the interfacial tension [24]. The interfacial tension tends to 0 as the critical point of demixing is approached, and near the critical point it varies as a power law. See the review of Widom [24] for an excellent introduction to interfaces near critical points. Sufficiently close to the critical point the scaling of the interfacial tension will be dominated by fluctuations and then the exponent μ will take the value for the Ising model in three dimensions, $\mu = 1.26$ [19,24]. However, for very long polymers $R_E \gg \sigma$ the effective interaction is long ranged and long-range interactions suppress fluctuations and make the system mean field like. The mean field value of the exponent μ is $3/2$ [24]. Which value of the exponent, Ising or mean-field, is observed is determined by whether or not the Ginzburg criterion is obeyed or not; see Ref. [19] or any introduction to critical phenomena for a definition of the Ginzburg criterion. Note that Eq. (3), belonging as it does to a mean-field theory, will yield an interfacial tension that tends to 0 with an exponent $\mu = 3/2$, its mean-field value.

III. NUCLEATION AND OTHER FLUCTUATIONS

Now consider a single phase mixture of spheres and polymer quenched into the two-phase coexistence region. For definiteness assume that the single phase is the polymer-rich one. Then in order for the second, colloid-rich, phase to form and coexist with the polymer-rich one, this second phase must form. The dynamics of the formation of a new phase fall into two broad categories: nucleation then growth, and spinodal decomposition. See Refs. [18–20] for an introduction to the dynamics of first-order phase transitions. For example, a mixture of simple liquids such as water and an alcohol phase separate via nucleation of the new water-rich or alcohol-rich phase followed by growth of the nuclei, whereas polymer blends phase separate via spinodal decomposition. Here we show that for large ideal polymers and spheres, nucleation becomes very difficult, so mixtures of large ideal polymers and much smaller spheres will start to phase separate via spinodal decomposition.

The rate of nucleation N_n can be estimated using classical nucleation theory, see the book of Debenedetti [18] for a comprehensive discussion, see also Refs. [19,20]. N_n is the number of nuclei crossing the barrier per unit time per unit

volume. The classical nucleation theory expression for the rate N_n is

$$N_n = \Gamma \exp(-\Delta F^*/kT), \quad (8)$$

where Γ is an attempt frequency per unit volume, generally slowly varying, and ΔF^* is the free-energy barrier that must be crossed in order for a new phase to nucleate. The variation in the rate is generally dominated by that in ΔF^* so we focus on this. The free-energy barrier comes from the free energy needed to form a microscopic droplet of the new phase, here a colloid-rich phase. This droplet is the nucleus of the new phase. Within classical nucleation theory the free energy of formation of a microscopic droplet is the sum of two terms, a bulk term and a surface term,

$$\Delta F = \frac{4}{3} \pi R^3 \Psi_n + 4 \pi R^2 \gamma, \quad (9)$$

where R is the radius of the droplet and

$$\Psi_n = \omega(\rho_C^{(n)}) - \omega(\rho_C) - \mu_C(\rho_C^{(n)} - \rho_C) \quad (10)$$

is the difference between the grand potential inside the nucleus and the grand potential of the phase in which the nucleus forms, ρ_C is the density of colloid in the phase in which the nucleus forms, and $\rho_C^{(n)}$ is the density of colloid inside the nucleus. So long as we do not approach the spinodal too closely, we can express Ψ_n as a Taylor expansion in chemical potential, around the chemical potential of the colloid at coexistence μ_{co} . Truncating the Taylor series after the linear term, we get

$$\Psi_n \approx \Psi'(\mu_C - \mu_{co}), \quad (11)$$

as $\Psi_n = 0$ at coexistence, with

$$\Psi' = \left(\frac{\partial \Psi_n}{\partial \mu_C} \right)_{\mu_C = \mu_{co}}, \quad (12)$$

the derivative of Ψ_n at coexistence.

The barrier is given by the free energy of the droplet whose free energy is highest, which occurs when the two terms in Eq. (9) are comparable, $R^3 \Psi_n \sim R^2 \gamma$. Thus, $R \sim \gamma / [\Psi'(\mu_C - \mu_{co})]$, and

$$\Delta F^* \sim \frac{\gamma^3}{[\Psi'(\mu_C - \mu_{co})]^2}. \quad (13)$$

From Eq. (12), Ψ' scales as $1/R_E^2 \sigma$. Using this scaling together with that of γ , we find that at the top of the barrier the size of the nucleus is of order R_E , for $\mu_C - \mu_{co}$ not too much

less than kT . Using these same scalings in Eq. (13), we obtain the principle result of this section, the scaling of the nucleation barrier ΔF^* ,

$$\frac{\Delta F^*}{kT} \sim \left(\frac{\mu_{co}}{\mu_C - \mu_{co}} \right)^2 \frac{R_E}{\sigma}, \quad (14)$$

the barrier scales as R_E/σ and so increases as the size of the polymer molecules relative to that of the colloidal spheres increases. The factor in parentheses is a dimensionless measure of the supersaturation: how far we are into the two-phase region.

For sufficiently large R_E of the polymers the nucleation barrier will become so large that nucleation cannot occur. The mixture will be metastable up to very close to the spinodal [20,25–27]. Thus, the mixture will only start to demix when quenched beyond the spinodal, where the phase separation will start with spinodal decomposition. This is precisely analogous to polymer blends and systems of particles in which the particle-particle attractions are long ranged. In these systems the nucleation barrier scales as $N^{1/2}$ and as r^3 , where N is the length of the polymer and r is the range of the attraction [27]. The phase transition dynamics of systems of polymers and of particles with long-range attractions, were studied extensively in the early 1980s by Binder and Klein and their co-workers [25–27]. Many of the conclusions of that work also apply to the demixing of mixtures of hard spheres and much larger ideal polymers.

Finally, we note that our finding that nucleation is suppressed is equivalent to saying that our mixture satisfies the Ginzburg criterion for the irrelevance of fluctuations [19]. Essentially, nucleation is a fluctuation so when fluctuations are weak nucleation is suppressed and vice versa, again this was found for polymer blends/particles with long-range attractions [28,27]. For our mixtures, the Ginzburg criterion is essentially that the root-mean-square (rms) fluctuations in the number of colloidal spheres or of polymer molecules, in a volume R_E^3 , are much less than the mean number in that volume. The volume R_E^3 is the volume over which a pair of spheres or polymer interact (the sphere-sphere interaction is mediated by the polymer molecules, and the polymer-polymer interaction is mediated by the spheres). The rms fluctuations scale as the square root of the number of spheres in a volume R_E^3 , which is $\sim (R_E/\sigma)^{1/2}$, whereas the mean number scales as R_E/σ . Thus for large values of the ratio of the sizes, R_E/σ , the rms fluctuations in the number of spheres (or polymer molecules) inside the interaction volume is a small fraction of the mean number. Fluctuations about the mean are small and so mean-field theory applies and nucleation, which is a fluctuation, has a very high free-energy cost.

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