Adsorption Dynamics in Pickering Emulsions

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We investigate the adsorption dynamics of colloidal particles to a liquid/liquid interface. Such an analysis is important in the formation of Pickering emulsions. Using a free energy formulation that has been used for adsorption of surfactants, we obtain the time evolution of the surface coverage and dynamic surface tension. We estimate the characteristic time for adsorption, and show that it corresponds to a diffusion-limited adsorption case. The asymptotic values of the surface coverage and surface tension with respect to their equilibrium values is shown to decrease as $t^{-1/2}$. We also show that the equilibrium equation of state relating surface tension to surface coverage holds also in nonequilibrium situations.

§1. Introduction

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"[1] and have been used in various food and cosmetic products.[2] 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 micro-structured hollow spheres[3] or ribosome-like nano-capsules ("colloidsomes").[4] In addition to spherical droplets, the particles form several self-assembling structures such as network structures or non-spherical aggregates.[5),6]

Pickering emulsions are not only useful but also interesting from the fundamental point of view. When a molecule exhibits a surface activity, it is conventionally believed that both hydrophobic and hydrophilic groups should exist in a single molecule. However, this is not the case for a colloidal particle whose surface is chemically uniform. The particles adsorb only when the relative wettability between the particle and the two liquids balances each other.[7),8] Moreover, colloidal particles can adjust their position with respect to the interface in order to reduce the interfacial energy.

One of the important aspects of Pickering emulsions resides in their nonequilibrium properties. This is the reason why it was a surprise when thermodynamically stable Pickering emulsions have been reported recently.[9] For example, the coalescence frequency of droplets is shown to depend on time and particle concentration.[10] Computer simulations of phase separation of a binary solvent containing nanoparticles have been also performed.[11] It was shown that colloidal particles with equal affinity for two liquids form a bicontinuous interfacially jammed emulsion gel ("bijel").[12] Soon after this study, microscopy study of Pickering emulsions revealed that quenching into the demixed region leads to the formation of domains which are sta-

ble due to a jammed, semisolid, multilayer of colloids.[13),14)] Recently, the kinetics of nanoparticle self-assembly at liquid-liquid interfaces has been reported.[15)] They measured changes in the interfacial tension from the early to late stages of nanoparticle adsorption.

In this paper, we discuss the adsorption dynamics of solid particles to liquid-liquid interfaces. We use a theory that has been developed to describe the kinetics of surfactant adsorption.[16),17)] This theory relies on a free energy formulation and has been successful in explaining the observed dynamic interfacial tensions of surfactant solutions. Our primary interest is to understand how the wettability (affinity) of the colloidal particle with respect to the two liquids would affect the adsorption dynamics. We discuss the characteristic time for the particle adsorption and will show that it is a diffusion-limited process. We also calculate the dynamic surface tension which will be compared with the recent experimental result of nanoparticle adsorption.[15)] It will be argued that the equilibrium equation of state holds also in nonequilibrium cases.

In the next section, we first define the wettability of a colloidal particle and derive its adsorption energy. In §3, the free energy of the system is defined and some equilibrium properties are derived including the adsorption isotherm. In §4, we present the basic equations describing the adsorption kinetics. Section 5 gives the results of the numerical calculation together with some discussions. Finally, we shall conclude in §6.

§2. Wettability of a spherical particle

We start our discussion by considering a spherical particle of diameter a residing at a flat interface between liquid 1 and liquid 2, as shown in Fig. 1(a). Let θ be the contact angle defined in liquid 1, and $\sigma_{1\mathrm{p}}$, $\sigma_{2\mathrm{p}}$, σ_{12} be the 1-particle, 2-particle, 1-2 interfacial tensions, respectively. In this paper, we define the following dimensionless quantity to characterize the wettability of the particle:

$$\gamma = \frac{\sigma_{1\mathrm{p}} - \sigma_{2\mathrm{p}}}{\sigma_{12}}. \tag{2·1}$$

Neglecting external forces and a finite thickness of the interface, the interfacial energy attributed to the particle is $A = \sigma_{1\mathrm{p}} S_{1\mathrm{p}} + \sigma_{2\mathrm{p}} S_{2\mathrm{p}} - \sigma_{12} S_{12}$, where $S_{1\mathrm{p}}$ and $S_{2\mathrm{p}}$ are the 1-particle and 2-particle contact areas, respectively, while S_{12} is the eliminated area of the 1-2 interface due to the presence of the particle.[7),18)] These areas are given by

$$S_{1\mathrm{p}} = \frac{\pi a^2}{2}(1+\cos\theta), \qquad S_{2\mathrm{p}} = \frac{\pi a^2}{2}(1-\cos\theta), \qquad S_{12} = \frac{\pi a^2}{4}\sin^2\theta. \tag{2·2}$$

Then the total adsorption energy per particle is expressed as

$$A(\theta,\gamma) = \frac{\pi a^2 \sigma_{12}}{2}\left[\sigma + \gamma\cos\theta - \frac{\sin^2\theta}{2}\right], \tag{2·3}$$

where $\sigma = (\sigma_{1\mathrm{p}} + \sigma_{2\mathrm{p}})/\sigma_{12}$.

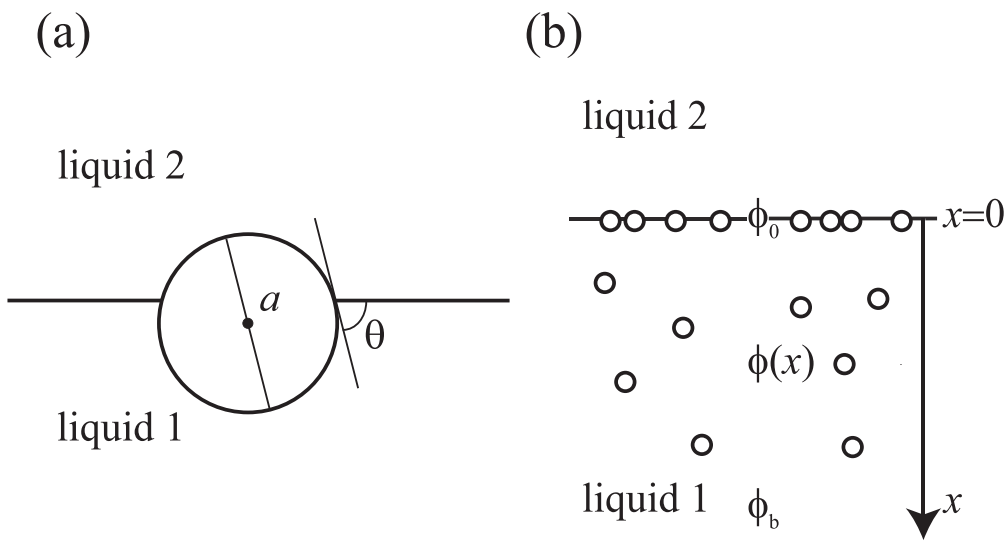

Fig. 1. (a) A spherical particle of diameter a adsorbed to a flat interface between liquid 1 and liquid 2. The contact angle taken in liquid 1 is denoted by θ. (b) Colloidal particles adsorbing at the liquid/liquid interface. The particles are contained only in liquid 1 which occupies $x > 0$. Here ϕ_0 is the surface coverage, $\phi(x)$ the volume fraction at x, and ϕ_b the bulk volume fraction at $x \to \infty$.

The contact angle θ which gives the equilibrium position of the particle is determined by minimizing $A(\theta, \gamma)$ with respect to θ. This leads to the conventional Young's equation:[7)]

$$\theta = \arccos(-\gamma). \tag{2·4}$$

By substituting this relation into Eq. (2·3), the minimized interfacial energy or the adsorption energy (as a function of γ) is given by[18)]

$$A(\gamma) = \frac{\pi a^2 \sigma_{12}}{2} \left[\sigma - \frac{1}{2}(1+\gamma^2) \right], \tag{2·5}$$

as long as $|\gamma| < 1$. In other cases, the particle prefers to stay either in liquid 1 when $\gamma < -1$ or in liquid 2 when $\gamma > 1$.

§3. Adsorption isotherm

Next we discuss the equilibrium adsorption isotherm of the interface. As depicted in Fig. 1(b), we assume that a flat interface between the two liquids spans the plane $x = 0$, and the particles are contained only in liquid 1 which occupies $x > 0$. Liquid 1 is in contact with a bulk reservoir of particles where the particle volume fraction and chemical potential are given by ϕ_b and μ_b, respectively.

The particle volume fraction in the bulk is denoted by $\phi(x)$, and its value at the interface by ϕ_0. Following Refs. 16) and 17), we start from the excess free energy

per unit area written as

$$\Delta\Gamma[\phi(x)] = \int_0^\infty \Delta f[\phi(x)]\,dx + f_0(\phi_0), \tag{3·1}$$

where Δf is the excess free energy per unit volume in the bulk, and f_0 is the free energy per unit area at the interface. The former is given by

$$\begin{aligned}\Delta f[\phi(x)] = \frac{1}{a^3}\big\{&k_{\rm B}T[\phi\ln\phi - \phi - (\phi_{\rm b}\ln\phi_{\rm b} - \phi_{\rm b})]\\ &+4\pi(a/2)^2\sigma_{1\rm p}(\phi-\phi_{\rm b}) - \mu_{\rm b}(\phi-\phi_{\rm b})\big\},\end{aligned} \tag{3·2}$$

where $k_{\rm B}$ is the Boltzmann constant and T the temperature. The first contribution is the entropy of mixing with respect to the bulk, and the second contribution comes from the contact of the particles with liquid 1 (hence the surface tension $\sigma_{1\rm p}$). It is assumed here that the bulk volume fraction $\phi(x)$ is much smaller than unity. On the other hand, f_0 in Eq. (3·1) has the form

$$\begin{aligned}f_0(\phi_0) = \frac{1}{a^2}\Big\{&k_{\rm B}T[\phi_0\ln\phi_0 + (1-\phi_0)\ln(1-\phi_0)]\\ &+A(\gamma)\phi_0 - \frac{B}{2}\phi_0^2 - \mu_1\phi_0\Big\}.\end{aligned} \tag{3·3}$$

In the above, the terms in the square brackets is the full entropy of mixing since $\phi_0 \gg \phi(x)$. Moreover $A(\gamma)$ is the particle adsorption energy defined by Eq. (2·5), and the term proportional to B describes the interactions between particles at the interface. The overall particle interaction is attractive when $B > 0$. Finally, the chemical potential is defined as $\mu_1 \equiv \mu(x \to 0)$.

Variation of $\Delta\Gamma$ with respect to $\phi(x)$ leads to the chemical potential given by $\mu(x) = k_{\rm B}T\ln\phi(x) + \pi a^2\sigma_{1\rm p}$. Hence we have $\mu_1 = k_{\rm B}T\ln\phi_1 + \pi a^2\sigma_{1\rm p}$, where $\phi_1 \equiv \phi(x \to 0)$ is the particle volume fraction at the subsurface layer. Note that, in equilibrium, we have $\phi(x) = \phi_{\rm b}$ for $x > 0$. On the other hand, minimization of $\Delta\Gamma$ with respect to ϕ_0 (hence $\mu_0 = \mu_1$, where μ_0 is the chemical potential at the interface) and the condition $\mu_1 = \mu_{\rm b}$ gives the equilibrium adsorption isotherm

$$\phi_{0,\rm eq} = \frac{\phi_{\rm b}}{\phi_{\rm b} + \exp[-\alpha(1+\gamma)^2 - \beta\phi_{0,\rm eq}]}, \tag{3·4}$$

where $\alpha \equiv \pi(a/2)^2\sigma_{12}/k_{\rm B}T$ and $\beta \equiv B/k_{\rm B}T$ are dimensionless energy parameters. This equation is called the Frumkin adsorption isotherm which reduces to the Langmuir adsorption isotherm when $\beta = 0$.[19] In Fig. 2(a), we plot $\phi_{0,\rm eq}$ as a function of $\phi_{\rm b}$ for various values of β. The other parameters are chosen to be $\alpha = 10$ and $\gamma = -0.5$. When $\beta < 4$, the equilibrium surface coverage $\phi_{0,\rm eq}$ increases monotonically. For $\beta > 4$, however, $\phi_{0,\rm eq}$ changes non-monotonically so that a two-phase coexistence is implied.[19] We have determined the vertical dashes lines by the condition that $\phi_{\rm b}$ minimizes the surface free energy of Eq. (3·3). Such a discontinuous jump of the surface coverage in the presence of a lateral interaction is also predicted for athermal polymer-nanoparticle blends near a substrate.[20] In the following, we

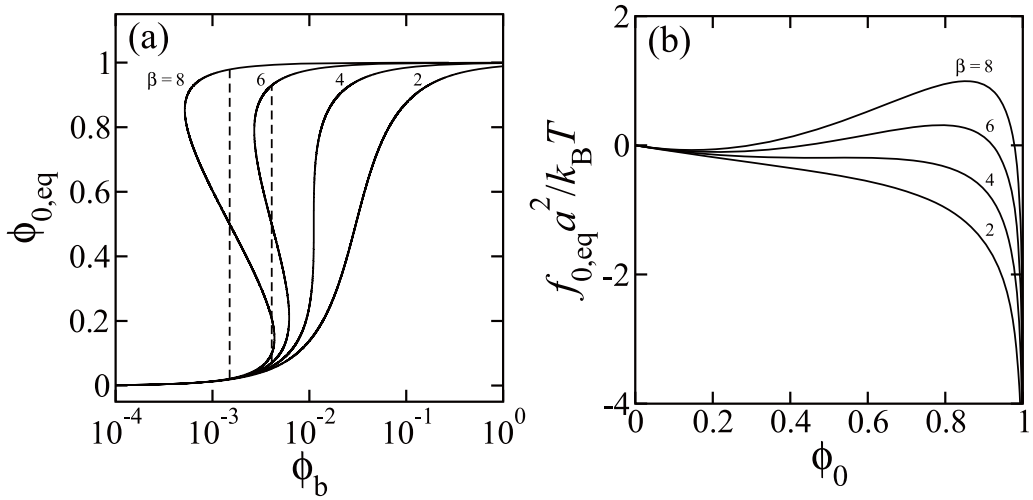

Fig. 2. (a) Equilibrium surface coverage $\phi_{0,\mathrm{eq}}$ as a function of the bulk volume fraction ϕ_b for different values of β (adsorption isotherms). The other parameters are $\alpha = 10$ and $\gamma = -0.5$. For $\beta > 4$, $\phi_{0,\mathrm{eq}}$ changes discontinuously according to the dashed lines. (b) The equilibrium interfacial energy $f_{0,\mathrm{eq}}$ as a function of ϕ_0.

shall mainly deal with the case of $\beta < 4$ for which the phase transition does not occur. The case of $\beta > 4$ will be briefly discussed later in §5.

From Eqs. (3·3) and (3·4), the equilibrium interfacial energy becomes[16),17)]

$$f_{0,\mathrm{eq}} = \frac{k_\mathrm{B}T}{a^2}\left[\ln(1-\phi_{0,\mathrm{eq}}) + \frac{\beta}{2}\phi_{0,\mathrm{eq}}^2\right]. \tag{3·5}$$

This provides the equilibrium equation of state relating the surface tension to the surface coverage. Notice that Δf in Eq. (3·2) completely vanishes in equilibrium. In Fig. 2(b), we show $f_{0,\mathrm{eq}}$ as a function of ϕ_0 for various values of β. As a result of the competition between the entropy and interaction terms, the above equilibrium surface energy decreases only slightly for small ϕ_0, but drops off when $\phi_0 \to 1$. We also see that a maximum appears when $\beta > 4$.

§4. Adsorption dynamics

In order to discuss nonequilibrium situations, we follow the formulation that has been developed for surfactant molecules.[16),17),21)] Assuming the proportionality between the velocities and potential, we employ an ordinary diffusion equation in the bulk:

$$\frac{\partial\phi}{\partial t} = D\frac{\partial^2\phi}{\partial x^2}, \tag{4·1}$$

where D is the diffusion constant of the colloidal particle. We further assume here that the colloidal particles do not leave the interface toward liquid 2. Then the

condition of the particle conservation at the subsurface layer can be written as

$$\frac{\partial \phi_1}{\partial t} = \frac{D}{a}\frac{\partial \phi}{\partial x}\bigg|_{x=a} - \frac{\partial \phi_0}{\partial t}, \tag{4·2}$$

where we have assumed that the subsurface layer exists at $x = a$.

By applying the Laplace transform to Eqs. (4·1) and (4·2), we recover the so-called Ward-Tordai equation:[22),23)]

$$\phi_0(t) + \phi_1(t) = \frac{1}{a}\sqrt{\frac{D}{\pi}}\left[2\phi_{\rm b}\sqrt{t} - \int_0^t \frac{\phi_1(\tau)}{\sqrt{t-\tau}}\,d\tau\right] + 2\phi_{\rm b}, \tag{4·3}$$

where we have used $\phi(x, t = 0) = \phi_{\rm b}$ for the initial condition. This equation describes the time evolution of the surface plus subsurface volume fraction $(\phi_0 + \phi_1)$ due to a diffusive transport of colloidal particles from the bulk to the interface. The second term in the brackets accounts for the desorption of the particles from the subsurface layer. The dynamics at the interface itself is proportional to the variation of f_0 with respect to ϕ_0. This gives the following equation:

$$\frac{\partial \phi_0}{\partial t} = \frac{D}{a^2}\phi_1\left[\ln\frac{\phi_1(1-\phi_0)}{\phi_0} + \alpha(1+\gamma)^2 + \beta\phi_0\right]. \tag{4·4}$$

Equations (4·3) and (4·4) provide a complete set of equations to determine $\phi_0(t)$ and $\phi_1(t)$ independently. Although the diffusivities at the interface can be different from those inside the aqueous solution, the two diffusion constants D in the above equations are assumed to be the same. Using the numerical scheme described in Ref. 24), we calculate the full solution of the coupled equations numerically.

§5. Results and discussion

In this section, we present the results obtained from the numerical solutions of Eqs. (4·3) and (4·4). Our primary interest is to understand how the particle wettability parameter γ affects the adsorption kinetics. In Fig. 3(a), we have plotted the time evolution of the particle volume fraction $\phi_0(t)$ at the interface as a function of the scaled time $\tilde{t} = Dt/a^2$ for various values of γ. The other parameters are chosen to be $\phi_{\rm b} = 10^{-2}$, $\alpha = 10$, and $\beta = 1$. For all the cases, $\phi_0(t)$ increases monotonically with time approaching to the respective equilibrium values $\phi_{0,\rm eq}$ (see Eq. (3·4)) which are indicated by the open circles on the right axis of Fig. 3(a). We see that $\phi_0(t)$ becomes larger when the value of γ is increased from -0.5 to 0. This tendency is reasonable because the particles have more affinity to liquid 2 when γ is made larger. In the intermediate time range, ϕ_0 increases almost as $t^{1/2}$ at least for larger γ, which is consistent with the Ward-Tordai equation. In Fig. 3(b), we have shown $\phi_{0,\rm eq} - \phi_0(t)$ as a function of $\tilde{t}$ in the large time region to see the asymptotic adsorption behavior. We see here a clear power-law dependence obeying $\sim t^{-1/2}$. The physical explanation of this behavior will be discussed soon after.

In order to estimate a typical time which is necessary for the particles to approach the equilibrium state, we determined the points which satisfy the condition

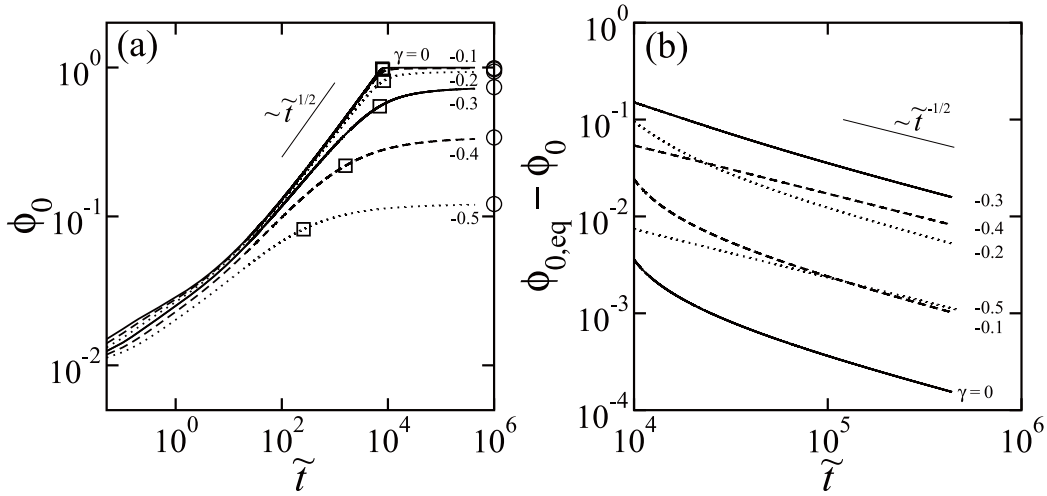

Fig. 3. (a) The time evolution of the surface coverage ϕ_0 as a function of the scaled time $\tilde{t} = Dt/a^2$ for different values of γ. The other parameters are $\phi_b = 10^{-2}$, $\alpha = 10$, and $\beta = 1$. The open circles on the right axis indicate the respective equilibrium values $\phi_{0,eq}$. The open squares are the points at which the condition $d^3(\log\phi_0)/d(\log\tilde{t})^3 = 0$ is satisfied. (b) The asymptotic behavior of $\phi_{0,eq} - \phi_0$ in the large time regions.

$d^3(\log\phi_0)/d(\log\tilde{t})^3 = 0$ for each curve in Fig. 3(a). These points are marked by open squares in the figure, and the corresponding characteristic time is denoted by $\tilde{\tau}_c$. Needless to say, this is not the only possibility to define the characteristic time, but other definitions would not alter the present result qualitatively. In Fig. 4, we summarized the obtained $\tilde{\tau}_c$ as a function of γ by open squares. The characteristic time $\tilde{\tau}_c$ increases as γ is made larger from -1, and it almost saturates when $\gamma \geq -0.3$ for the present choice of the parameters.

It was argued before that there can be two limiting cases describing the relative time scales of the two processes, namely, the kinetics inside the bulk solution described by Eq. (4·3) and the kinetics at the interface described by Eq. (4·4).[16),17)] The first case is the *diffusion-limited adsorption* (DLA) which occurs when the dynamics inside the solution is much slower than the one at the interface. Here the interface is in constant equilibrium with the adjacent solution. This means that, in a DLA, the interface is always at the minimum of $f_0(\phi_0)$ although the free energy curve changes with time. In this situation, the asymptotic time dependence of the surface coverage is predicted to be[25)]

$$\phi_{0,eq} - \phi_0(t) \sim \sqrt{\tau_d/t}. \tag{5·1}$$

Here the characteristic time scale of diffusion is determined by

$$\tau_d = \frac{a^2}{D}\left(\frac{\phi_{0,eq}}{\phi_b}\right)^2. \tag{5·2}$$

The second case is the *kinetically limited adsorption* (KLA) which applies when the dynamics at the interface is much slower. In a KLA, the shape of $f_0(\phi_0)$ does

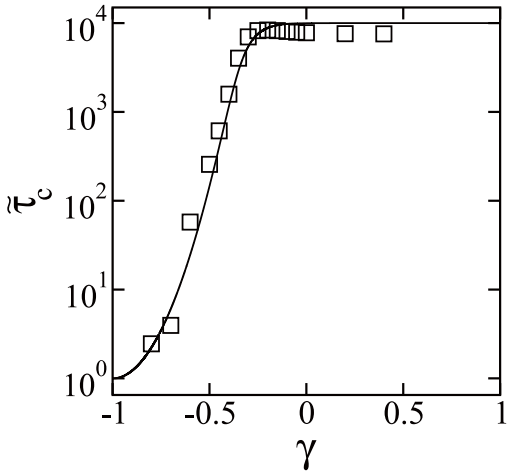

Fig. 4. The characteristic time $\tilde{\tau}_c$ obtained from Fig. 3(a). The solid line represents the scaled characteristic time of diffusion $\tilde{\tau}_d = (\phi_{0,eq}/\phi_b)^2$ as given by Eq. (5·2).

not change with time, but the surface coverage increases toward $\phi_{0,eq}$. Therefore ϕ_0 evolves with time according to Eq. (4·4), and its asymptotic behavior is given by[16),17)]

$$\phi_{0,eq} - \phi_0(t) \sim e^{-t/\tau_k}, \tag{5·3}$$

with a different characteristic time

$$\tau_k = \frac{a^2}{D}\left(\frac{\phi_{0,eq}}{\phi_b}\right)^2 \exp[-\alpha(1+\gamma)^2 - \beta\phi_{0,eq}]. \tag{5·4}$$

In general, KLA is realized when there is a potential barrier that might lead to kinetic limitations.

Comparing Eqs. (5·2) and (5·4), we find that $\tau_d > \tau_k$ holds when the lateral interaction is attractive ($\beta > 0$). Hence we expect that colloidal particles without any surface charge exhibit a DLA rather than a KLA. In Fig. 4, τ_d is represented by a solid line. We see that the characteristic time τ_c obtained from the numerical calculation (open squares) is well-described by the diffusive characteristic time τ_d. We have also checked that τ_k is much smaller than τ_d in the present parameter choice. In Fig. 3(b), we have shown that the asymptotic behavior of $\phi_{0,eq} - \phi_0$ obeys the $t^{-1/2}$ behavior as described by Eq. (5·1). All these results indicate that the adsorption of colloidal particles in Pickeirng emulsions is governed by a diffusion-limited process.

Since most of the experiments measure surface tension rather than surface coverage, we next look at the dynamical surface tension of an interface adsorbed by colloidal particles. We remind that the total excess free energy per unit area is given by Eq. (3·1). For simplicity, we neglect here the contribution from the bulk solution (the first term) which is considered to be relatively small. Hence we are left with only the second term, i.e., the contribution from the interface. In Fig. 5(a), we show the time evolution of $f_0(\phi_0)$ for various values of γ while the other parameters are the same with those in Fig. 2. One typically sees a slow decrease in the beginning

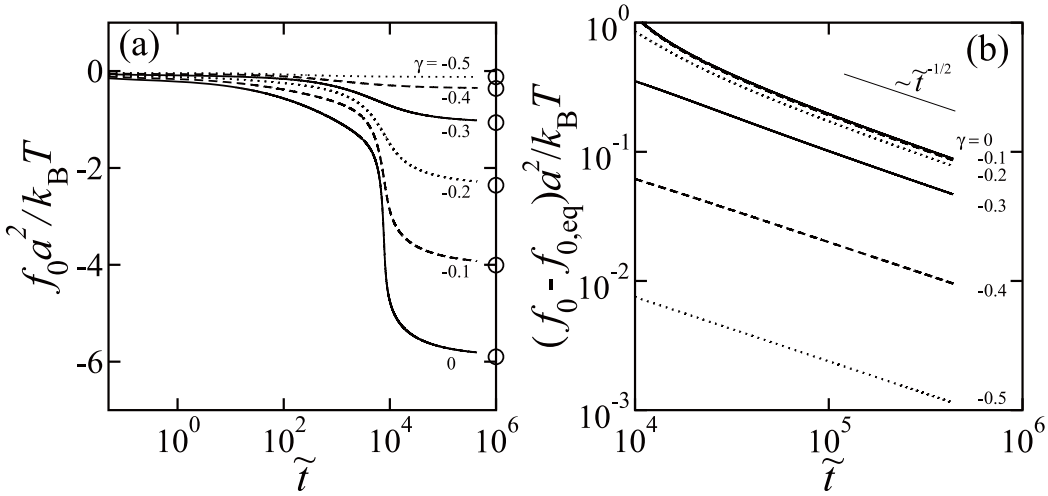

Fig. 5. (a) The time evolution of the surface energy f_0 as a function of the scaled time $\tilde{t}$ for different values of γ. The open circles on the right axis indicate the respective equilibrium values $f_{0,\mathrm{eq}}$. (b) The asymptotic behavior of $f_0 - f_{0,\mathrm{eq}}$ in the large time regions.

and a rapid drop followed by a slow relaxation toward the equilibrium. The decrease of the surface energy becomes larger as the value of γ is approached from negative to zero. Notice that the rapid drop of f_0 occurs around $t \approx \tau_\mathrm{c} \approx \tau_\mathrm{d}$. To investigate the long time asymptotic behavior, we present in Fig. 5(b) the difference $f_0(\phi_0) - f_{0,\mathrm{eq}}$ for large t. This plot implies that the dynamic surface tension also decreases as $t^{-1/2}$ similar to the behavior of $\phi_0(t)$ in Fig. 3(b). Such a power-law dependence is characteristic for DLA and should be contrasted with an exponential decay expected for KLA.

In the case of DLA, we mentioned that $f_0(\phi_0)$ is all the time at its minimum so that $\mu_0 = \mu_1$ holds even if the free energy is dependent on time ($\mu_1 \neq \mu_\mathrm{b}$). When this is true, the surface energy can be further written as

$$f_0[\phi_0(t)] = \frac{k_\mathrm{B}T}{a^2}\left[\ln[1-\phi_0(t)] + \frac{\beta}{2}[\phi_0(t)]^2\right], \tag{5·5}$$

so that f_0 is now a functional of $\phi_0(t)$. This relation means that the equilibrium equation of state as previously given by Eq. (3·5) also holds for nonequilibrium situations.[17] In order to check the validity of this argument, we have plotted in Fig. 6 both Eqs. (3·3) and (5·5) by the solid and dashed lines, respectively. We present here only the case of $\gamma = 0$ and the other parameters are the same as those in Fig. 3. We can see that the two curves coincide almost perfectly for $t \geq \tau_\mathrm{d}$. Hence the extension of the equation of state to the nonequilibrium cases can be justified for DLA in the long time limit.

In Refs. 16) and 17), it was pointed out that the adsorption of nonionic surfactants is described by a DLA. This fact has been experimentally confirmed for various types of nonionic surfactant which exhibit the asymptotic $t^{-1/2}$ decrease of the dynamical surface tension. For salt-free ionic surfactants, however, the adsorption is

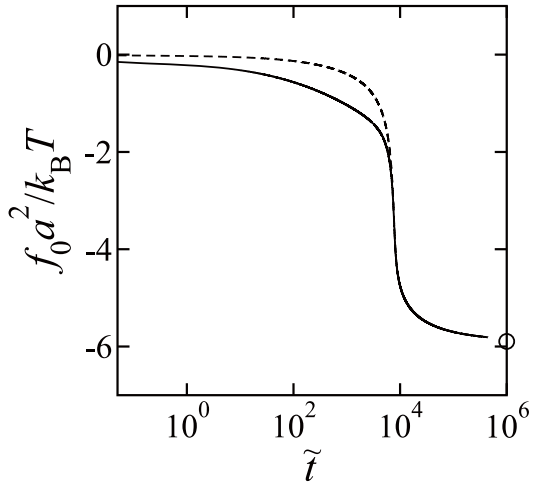

Fig. 6. The solid line is the time evolution of the surface energy f_0 as a function of the scaled time $\tilde{t}$ for $\gamma = 0$ (as presented in Fig. 5). The dashed line is the time evolution of Eq. (5·5). Both curves coincide in the large time region.

described by a KLA due to the electrostatic interaction. Interestingly, addition of salt to an ionic surfactant solution recovers a DLA. For colloidal particles, it is natural to expect that the adsorption deviates from a DLA when the particles are charged.

Recently, the adsorption dynamics of cadmium selenide nanoparticles at an oil/water interface has been investigated.[15] Using a pendant drop tensiometer, they measured changes in the interfacial tension for the early and late stages. The observed time dependence of the interfacial tension is very similar to that in Fig. 5(a), and its asymptotic long time behavior is indeed described by the $t^{-1/2}$ dependence as in Eq. (5·1). Hence the experimental result can be described as a DLA.

Finally we shall briefly argue the case when the interaction parameter satisfies $\beta > 4$ so that the phase transition occurs at the interface. In Fig. 7(a) and (b), we present the time evolutions of ϕ_0 and f_0, respectively, for different values of β. Other parameters are $\phi_b = 10^{-2}$, $\alpha = 10$, and $\gamma = -0.5$. When $\beta > 4$, we observe a steep increase of ϕ_0 in the late stages. Corresponding to this behavior, the surface energy f_0 increases transiently and then drops off toward equilibrium value as shown in Fig. 7(b). Such a unique time dependence of the surface energy is expected to be observed in the experiment.

§6. Conclusion

In this paper, we have discussed the adsorption dynamics of colloidal particles to liquid/liquid interfaces. We used a free energy formulation for the adsorption which has been applied to surfactants. By solving the coupled equations including the Ward-Tordai equation, we obtained the time evolution of the surface coverage and dynamic surface tension. From the estimation of the characteristic time, we showed that the adsorption process is a diffusion-limited one. In this situation, the

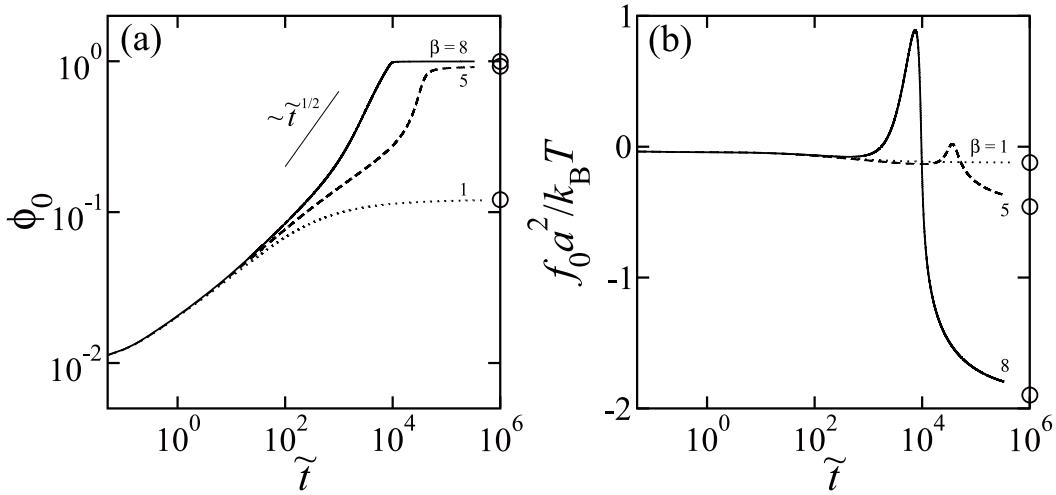

Fig. 7. (a) The time evolution of the surface coverage ϕ_0 as a function of $\tilde{t}$ for different values of β. The other parameters are $\phi_b = 10^{-2}$, $\alpha = 10$, and $\gamma = -0.5$. (b) The corresponding time evolution of the surface energy f_0 as a function of $\tilde{t}$.

asymptotic time dependencies of the surface coverage and surface tension close to their equilibrium values obey the $t^{-1/2}$ law. Our result is in agreement with a recent experiment using nanoparticles. We also showed that the equilibrium equation of state relating the surface tension to the surface coverage also holds for nonequilibrium situations.

Several extensions of the present work are under progress. For example, we are investigating the adsorption of two different types of colloidal particles characterized by different values of γ. One might also consider the case in which the adsorption occurs from both liquids. In this case, we allow the particles to leave the interface toward the other liquid.

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