

## Adsorption of colloidal particles to curved interfaces

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As a simple model for a Pickering emulsion droplet, we consider the adsorption of spherical particles to a spherical liquid-liquid interface in order to investigate the curvature effect on the particle adsorption. By taking into account both the surface and the volume energies due to the presence of a particle, we show that the equilibrium contact angle is determined by the classical Young's equation although the adsorption energy depends on the curvature. We also calculate the partitioning of the colloidal particles among the two liquids and the interface. The distribution of colloidal particles is expressed in terms of the interfacial curvature as well as the relative wettability of the particle. © 2006 American Institute of Physics. [DOI: 10.1063/1.2216697]

Small particles such as lamp black or hydrophobic silica adsorb to an oil-water interface and act as stabilizers of emulsions. Such emulsions are called "Pickering emulsions"<sup>1</sup> and have been used in various food and cosmetic products.<sup>2</sup> For instance, lipoprotein particles and fatty acid crystals stabilize the emulsion state in mayonnaise or margarine. A modern application of Pickering emulsion is to use them as templates of functional composite materials. For example, spherical emulsion droplets are used to produce microstructured hollow spheres<sup>3</sup> or ribosome-like nano-capsules ("colloidsomes").<sup>4</sup> In addition to spherical droplets, the particles form several self-assembling structures such as network structures or ball-like aggregates.<sup>5</sup> Quite recently, colloidal particles with equal affinity for two liquids are shown to form a bicontinuous interfacially jammed emulsion gel ("bijel").<sup>6</sup>

Pickering emulsions are not only useful but also very interesting from the fundamental point of view. When a molecule exhibits a surface activity, it is conventionally recognized that both hydrophobic and hydrophilic groups should exist in a single molecule. This is not the case for colloidal particles whose surface is chemically uniform. The particles adsorb only when the relative wettability between the particle and the two liquids balances each other.<sup>7,8</sup> Moreover, the connecting point between the hydrophobic and hydrophilic groups in a surfactant molecule is localized at the interface between the two liquids. Colloidal particles, on the other hand, can adjust their position with respect to the interface in order to reduce the interfacial energy.

In this Communication, we discuss the adsorption of spherical solid particles to a liquid-liquid interface. Special attention is paid to the effects of interfacial curvature on the adsorption behavior. For a spherically curved droplet interface, we show that the contact angle satisfies the classical Young's equation although the adsorption energy depends on the curvature. We also consider the partitioning of the colloidal

particles among the two liquids and the interface. In contrast to the previous work,<sup>9</sup> both the relative wettability and the interfacial curvature are shown to contribute to the equilibrium distribution of colloidal particles. The curvature effect on the adsorption behavior is important because most of the structures in Pickering emulsions are characterized by finite curvatures.

We start our discussion by considering a single spherical particle of radius  $a$  resting at a flat interface between liquid 1 and liquid 2, as shown in Fig. 1(a). Let  $\theta$  be the contact angle, and  $\sigma_{1p}$ ,  $\sigma_{2p}$ ,  $\sigma_{12}$  be the 1-particle, 2-particle, 1-2 interfacial tensions, respectively. Neglecting external forces and a finite thickness of the interface, the interfacial energy attributed to the particle is  $w_0 = \sigma_{1p}A_{1p} + \sigma_{2p}A_{2p} - \sigma_{12}A_{12}$ , where  $A_{1p}$  and  $A_{2p}$  are the 1-particle and 2-particle contact areas, respectively, while  $A_{12}$  is the eliminated area of the 1-2 interface due to the presence of the particle.<sup>7</sup> For a flat interface, these areas are given by

$$A_{1p} = 2\pi a^2(1 + \cos \theta), \quad A_{2p} = 2\pi a^2(1 - \cos \theta), \quad (1)$$

$$A_{12} = \pi a^2 \sin^2 \theta.$$

Hereafter, it is convenient to introduce the following dimensionless quantities:

$$\sigma = \frac{\sigma_{1p} + \sigma_{2p}}{\sigma_{12}}, \quad \gamma = \frac{\sigma_{1p} - \sigma_{2p}}{\sigma_{12}}. \quad (2)$$

Then the dimensionless adsorption energy defined by  $g_0(\theta) = w_0 / (2\pi a^2 \sigma_{12})$  is written as

$$g_0(\theta) = \sigma + \gamma \cos \theta - \frac{\sin^2 \theta}{2}. \quad (3)$$

The equilibrium position (or the contact angle) of the particle is determined by minimizing  $g_0(\theta)$  with respect to  $\theta$ , i.e.,  $dg_0/d\theta = 0$ . This results in the conventional Young's equation:<sup>7</sup>

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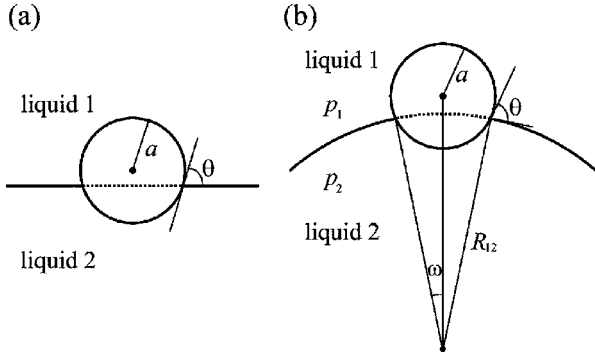


FIG. 1. (a) A spherical particle of radius  $a$  adsorbed to a flat interface between liquid 1 and liquid 2. The contact angle is denoted by  $\theta$ . (b) A spherical particle adsorbed to a spherical interface whose radius of curvature is  $R_{12}$ . The pressures in liquids 1 and 2 are  $p_1$  and  $p_2$ , respectively.  $\omega$  is the central angle.

$$\theta_{\min} = \arccos(-\gamma). \quad (4)$$

By substituting this relation to Eq. (3), the minimized interfacial energy is obtained as  $g_0(\theta = \theta_{\min}) = \sigma - (1 + \gamma^2)/2$  when  $|\gamma| < 1$ . On the other hand, the particle prefers to stay either in liquid 1 when  $\gamma < -1$  or in liquid 2 when  $\gamma > 1$ .

Next we discuss the adsorption of a spherical particle to a curved interface between liquids 1 and 2. For simplicity, we consider a spherical 1-2 interface whose radius is denoted by  $R_{12}$  as depicted in Fig. 1(b). Here the dimensionless curvature  $\epsilon = a/R_{12}$  is taken to be positive when the interface is curved toward liquid 1. In the following, we generally assume that  $\epsilon \ll 1$ . When the interface is curved, one has to take into account the pressure in each liquid denoted by  $p_1$  and  $p_2$ . According to Laplace's law for a spherical interface, the pressure difference is maintained by the surface tension;  $p_2 - p_1 = 2\sigma_{12}/R_{12}$ . For a given droplet curvature  $\epsilon$ , we now calculate the energy per particle by  $w = \sigma_{1p}A_{1p} + \sigma_{2p}A_{2p} - \sigma_{12}A_{12} + p_1V_1 + p_2V_2$ , where  $V_1$  and  $V_2$  are the volumes occupied by the particle in liquids 1 and 2, respectively. After some geometrical considerations, we obtain these areas and volumes as

$$A_{1p} = 2\pi a^2[1 + \cos(\theta - \omega)],$$

$$A_{2p} = 2\pi a^2[1 - \cos(\theta - \omega)], \quad (5)$$

$$A_{12} = 2\pi R_{12}^2(1 - \cos \omega),$$

$$V_1 = \pi a^3 \left[ \frac{2}{3} + \cos(\theta - \omega) - \frac{1}{3} \cos^3(\theta - \omega) \right]$$

$$- \pi R_{12}^3 \left[ \frac{2}{3} - \cos \omega + \frac{1}{3} \cos^3 \omega \right], \quad (6)$$

$$V_2 = \pi a^3 \left[ \frac{2}{3} - \cos(\theta - \omega) + \frac{1}{3} \cos^3(\theta - \omega) \right]$$

$$+ \pi R_{12}^3 \left[ \frac{2}{3} - \cos \omega + \frac{1}{3} \cos^3 \omega \right], \quad (7)$$

where

$$\omega = \arctan \left( \frac{\epsilon \sin \theta}{1 + \epsilon \cos \theta} \right) \quad (8)$$

is the central angle defined in Fig. 1(b). Then the dimensionless energy  $g(\theta, \epsilon) = w/(2\pi a^2 \sigma_{12})$  which now depends on  $\theta$  and  $\epsilon$  becomes

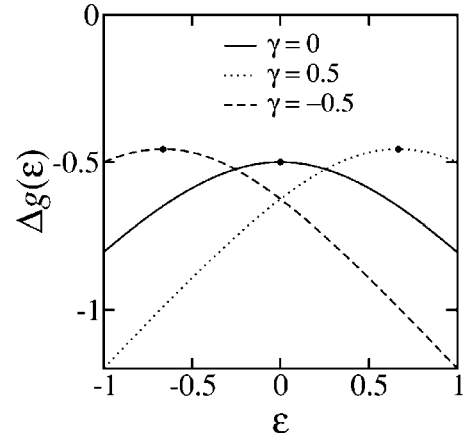


FIG. 2. The minimized scaled interfacial energy difference  $\Delta g(\epsilon)$  (see the text) as a function of  $\epsilon = a/R_{12}$  for  $\gamma = 0, \pm 0.5$ . Filled circles on each curve correspond to the maximum points.

$$g(\theta, \epsilon) = \sigma + \frac{a(p_1 + p_2)}{3\sigma_{12}} + \gamma \cos(\theta - \omega)$$

$$- \frac{1 - \cos^3 \omega}{3\epsilon^2} - \frac{\epsilon}{3} [3 \cos(\theta - \omega) - \cos^3(\theta - \omega)]. \quad (9)$$

Since  $\omega \approx \epsilon \sin \theta$  up to the lowest order in  $\epsilon$ , it is easy to see that Eq. (9) reduces to Eq. (3) in the limit  $\epsilon \rightarrow 0$  except the constant term related to the pressure. We note here that a similar calculation was done before,<sup>10</sup> but the volume energies were not considered there.

As we did for a flat interface, the equilibrium position of the particle is obtained by minimizing  $g(\theta, \epsilon)$  with respect to  $\theta$  while  $\epsilon$  is fixed, i.e.,  $(\partial g / \partial \theta)_\epsilon = 0$ . Then we obtain the same Young's equation as in Eq. (4). This means that the equilibrium contact angle does *not* depend on the curvature of the interface. The present result is consistent with the other work.<sup>11</sup> Notice that we have fixed the curvature  $\epsilon$  and allowed the area and volume to change. In a different treatment,<sup>12</sup> the same Young's equation was recovered even when the volume is conserved.

We now substitute back the Young's equation into Eq. (9), and obtain  $g(\epsilon) = g(\theta = \theta_{\min}, \epsilon)$  which is a function of  $\epsilon$  only. In Fig. 2,  $\Delta g(\epsilon) \equiv g(\epsilon) - \sigma - a(p_1 + p_2)/(3\sigma_{12})$  is plotted for  $\gamma = 0$  and  $\pm 0.5$ . We see that  $g(\epsilon)$  takes a maximum value at a certain value of  $\epsilon$  (denoted by  $\epsilon^*$ ) for each different values of  $\gamma$ . Since the absolute value of  $g(\epsilon)$  corresponds to the work needed to remove a particle from the interface, the particles are most weakly adsorbed when  $\epsilon = \epsilon^*$ .

When the size of the droplet is large ( $\epsilon \ll 1$ ), one can expand  $g(\epsilon)$  in terms of  $\epsilon$  to obtain

$$g(\epsilon) \approx \sigma + \frac{a(p_1 + p_2)}{3\sigma_{12}} - \frac{1}{2}(1 + \gamma^2) + \gamma \left( 1 - \frac{\gamma^2}{3} \right) \epsilon$$

$$- \frac{3}{8}(-1 + \gamma^2)^2 \epsilon^2 + \dots \quad (10)$$

Again,  $g(\epsilon)$  reduces to  $g_0(\epsilon)$  in the limit  $\epsilon \rightarrow 0$  apart from the constant term. Within this quadratic approximation we obtain  $\epsilon^* \approx (4/9)\gamma(3 - \gamma^2)/(-1 + \gamma^2)^2$ , which is valid when  $\gamma$  is close

to zero. Being consistent with the symmetry consideration,  $\epsilon^*$  is an odd function of  $\gamma$ . It should be noted that even the equilibrium contact angle is independent of the interfacial curvature, the minimized interfacial energy  $g(\epsilon)$  is a function of  $\epsilon$ . This is the main result of the paper. Such a curvature effect becomes important when we consider, for example, the partitioning of the particles as discussed below.

In the following, we adopt the formalism to discuss the thermodynamics of the surfactant films which are in equilibrium with surfactant in solution.<sup>13</sup> Here the particles play the role of surfactants. Consider a ternary mixture in which the total volume fractions of liquid 1 and liquid 2 are  $\phi_1$  and  $\phi_2$ , respectively, and the total volume fraction of colloidal particles in the system is  $\phi_p$ . These volume fractions satisfy the condition  $\phi_1 + \phi_2 + \phi_p = 1$ . The particles are partitioned among the liquid 1, liquid 2, and the monolayer films with volume fractions  $\phi_{p,1}$ ,  $\phi_{p,2}$  and  $\phi_{p,m}$ , respectively. Such a partitioning was indeed observed in the experiment.<sup>14</sup> Since the total amount of the particle should be conserved, they satisfy

$$\phi_{p,1} + \phi_{p,2} + \phi_{p,m} = \phi_p. \quad (11)$$

Next we denote the local volume fractions of particles in liquid 1 and liquid 2 by  $\psi_1$  and  $\psi_2$ , respectively. When the segregation between the two liquids is strong enough, the total and the local volume fractions are related by

$$\frac{\phi_{p,i}}{\phi_i} = \frac{\psi_i}{1 - \psi_i}, \quad (12)$$

where  $i=1,2$ . It is assumed here that the local concentration of particle in the film is unity. This assumption is justified because the interfaces in Pickering emulsions consist of monolayers of almost hexagonally close-packed particles.<sup>15,16</sup>

In the liquid regions containing colloidal particles, each free energy per particle is given by

$$f_i = \psi_i \log \psi_i + (1 - \psi_i) \log(1 - \psi_i) + \mu_i \psi_i + \frac{\chi_i}{2} \psi_i^2, \quad (13)$$

where the first two terms represents the entropy,  $\mu_i$  is the energy of one particle in liquid  $i$ , and  $\chi_i$  is the second virial coefficient among the particles in liquid  $i$ . Here and in the following, all the energies are expressed in units of the thermal energy  $k_B T$ . We consider the case of  $\chi_i \geq 0$  in order to investigate the effect of the repulsion between the particles. For attractive cases ( $\chi_i < 0$ ), one needs to include the higher order terms in  $\psi_i$ , which will be reported elsewhere. In the case of a spherical particle, we simply have

$$\mu_i = \frac{4\pi a^2 \sigma_{ip}}{k_B T} + \frac{4\pi a^3 p_i}{3k_B T}, \quad (14)$$

and  $\chi_i = 8$  for hard spheres.<sup>17</sup> Since the two liquid phases consisting of both liquid and particles occupy fractions of  $\phi_1 + \phi_{p,1}$  and  $\phi_2 + \phi_{p,2}$  of the total volume, the total free energy per particle is written as

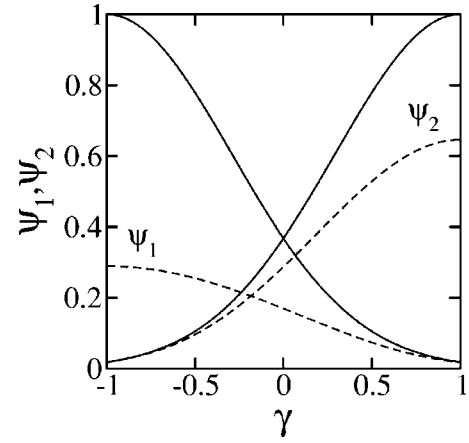


FIG. 3. Equilibrium local volume fractions of particles in liquid 1 ( $\psi_1$ ) and in liquid 2 ( $\psi_2$ ) as a function of  $\gamma$ . The second virial coefficients are  $(\chi_1, \chi_2) = (0, 0)$  (solid lines) and  $(\chi_1, \chi_2) = (5, 1)$  (dashed lines). The other parameters are  $\epsilon = 0$  and  $\pi a^2 \sigma_{12} / k_B T = 1$ .

$$f_{\text{total}} = (\phi_1 + \phi_{p,1})f_1 + (\phi_2 + \phi_{p,2})f_2 + \phi_{p,m}f_m, \quad (15)$$

where  $f_m = (2\pi a^2 \sigma_{12} / k_B T)g(\epsilon)$  is the interfacial energy per particle consisting the monolayer [see Eq. (10)].

To obtain the equilibrium partition, we minimize  $f_{\text{total}}$  with respect to  $\psi_1$ ,  $\psi_2$ , and  $\phi_{p,m}$  subject to the constraint of conservation of the total amount of the particle [see Eq. (11)]. Such a constraint minimization can be performed using the method of Lagrange multiplier. The resulting equilibrium conditions are provided by

$$2 \log \psi_i - 2(f_m - \mu_i) + \chi_i \psi_i (2 - \psi_i) = 0, \quad (16)$$

with  $i=1,2$ . Elimination of  $f_m$  from Eq. (16) yields the relation between  $\psi_1$  and  $\psi_2$  such that

$$\psi_1 = \psi_2 \exp \left[ \mu_2 - \mu_1 + \chi_2 \left( \psi_2 - \frac{\psi_2^2}{2} \right) - \chi_1 \left( \psi_1 - \frac{\psi_1^2}{2} \right) \right]. \quad (17)$$

This relation is reminiscent of the Frumkin adsorption isotherm.<sup>18</sup>

In the case of a spherical particle adsorbing to a spherical interface, one can show from Eqs. (10) and (14) that  $f_m - \mu_i$  in Eq. (16) are given by

$$f_m - \mu_1 = \frac{2\pi a^2 \sigma_{12}}{k_B T} \left[ -\frac{1}{2}(1 + \gamma)^2 + \left( \frac{2}{3} + \gamma - \frac{\gamma^3}{3} \right) \epsilon + \dots \right], \quad (18)$$

$$f_m - \mu_2 = \frac{2\pi a^2 \sigma_{12}}{k_B T} \left[ -\frac{1}{2}(1 - \gamma)^2 - \left( \frac{2}{3} - \gamma + \frac{\gamma^3}{3} \right) \epsilon + \dots \right], \quad (19)$$

up to the lowest order in  $\epsilon$ . Once we obtain  $\psi_i$  by solving Eq. (16),  $\phi_{p,i}$  is calculated from Eq. (12). Then  $\phi_{p,m}$  is determined according to Eq. (11) provided  $\phi_i$  and  $\phi_p$  are given. The partitioning of the particle is determined not only by the relative wettability  $\gamma$  but also the interfacial curvature  $\epsilon$ .

We first consider the adsorption to a flat interface ( $\epsilon = 0$ ). In the absence of repulsion between the particles in both liquids ( $\chi_1 = \chi_2 = 0$ ), Eq. (16) can be easily solved for  $\psi_i$ :

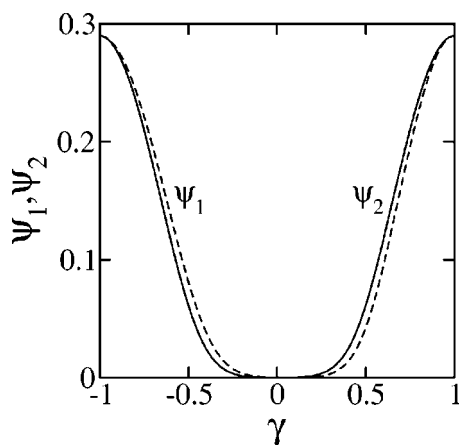


FIG. 4. Equilibrium local volume fractions of particles in liquid 1 ( $\psi_1$ ) and in liquid 2 ( $\psi_2$ ) as a function of  $\gamma$  when  $\epsilon=0$  (solid lines) and  $\epsilon=0.1$  (dashed lines). The other parameters are  $(\chi_1, \chi_2)=(5, 5)$  and  $\pi a^2 \sigma_{12}/k_B T=10$ .

$$\psi_i = \exp(f_m - \mu_i). \quad (20)$$

This result for  $\psi_1$  and  $\psi_2$  are plotted as solid lines in Fig. 3 when  $\pi a^2 \sigma_{12}/k_B T=1$ . As is consistent with the physical meaning of the relative wettability,  $\psi_1$  decreases and  $\psi_2$  increases as  $\gamma$  is changed from  $-1$  to  $1$ . When  $\gamma=0$ , the adsorption is purely determined by the ratio  $\pi a^2 \sigma_{12}/k_B T$ .<sup>6</sup> Practically, the fraction of the particles in the bulk liquids are negligibly small when  $\pi a^2 \sigma_{12}/k_B T > 10$ . In the presence of repulsive interactions, on the other hand, Eq. (16) needs to be solved numerically. As an example, we show the result of  $(\chi_1, \chi_2)=(5, 1)$  as dashed lines in Fig. 3. The repulsive interactions dramatically suppress  $\psi_i$ , which in turn leads to an enhanced particle adsorption. This suppression is more pronounced in liquid 1.

Next we look at the effect of a finite interfacial curvature. In Fig. 4, we have plotted  $\psi_1$  and  $\psi_2$  for  $\epsilon=0$  (solid lines) and  $0.1$  (dashed lines). The other parameter values are chosen here as  $(\chi_1, \chi_2)=(5, 5)$  and  $\pi a^2 \sigma_{12}/k_B T=10$ . Due to the latter choice of the parameter, both  $\psi_1$  and  $\psi_2$  almost vanish for  $\gamma \geq 0$  and  $\gamma \leq 0$ , respectively (not visible in Fig. 4). For a positive curvature as considered here,  $\psi_1$  is larger and  $\psi_2$  is smaller than those of the flat interface. This result is in accordance with the fact that the particles prefer to stay in liquid 1 because the pressure in liquid 2 is larger when  $\epsilon > 0$ . The shifts of the distribution curves become larger as the curvature is increased (not shown here).

Finally, we comment that the interfacial curvature  $\epsilon$  is primarily determined by the total volume fractions  $\phi_1$ ,  $\phi_2$ , and  $\phi_p$ . Assuming strong adsorption of the particles, the cur-

vature of a spherical droplet consisting of liquid 2 is roughly given by  $\epsilon \sim \phi_p / \phi_2$ .<sup>17</sup> This means that the partition of the particles is completely determined provided we know the total volume fractions of each component. The macroscopic phase behavior of a Pickering emulsion is characterized by the competition between  $\epsilon$  and the spontaneous curvature of the interface saturated with particles.<sup>10</sup>

In summary, we have discussed the adsorption of spherical particles to a spherically curved interface. We showed that equilibrium contact angle is given by the Young's equation, whereas the minimized adsorption energy is a function of curvature. Such a curvature effect affects the equilibrium distribution of the particles. Currently, we are investigating analogous problems for a spherical colloidal particle with hydrophilic and hydrophobic hemispheres ("Janus bead").<sup>19</sup>

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