

Surface activity of solid particles with extremely rough surfaces

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Abstract

The solid particles are adsorbed at liquid–liquid interfaces and form self-assembled structures when the particles have suitable wettability to both liquids. Here, we show theoretically how the extreme roughness on the particle surface affects their adsorption properties. In our previous work, we discussed the adsorption behavior of the solid particles with microstructured surfaces using the so-called Wenzel model [Y. Nonomura et al., *J. Phys. Chem. B* 110 (2006) 13124]. In the present study, the wettability and the adsorbed position of the particles with extremely rough surfaces are studied based on the Cassie–Baxter model. We predict that the adsorbed position and the interfacial energy depend on the interfacial tensions between the solid and liquid phases, the radius of the particle, and the fraction of the particle surface area that is in contact with the external liquid phase. Interestingly, the initial state of the system governs whether the particle is adsorbed at the interface or not. The shape of the particle is also an important factor which governs the adsorbed position. The disk-shaped particle and the spherical particle which is partially covered with the extremely rough surface, i.e. Janus particle, are adsorbed at the liquid–liquid interface in an oriented state. We should consider not only the interfacial tensions, but also the surface structure and the particle shape to control the adsorption behavior of the particle.

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1. Introduction

Interfaces adsorbing solid particles have recently attracted great attentions in the field of materials science [1,2]. The solid particles are adsorbed at the interfaces and form self-assembled structures, i.e. emulsions, ball-like aggregates and foams, when the particles have suitable wettability to both liquids [3–5]. In recent years, some scientists have used the emulsions as a template of functional composite materials [6–8]. The mechanism for the adsorption of the surface-active particle has been discussed based on the interfacial energy argument [9]. The particle is adsorbed at the interface when the interfacial tensions among the three phases are balanced according to the Young's equation. The effects of the particle shape and the curvature of the liquid–liquid interface on the adsorption were also described elsewhere [10–12].

The interfacial properties of particles with a rough surface are interesting, because complicated rough structures existing on the solid surfaces change their wettability drastically [13]. For example, Tsujii et al. showed that fractal surfaces are super water-repellent [14,15]. It is then natural to expect that the roughness might affect the behavior of surface-active particles.

Here, we show theoretically how the extreme roughness on the particle surface affects their adsorption properties. The extreme roughness changes drastically the wettability and the adsorbed position of the particle. In the present work, we consider the interfacial energy of the liquid–liquid interface adsorbing spherical particles with an extremely rough surface as illustrated in Fig. 1a. In many cases, wettability of the rough surface has been discussed using the so-called Wenzel model [16–18]. In this model, the interfacial energy is considered to be proportional to the effective surface area. However, the Wenzel model is not appropriate for extremely rough surfaces and the Cassie–Baxter model is more suitable, because the liquid in holes on the particle surfaces is not replaced by another liquid [19]. We assume that the holes on the surface are filled by the liquid and

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the rough surface consists of two parts, i.e., the particle surface and the liquid in the holes. We predict the adsorbed position and the energy of the interface based on the Cassie–Baxter model. In addition, we discuss the effect of the asymmetry of the particle shape on the surface activity. The disk-shaped particles are widely used in various industrial fields, while the Janus particles which are partially covered with the extremely rough surface are expected as building blocks for supraparticular assemblies and dual-functionalized devices [20]. In general, the disk shape of the particle and the partial modification of the particle surface cause the particle to be adsorbed with a fixed orientation at the liquid–liquid interface [10,11]. The interfacial energy of the liquid–liquid interface adsorbing the disk-shaped particle, and the Janus particle is derived in the present study. We demonstrate here that the asymmetry of the particle surface is one of the most effective factors to control the adsorbed state of the particle.

This paper is organized as follows. We first discuss the effect of the surface roughness on the surface activity. We calculated

the interfacial energy of the liquid–liquid interface adsorbing the spherical particle with extremely rough surfaces. The effect of the asymmetry of the particle on the adsorbing behavior is considered in the next section. The interfacial energy of the interface adsorbing the disk-shaped particle and the Janus particle is calculated. In the discussion, we predict the requirements for the adsorption of the particle with extremely rough surface.

2. Results

2.1. The adsorption energy of a solid particle with extremely rough surface

We now discuss the adsorption of a spherical particle P at an interface between liquids A and B as shown in Fig. 1a Scheme 1. We assume that there are many tube-like holes on the particle surface. The particle P which has higher affinity with the liquid A than the liquid B is adsorbed at the interface between the liquids A and B. When the particle is adsorbed to

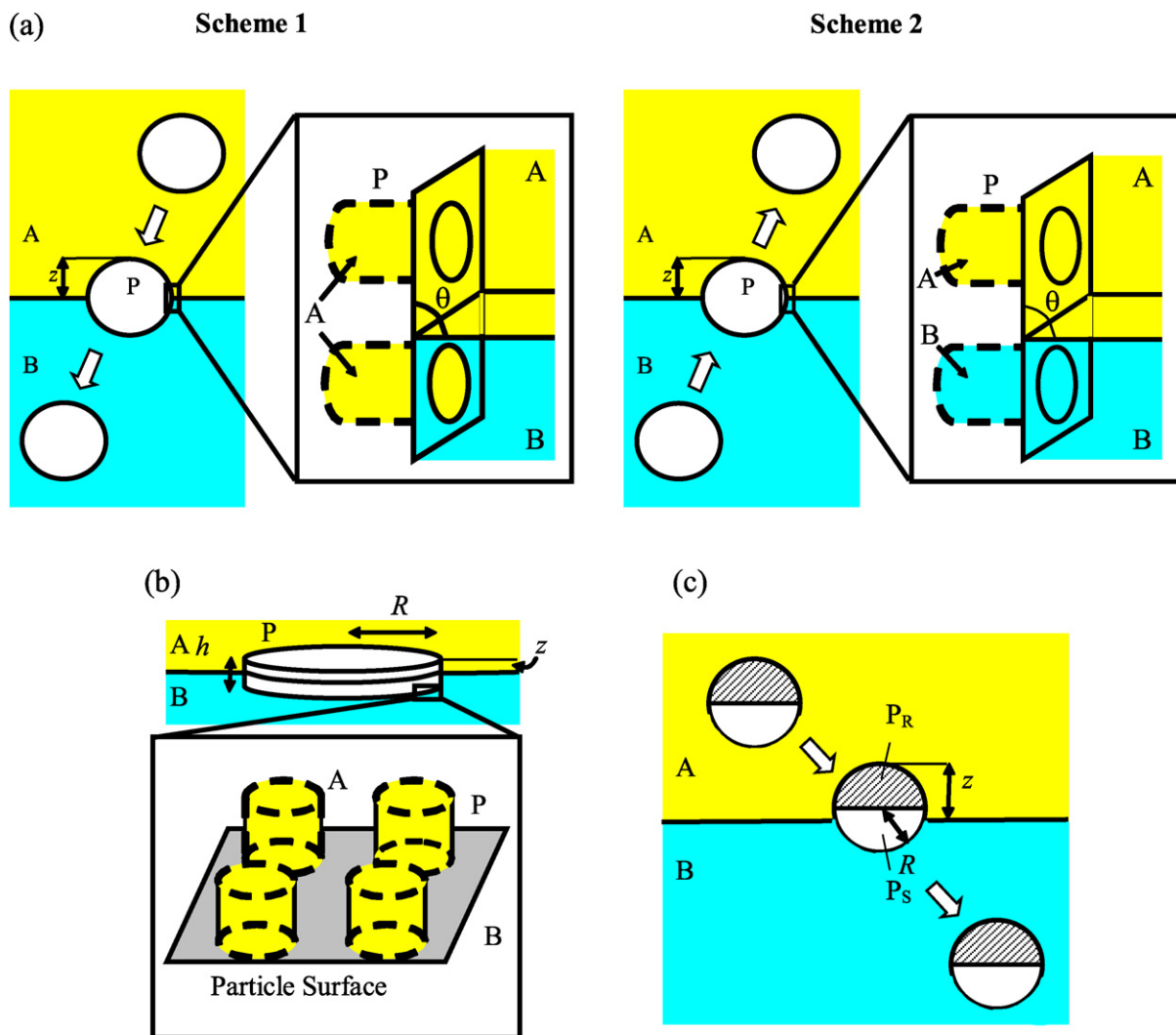


Fig. 1. The schematic illustrations of the interface adsorbing (a) a spherical particle, (b) a disk-shaped particle, and (c) a partially rough particle. The particles P are adsorbed at the interfaces between liquids A and B. In the illustrations, R is the radius of the spherical particle and the disk-shaped particle. The length h is the thickness of the disk-shaped particle, whereas z is the immersion depth of the particle. The angle θ is the contact angle at the three phase contact line.

the A/B interface from the liquid A side, the liquid A is not replaced by the liquid B, and it remains in the holes. Let F be the interfacial energy per particle when it is adsorbed at the interface between liquids A and B. Now, we consider the case when the particle is originally immersed in the liquid A. The interfacial energy F is defined as

$$F = F_1 + F_2 + F_3 + F_4. \quad (1)$$

Here, F_1 is the energy when the whole particle is immersed in the liquid A and is given by $F_1 = 4\pi r R^2 \gamma_{AP}$. In this equation, R is the radius of the particle and γ_{ij} is the interfacial tension between the phases i and j . The surface area of the spherical particle is r times larger than that of the spherical particle having a smooth surface. The energies F_2 , F_3 , and F_4 are energy changes with the contact of the particle surface with the liquid B, the elimination of the interface between the liquids A and B, and the formation of the interface between the liquids A and B at the holes, respectively. In this case, the energies F_2 , F_3 , and F_4 are given by $F_2 = -2\pi\phi R(2R - z)(\gamma_{AP} - \gamma_{BP})$, $F_3 = -\pi(2Rz - z^2)\gamma_{AB}$, $F_4 = 2\pi(1 - \phi)R(2R - z)\gamma_{AB}$. Here, the quantity z is the depth of immersion into the liquid A, and ϕ is the fraction of the particle surface area that is in contact with the external liquid phase. The interfacial energy for the interface adsorbing the spherical particle is given by

$$F = F_1 + 4\pi R^2 \gamma_{AB} \{1 - \phi(1 + \Sigma)\} - 2\pi R \gamma_{AB} \{2 - \phi(1 + \Sigma)\}z + \pi \gamma_{AB} z^2 \quad (2)$$

with $\Sigma = (\gamma_{AP} - \gamma_{BP})/\gamma_{AB}$. In this equation, the second and the third terms are multiplied by ϕ , not by r . This result shows that ϕ affects the energy change due to the particle adsorption. On the other hand, the surface magnification r does not affect the energy change, because the increase of the surface corresponds to the side surface of the tube-like holes which are covered with the liquid A. We plot the dimensionless quantity $F/(\pi R^2 \gamma_{AB})$ against z/R when $\gamma_{AP}/\gamma_{AB} = 0.4$, $\gamma_{BP}/\gamma_{AB} = 0.5$, $r = 30$, and $\phi = 0.3$ in Fig. 2a. The above energy F attains a minimum

at z_{\min} :

$$z_{\min} = \{2 - \phi(1 + \Sigma)\}R. \quad (3)$$

The corresponding minimized energy F_{\min} is given by

$$F_{\min} = F_1 - \pi\phi^2 R^2 \gamma_{AB} (1 + \Sigma)^2, \quad (4)$$

where the first term is the energy when the particle is immersed in the liquid A, and the second term is the energy change due to the adsorption of a particle at the liquid–liquid interface. Here, we define the energy gap between F_{\min} and the energy when the particle is immersed in the liquid B [A] as ΔF_1 [ΔF_2]. For a spherical particle, they are given by $\Delta F_1 = 4\pi R^2 \gamma_{AB} (1 - \phi - \phi\Sigma) + \pi\phi^2 R^2 \gamma_{AB} (1 + \Sigma)^2$ and $\Delta F_2 = \pi\phi^2 R^2 \gamma_{AB} (1 + \Sigma)^2$. The quantities ΔF_1 , ΔF_2 , and z_{\min} are plotted against $1 - \phi$ in Fig. 2b. Note that ΔF_1 and ΔF_2 are proportional to ϕ^2 , whereas z_{\min} is linear in ϕ . The particle is adsorbed at the liquid–liquid interface when $\Delta F_1, \Delta F_2 > 0$.

Next, we consider the case when the particle is originally immersed in the liquid B. The schematic illustration is shown in Fig. 1a Scheme 2. When the particle has a higher affinity with the liquid A than with the liquid B, the liquid B in the holes is replaced by the liquid A. In this case, the adsorbed state can be described by the Wenzel model [16,17]. Then, F is given by

$$F = 4\pi r R^2 \gamma_{BP} - 2\pi R \gamma_{AB} (1 - r\Sigma)z + \pi \gamma_{AB} z^2. \quad (5)$$

We plot $F/(\pi R^2 \gamma_{AB})$ against z when $\gamma_{AP}/\gamma_{AB} = 0.4$, $\gamma_{BP}/\gamma_{AB} = 0.5$, and $r = 30$ in Fig. 2a. The energy F decreases with increasing z , and the minimum does not exist. This means that the particle is not adsorbed at the interface and is dispersed in the liquid A.

2.2. The effect of asymmetry of the particle with extremely rough surface

We discuss the adsorption of the disk-shaped particle at the liquid–liquid interface as shown in Fig. 1b. The interfacial energy F is given by $F_1 = 2\pi r R(R + h)\gamma_{AP}$ when the whole particle is immersed in the liquid A. Here, R and h are the radius

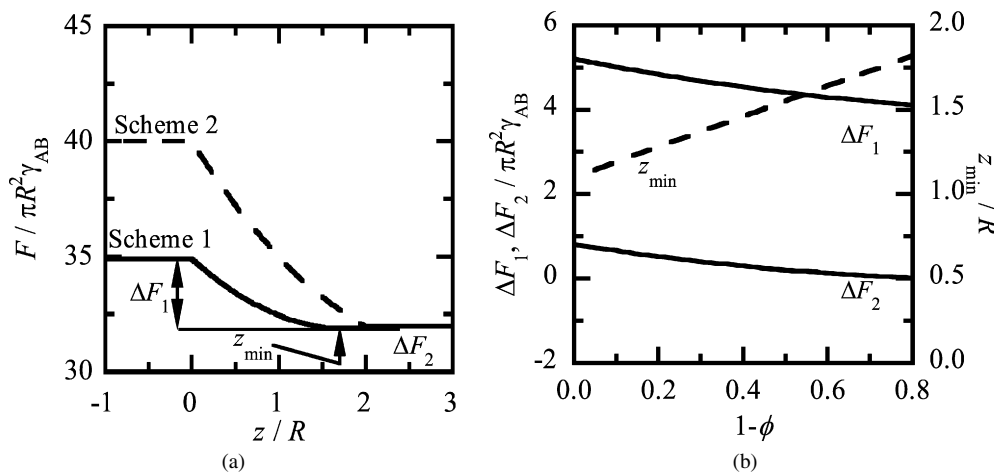


Fig. 2. Adsorbed state of the spherical particle P. (a) The dimensionless adsorption energy $F/(\pi R^2 \gamma_{AB})$ against immersion depth z/R for the particle P at constant radius R of the particle and the interfacial tensions γ_{ij} . The parameters are as follows, $\gamma_{AP}/\gamma_{AB} = 0.4$, $\gamma_{BP}/\gamma_{AB} = 0.5$, $r = 30$, and $\phi = 0.3$. (b) The energy gaps ΔF_1 and ΔF_2 and the adsorbed position of the particle z_{\min} against the ratio of the particle surface area ϕ when the particle is adsorbed at the A/B interface from the liquid A side. The parameters are as follows, $\gamma_{AP}/\gamma_{AB} = 0.4$, $\gamma_{BP}/\gamma_{AB} = 0.5$.

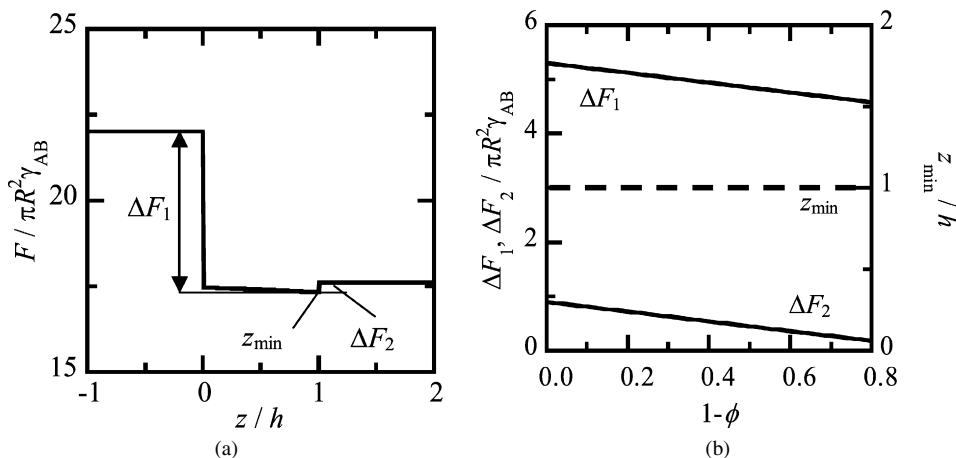


Fig. 3. Adsorbed state of the disk-shaped particle P. (a) The dimensionless adsorption energy $F/(\pi R^2 \gamma_{AB})$ against immersion depth z/h at constant radius R and height h of the particle and the interfacial tensions γ_{ij} . The parameters are as follows, $\gamma_{AP}/\gamma_{AB} = 0.4$, $\gamma_{BP}/\gamma_{AB} = 0.5$, $r = 20$, $h/R = 0.1$, and $\phi = 0.3$. (b) The energy gaps ΔF_1 and ΔF_2 and the adsorbed position of the particle z_{\min} against the ratio of the particle surface area ϕ when the particle is adsorbed at the A/B interface from the liquid A side. The parameters are as follows, $\gamma_{AP}/\gamma_{AB} = 0.4$, $\gamma_{BP}/\gamma_{AB} = 0.5$, and $h/R = 0.1$.

and the thickness of the particle, respectively. When the particle is in contact with the liquid–liquid interface, the energy changes F_2 , F_3 , and F_4 are given by $F_2 = -\pi\phi R(R + 2h - 2z)(\gamma_{AP} - \gamma_{BP})$, $F_3 = -\pi R^2 \gamma_{AB}$ and $F_4 = \pi(1 - \phi)R(R + 2h - 2z)\gamma_{AB}$. The interfacial energy for the interface adsorbing the disk-shaped particle is given by

$$F = F_1 + 2\pi R h \gamma_{AB} - \pi\phi R(R + 2h)\gamma_{AB}(\Sigma + 1) + 2\pi R \gamma_{AB}(\phi\Sigma + \phi - 1)z. \quad (6)$$

This interfacial energy changes with z as shown in Fig. 3a. We note that the energy changes discontinuously at $z = 0$, that is, when the plane surface of the particle contacts with the liquid–liquid interface. The energy changes linearly with z as a result of the contact of the side surface of the particle with the liquid B and attains the minimum at $z = h$. The corresponding minimized energy is given by

$$F_{\min} = F_1 - \pi\phi R^2 \gamma_{AB}(\Sigma + 1). \quad (7)$$

For the disk-shaped particle, the energy changes ΔF_1 and ΔF_2 are given by $\Delta F_1 = \pi\phi R^2 \gamma_{AB}(\Sigma + 1) - 2\pi R(R + h)\gamma_{AB}\Sigma$ and $\Delta F_2 = \pi\phi R^2 \gamma_{AB}(\Sigma + 1)$, respectively. They are proportional to ϕ , whereas z_{\min} does not depend on ϕ , because the interfacial energy is minimized when the plane surface is in contact with the liquid–liquid interface irrespective of the surface roughness.

We now discuss the adsorption of a Janus particle at an interface between liquids A and B as shown in Fig. 1c. The hemisphere of the particle P_R is covered with many tube-like holes, while the other hemisphere P_S is covered with a smooth one. The surface area of the P_R region is r times larger than that of the smooth one, and the particle is more wettable to the liquid A than to the liquid B. Here, we assume that the liquid A is not replaced with the liquid B, and it remains in the holes when the particle is adsorbed to the A/B interface from the liquid A side. The interfacial energy per particle F is given by $F_1 = 2\pi(r + 1)R^2 \gamma_{AP}$ when the whole particle is immersed in the liquid A. When the particle approaches to the interface from

the P_S side, F is given as follows:

$$F = F_1 - 4\pi R^2 \gamma_{AB} \Sigma - 2\pi R \gamma_{AB}(1 - \Sigma)z + \pi \gamma_{AB} z^2, \quad R \leq z \leq 2R, \quad (8)$$

$$F = F_1 + 2\pi R^2 \gamma_{AB} \{1 - \phi - (1 + \phi)\Sigma\} - 2\pi R \gamma_{AB}(2 - \phi - \phi\Sigma)z + \pi \gamma_{AB} z^2, \quad 0 < z < R. \quad (9)$$

In the Eq. (8), ϕ and r do not affect the second and third terms. On the other hand, these terms are multiplied by ϕ in Eq. (9). We plot the dimensionless quantity $F/(\pi R^2 \gamma_{AB})$ against z/R when $\gamma_{AP}/\gamma_{AB} = 0.4$, $\gamma_{BP}/\gamma_{AB} = 0.5$, $r = 20$, and $\phi = 0.3$ in Fig. 4a. The above energy F attains a minimum at $z_{\min} = (1 - \Sigma)R$ and the corresponding energy is given as follows:

$$F_{\min} = F_1 - \pi R^2 \gamma_{AB}(1 + \Sigma)^2, \quad (10)$$

where the first term is the energy when the particle is immersed in the liquid A, and the second term is the energy change due to the adsorption of the particle at the liquid–liquid interface. Here, z_{\min} and F_{\min} are determined only by γ_{ij} and R . This result shows that the degree of the surface roughness does not affect the adsorbed state, because P_R region does not contact to liquid B in the energy minimized state.

We consider the case when the particle approaches to the interface from the P_R side. The energy F is given as follows:

$$F = F_1 + 4\pi R^2 \gamma_{AB}(1 - \phi - \phi\Sigma) - 2\pi R \gamma_{AB}(2 - \phi - \phi\Sigma)z + \pi \gamma_{AB} z^2, \quad R \leq z \leq 2R, \quad (11)$$

$$F = F_1 + 2\pi R^2 \gamma_{AB} \{1 - \phi - (1 + \phi)\Sigma\} - 2\pi R \gamma_{AB}(1 - \Sigma)z + \pi \gamma_{AB} z^2, \quad 0 < z < R. \quad (12)$$

We plot the dimensionless quantity $F/(\pi R^2 \gamma_{AB})$ against z/R when $\gamma_{AP}/\gamma_{AB} = 0.4$, $\gamma_{BP}/\gamma_{AB} = 0.5$, $r = 20$, and $\phi = 0.3$ in Fig. 4b. The energy F attains a minimum at $z_{\min} = (2 - \phi - \phi\Sigma)R$ and the corresponding energy is given as follows:

$$F_{\min} = F_1 - \pi R^2 \phi^2 \gamma_{AB}(1 + \Sigma)^2. \quad (13)$$

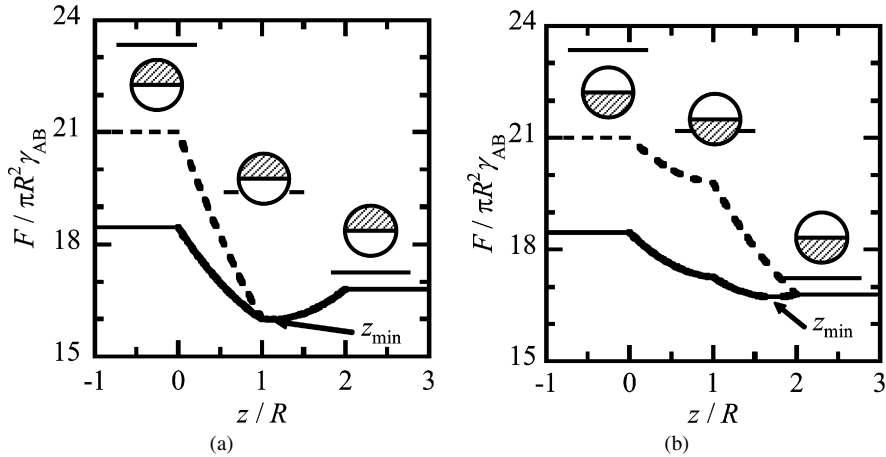


Fig. 4. The dimensionless adsorption energy $F/(\pi R^2 \gamma_{AB})$ against immersion depth z/R at constant radius R of the particle and the interfacial tensions γ_{ij} for the Janus particle. We show when the particle approaches to the A/B interface from P_S side (a) or P_R side (b). In these figures, the parameters are as follows, $\gamma_{AP}/\gamma_{AB} = 0.4$, $\gamma_{BP}/\gamma_{AB} = 0.5$, $r = 20$, and $\phi = 0.3$. The adsorption energies are derived based on Cassie–Baxter model when the particle is adsorbed at the A/B interface from the liquid A side (—), while they are derived based on the Wenzel model when the particle is adsorbed from the liquid B side (---).

Here, the second term contains ϕ and represents the energy change due to the particle adsorption.

Next, we consider the case when the particle is originally immersed in the liquid B. In this case, the adsorbed state can be described by the Wenzel model, because the liquid B in the holes is replaced by the liquid A [16,17]. When the particle approaches to the interface from the P_R side, F is given as follows:

$$F = F_1 - 4\pi R^2 \gamma_{AB} \Sigma - 2\pi R \gamma_{AB} (1 - \Sigma) z + \pi \gamma_{AB} z^2, \quad R \leq z \leq 2R, \quad (14)$$

$$F = F_1 - 2\pi R \gamma_{AB} (1 - r \Sigma) z + \pi \gamma_{AB} z^2, \quad 0 < z < R. \quad (15)$$

We plot $F/(\pi R^2 \gamma_{AB})$ against z when $\gamma_{AP}/\gamma_{AB} = 0.4$, $\gamma_{BP}/\gamma_{AB} = 0.5$, and $r = 30$ in Fig. 4a. The energy F attains a minimum at $z_{\min} = (1 - \Sigma)R$. The adsorbed position and the minimized interfacial energy agree with them when the whole particle is immersed in the liquid A at the initial state, because the P_R region is not in contact with the liquid A in these conditions.

When the particle approaches to the interface from the P_S side, F is given as follows:

$$F = F_1 - 4\pi r R^2 \gamma_{AB} \Sigma - 2\pi R \gamma_{AB} (1 - r \Sigma) z + \pi \gamma_{AB} z^2, \quad R \leq z \leq 2R, \quad (16)$$

$$F = F_1 - 2\pi R \gamma_{AB} (1 - r \Sigma) z + \pi \gamma_{AB} z^2, \quad 0 < z < R. \quad (17)$$

We plot $F/(\pi R^2 \gamma_{AB})$ against z when $\gamma_{AP}/\gamma_{AB} = 0.4$, $\gamma_{BP}/\gamma_{AB} = 0.5$, and $r = 30$ in Fig. 4b. The energy F decreases with increasing z , and the minimum does not exist. This means that the particle is not adsorbed at the interface and is dispersed in the liquid A.

3. Discussion

The adsorbed position of a particle and the adsorption energy are determined not only by the interfacial tension, but also the surface roughness. Equations (3) and (4) show that the adsorbed position z_{\min} shifts to the liquid A side, while the

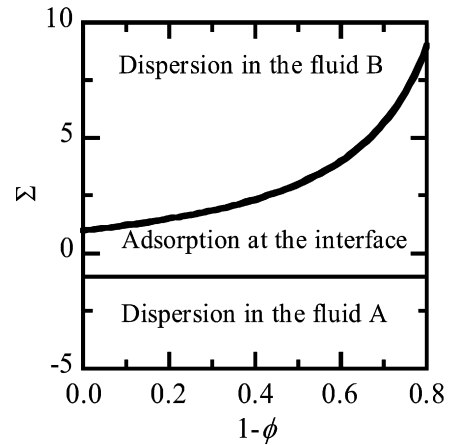


Fig. 5. The state diagram of the particle against the interfacial tensions γ_{ij} and the ratio of the particle surface area ϕ when the particle is adsorbed at the A/B interface from the liquid A side.

energy gaps ΔF_1 and ΔF_2 decrease when ϕ become smaller (Fig. 2b). These results indicate that the particle with a rough surface is more weakly held at the interface than that with a smooth surface. The wettability and the surface roughness of the particle determine whether it exhibits the surface activity or not. The spherical particle is adsorbed at the interface when $0 < z_{\min} < 2R$. The required condition to be adsorbed at the interface is derived from Eq. (4) and shown as equation:

$$-1 < \Sigma < 2/\phi - 1. \quad (18)$$

The above condition is drawn in Fig. 5. The particle is adsorbed at the liquid–liquid interface when the values ϕ and γ_{ij} satisfy the above condition. The particles are dispersed in the liquid A [B] if Σ is smaller than -1 (larger than $2/\phi - 1$). The allowed range of the interfacial tension extends with the increase of $1 - \phi$. For example, it is $-1 < \Sigma < 1$ when $1 - \phi = 0$, whereas it is $-1 < \Sigma < 5.666$ when $1 - \phi = 0.7$. Hence, we should consider not only the wettability, but also the surface structure in order to control the adsorption behavior of the particles with rough surfaces.

A contact angle hysteresis is expected for the surface-active particle. Here we consider how the contact angle θ varies as the particle is moved from the liquid A to the liquid B through the liquid–liquid interface. The contact angle is constant $\cos\theta = -\Sigma$ when the three phase contact line is on the normal particle surface. On the other hand, discontinuous change is expected at the edges of the holes. At these special positions, the contact angle can be an arbitrary value in the range of $\arccos(-\Sigma) < \theta < \arccos(-\Sigma) + \pi/2$, and it changes discontinuously due to the pinning effect at the edge. This unique behavior is characteristic of the particles with extremely rough surfaces and is not expected for the particle with smooth or microstructured surfaces.

We have shown that the adsorbed state of a particle with an extremely rough surface depends on the initial state of the system. The adsorbed position of the particle depends on whether the particle was in the liquid A or B in the initial state. This means that the system can be in a kinetically stable state, but not in a thermodynamically stable state. In the case of Fig. 2, the particle is dispersed in the liquid A if it was originally in the liquid B, although the interfacial energy is the lowest when the particle is adsorbed at the liquid–liquid interface. This is also important in the preparation of emulsions stabilized by the particles with rough surfaces. In the preparation of emulsions, we should be careful with the choice of the liquid to which we add the particles, because the mixed state can be different depending on the initial state.

The oriented adsorption is one of characteristic behaviors of Janus-particles. The second term of Eq. (13) is multiplied by the square of ϕ . Therefore, the energy F_{\min} is always larger than that obtained by Eq. (10). This indicates that the P_S region is oriented to the liquid B side at the liquid–liquid interface. The energy profile based on the Wenzel model is also shown in Fig. 4a. The adsorbed position and the corresponding energy coincide with those derived from the Wenzel model. When $R < z < 2R$, the profile overlaps with that of Cassie–Baxter model and F attains a minimum at $z_{\min} = (1 - \Sigma)R$.

The present theory is valid only when the particle has an extremely rough surface. The assumption that the rough surface consists of two parts does not work when the roughness is below a critical value r_c [19]. When $r < r_c$, the wettability of the particle can be described by the Wenzel model as in our previous study [16,17]. We obtain the critical value for the spherical particle r_c from the energy derived from Eq. (6) and the energy derived from the Wenzel model [16,17]. This examination shows $r_c = \phi - (\phi - 1)/\Sigma$ which is close to $1/\Sigma$ [21,22]. For example, $r_c = 10$ when $\gamma_{AP} = 16 \text{ mN m}^{-1}$, $\gamma_{BP} = 20 \text{ mN m}^{-1}$, and $\gamma_{AB} = 40 \text{ mN m}^{-1}$.

4. Conclusions

In the present study, we examined the energy of the interface adsorbing the particle with extremely rough surfaces based

on the Cassie–Baxter model. The results predict that the adsorbed state at the liquid–liquid interface depends on the roughness of the particle surface. The shape of the particle is also an important factor which governs the adsorbed position. The disk-shaped particle and the Janus particle are adsorbed at the liquid–liquid interface in an oriented state.

The present theory is suitable to explain the behavior of the particles in nano or micro meter scale, and is not suitable for the particles whose size is above 100 μm . Because the effect of gravity on the shape of the liquid–liquid interface is neglected in this work. It has been difficult to check the validity of the present theory by experimental works. However, we can inscribe the structure on the particle surface [23]. Further experimental and theoretical studies are necessary to understand the behavior of the surface-active particles.

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