

Adsorption of Janus particles to curved interfaces

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We investigate the adsorption of a spherical Janus particle to a spherically curved liquid-liquid interface. We show that the equilibrium contact angle is determined by the geometry of the particle, its wettability, and also the interfacial curvature. In contrast with a homogeneous particle, there is a preferred interfacial curvature (spontaneous curvature) due to the Janus particle when the particle satisfies certain conditions. © 2007 American Institute of Physics. [DOI: 10.1063/1.2756828]

Particles which have two distinct parts are called “Janus particles” in the name of the dual-faced Janus god.^{1,2} By providing two different chemical and/or physical properties to a single particle, one can produce various kinds of Janus particles which are useful in many modern technologies.^{3–6} For example, design and synthesis of bicompartamental particles, dumbbell-like particles, acornlike particles, or snowmanlike particles are reviewed in Ref. 7. In addition to use them as elementary building blocks for supraparticular assemblies, Janus particles can be very useful in various applications. For example, they can be used for the stabilization of water-in-oil or oil-in-water emulsions similar to surfactants.⁸ When bichromal Janus particles were made to have charge segregation on the surface, they could be useful for electronic displays such as the electric reusable paper. Other applications of Janus particles are catalysis, sensing, drug delivery, etc.

Here we focus on the Janus particles which are analogous to surfactant molecules having both hydrophilic and hydrophobic parts. Such amphiphilic particles were obtained by Casagrande *et al.*¹ and Ondaçuhu *et al.*² from glass spherical particles. They studied the adsorption at oil/water interfaces, and showed that the Janus particles behave differently from ordinary solid particles. In contrast with a dense film made of conventional molecular surfactants, a film of Janus particles at the interface has some interstices between the particles so that it can “breathe.”⁹ Moreover, it was theoretically shown that Janus particles are more surface active compared to homogeneous surface particles.¹⁰

Not only Janus particles but also homogeneous surface particles can stabilize emulsions. Such emulsions are called Pickering emulsions.^{11–13} In our previous paper, we investigated the adsorption of such homogeneous spherical particles to a liquid-liquid interface.¹⁴ In particular, we looked at the effect of the curvature of the interface on the particle adsorption. We showed that although the equilibrium contact angle is determined by the classical Young’s equation (being independent of the curvature), the adsorption energy is affected

by the interfacial curvature. The partitioning of the particles among the two liquids and the interface was also discussed.

In the present paper, a similar analysis is performed for Janus particles. We first discuss their equilibrium position at a liquid-liquid interface, and examine the effect of the interfacial curvature. Due to the inhomogeneous nature of the Janus particles, they exhibit completely different adsorption behavior compared to the homogeneous particles. Especially, we show that there is a preferred curvature (spontaneous curvature) in the presence of a Janus particle when certain conditions are satisfied. It is known that the spontaneous curvature of a molecular surfactant plays an essential role in emulsifying two immiscible liquids.¹⁵ This property is in sharp contrast compared with the homogeneous particles for which the spontaneous curvature does not exist.¹⁴

We first consider the equilibrium position of a Janus particle at an interface between two immiscible liquids. As shown in Fig. 1(a), the isolated particle is assumed to be perfectly spherical and its radius is denoted by a . The particle surface has two chemically distinct regions, say, “A” and “B” corresponding to hydrophilic and hydrophobic regions, respectively. The borderline between these two regions is parametrized by an angle α , as defined in Fig. 1(a). Then the areas of each region are given by

$$S_A = 2\pi a^2(1 + \cos \alpha) \quad (1)$$

and

$$S_B = 2\pi a^2(1 - \cos \alpha), \quad (2)$$

for A and B, respectively. Extreme cases are $\alpha=0$ for which the particle is homogeneously coated with region A, or $\alpha=\pi$ when region B covers the whole surface.

Next we discuss the adsorption of such a Janus particle to a spherically curved interface between liquids 1 and 2 which correspond to, for example, water and oil, respectively [see Fig. 1(b)]. Here liquid 2 forms a spherical droplet. We assume that the line connecting the centers of the droplet and the particle is perpendicular to the borderline of the particle, and the three phase contact line is perfectly regular without any distortion. We define θ as the contact angle (measured

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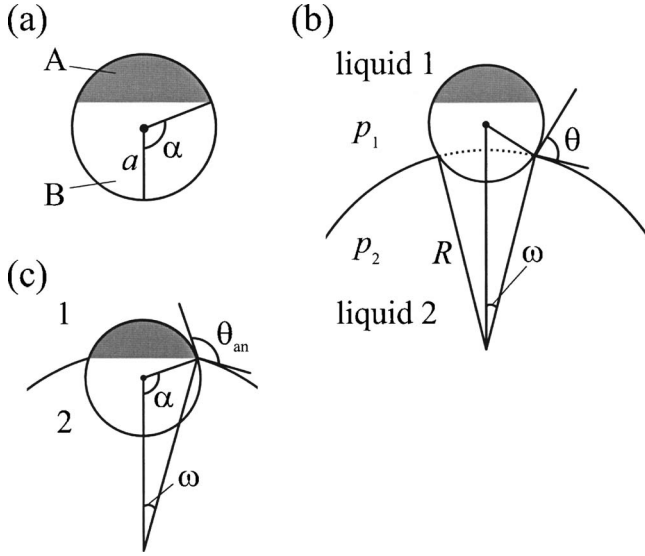


FIG. 1. (a) Geometry of a spherical Janus particle whose radius is a . Upper and lower regions are denoted by “A” and “B,” respectively. The angle α characterizes the borderline between A and B. (b) Janus particle adsorbed to a spherical interface between liquid 1 and liquid 2. The radius of the interfacial curvature is R . The pressures in liquids 1 and 2 are p_1 and p_2 , respectively. The angles θ and ω are the contact angle and the central angle, respectively. (c) Definition of the anchoring angle θ_{an} . The borderline between the two regions coincides with the liquid-liquid interface.

across liquid 1) which characterizes the position of the particle, and R is the radius of the liquid droplet. We introduce the dimensionless curvature $\epsilon = a/R$ which is taken to be positive when the interface is curved toward liquid 1 or negative when it is curved toward liquid 2. The central angle ω defined in Fig. 1(b) is given by

$$\omega = \arctan\left(\frac{\epsilon \sin \theta}{1 + \epsilon \cos \theta}\right), \quad (3)$$

in terms of ϵ and θ . From the geometrical relations, the borderline between the two regions on the particle coincides with the liquid-liquid interface when $\omega = \arcsin(\epsilon \sin \alpha)$. In this case, the contact angle is given by

$$\theta = \alpha + \omega = \alpha + \arcsin(\epsilon \sin \alpha) \equiv \theta_{\text{an}}. \quad (4)$$

As shown in Fig. 1(c), we call such a position of the particle as the *anchoring position* or the *anchoring angle* θ_{an} .

For the adsorption of a Janus particle, there are five different surface tensions characterizing the system. Let σ_{12} , σ_{1A} , and σ_{2A} be the 1-2, 1-A, and 2-A surface tensions. We use similar notations for σ_{1B} and σ_{2B} as well. When the interface is curved, as in Fig. 1(b), 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 1-2 surface tension σ_{12} ,

$$p_2 - p_1 = \frac{2\sigma_{12}}{R}. \quad (5)$$

We neglect external forces and a finite thickness of the interface. Then the interfacial energy attributed to the particle is given by either of the following two cases depending on the particle position with respect to the interface:

$$w_B = \sigma_{1A}S_A + \sigma_{2B}S_2 + \sigma_{1B}(S_1 - S_A) - \sigma_{12}S_{12} + p_1V_1 + p_2V_2, \quad (6)$$

when $0 \leq \theta \leq \theta_{\text{an}}$, or

$$w_A = \sigma_{1A}S_1 + \sigma_{2B}S_B + \sigma_{2A}(S_A - S_1) - \sigma_{12}S_{12} + p_1V_1 + p_2V_2, \quad (7)$$

when $\theta_{\text{an}} \leq \theta \leq \pi$. Here S_1 and S_2 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. Note that S_A and S_B are given in Eqs. (1) and (2), respectively. The volumes occupied by the particle in liquids 1 and 2 are denoted by V_1 and V_2 , respectively. After some geometrical calculations, these areas and volumes are obtained as

$$S_1 = 2\pi a^2[1 + \cos(\theta - \omega)], \quad (8)$$

$$S_2 = 2\pi a^2[1 - \cos(\theta - \omega)], \quad (9)$$

$$S_{12} = 2\pi R^2(1 - \cos \omega), \quad (10)$$

$$V_1 = \pi a^3\left[\frac{2}{3} + \cos(\theta - \omega) - \frac{1}{3}\cos^3(\theta - \omega)\right] - \pi R^3\left[\frac{2}{3} - \cos \omega + \frac{1}{3}\cos^3 \omega\right], \quad (11)$$

$$V_2 = \pi a^3\left[\frac{2}{3} - \cos(\theta - \omega) + \frac{1}{3}\cos^3(\theta - \omega)\right] + \pi R^3\left[\frac{2}{3} - \cos \omega + \frac{1}{3}\cos^3 \omega\right]. \quad (12)$$

Hereafter, we define the following dimensionless quantities using the above surface tensions:

$$\sigma = \frac{\sigma_{1A} + \sigma_{2B}}{\sigma_{12}}, \quad \tau = \frac{\sigma_{1A} - \sigma_{2B}}{\sigma_{12}}, \quad (13)$$

$$\gamma_A = \frac{\sigma_{1A} - \sigma_{2A}}{\sigma_{12}}, \quad \gamma_B = \frac{\sigma_{1B} - \sigma_{2B}}{\sigma_{12}}, \quad (14)$$

which characterize the wettability of the particle. Without loss of generality, we assume that region A prefers liquid 1 to liquid 2, and region B prefers liquid 2 to liquid 1. This means that the orientation of the particle with respect to the interface is such that shown in Fig. 1(b), and the case of the opposite orientation is excluded from our consideration. Since the conditions $\sigma_{1A} < \sigma_{2A}$ and $\sigma_{1B} > \sigma_{2B}$ hold in this situation, we can generally set

$$\gamma_A < 0, \quad \gamma_B > 0. \quad (15)$$

This condition means that the Janus particle is amphiphilic.

We now present the interfacial energy w_i ($i=A, B$) in the dimensionless form, and subtract the constant terms which do not depend on θ or ϵ ,

$$g_i(\theta, \epsilon) = \frac{w_i}{2\pi a^2 \sigma_{12}} - \sigma - \tau \cos \alpha - \frac{a(p_1 + p_2)}{3\sigma_{12}}. \quad (16)$$

Then we have

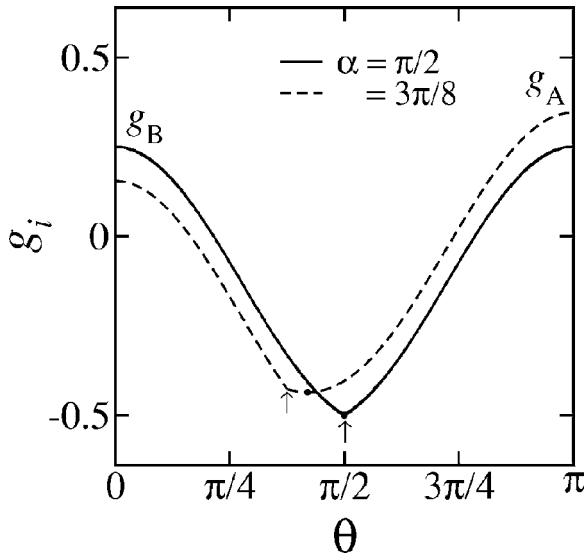


FIG. 2. The dimensionless adsorption energy g_i as a function of the contact angle θ for $\alpha = \pi/2$ and $3\pi/8$ when $\epsilon = a/R = 0$. The other parameters are $\gamma_A = -0.25$ and $\gamma_B = 0.25$. Filled circles correspond to the minimum and the arrows indicate the anchoring positions.

$$g_B(\theta, \epsilon) = \gamma_B [\cos(\theta - \omega) - \cos \alpha] - \frac{1 - \cos^3 \omega}{3\epsilon^2} - \frac{\epsilon}{3} [3 \cos(\theta - \omega) - \cos^3(\theta - \omega)] \quad (17)$$

for $0 \leq \theta \leq \theta_{\text{an}}$, and

$$g_A(\theta, \epsilon) = \gamma_A [\cos(\theta - \omega) - \cos \alpha] - \frac{1 - \cos^3 \omega}{3\epsilon^2} - \frac{\epsilon}{3} [3 \cos(\theta - \omega) - \cos^3(\theta - \omega)] \quad (18)$$

for $\theta_{\text{an}} \leq \theta \leq \pi$. Since $\omega \approx \epsilon \sin \theta$ up to the lowest order in ϵ [see Eq. (3)], the above expressions reduce to those for the flat interface when $\epsilon \rightarrow 0$.^{2,10} The equilibrium position of the particle is obtained by minimizing g_i with respect to θ while ϵ is fixed.

First we consider the case when the liquid-liquid interface is flat, i.e., $\epsilon = 0$. Then we have $\theta_{\text{an}} = \alpha$ from Eq. (4). In Fig. 2, we plot g_i as a function of θ for $\alpha = \pi/2$ and $3\pi/8$ when $\gamma_A = -0.25$ and $\gamma_B = 0.25$. Here the filled circles mark the minimum of g_i and the arrows indicate the anchoring angles. When $\alpha = \pi/2$, the minimum of g_i coincides with the anchoring position, whereas they differ for $\alpha = 3\pi/8$ although γ_A and γ_B are identical in these two cases. In the latter case, the minimum of g_A at $\theta \approx 1.32$ gives the smallest adsorption energy. A similar discussion for the adsorption of a Janus particle to a flat interface was given before,^{12,10} and our result agrees with theirs.

Next we examine the effect of the interfacial curvature on the adsorption of a Janus particle. In Fig. 3, we have plotted g_i for the cases $\epsilon = a/R = 0, 0.2$, and 0.4 . The rest of the parameters are the same as in Fig. 2 and hence the wettability of the particle is not changed here. As marked by the filled circles, the equilibrium position coincides with the anchoring position (indicated by an arrow) when $\epsilon = 0$ and 0.2 ,

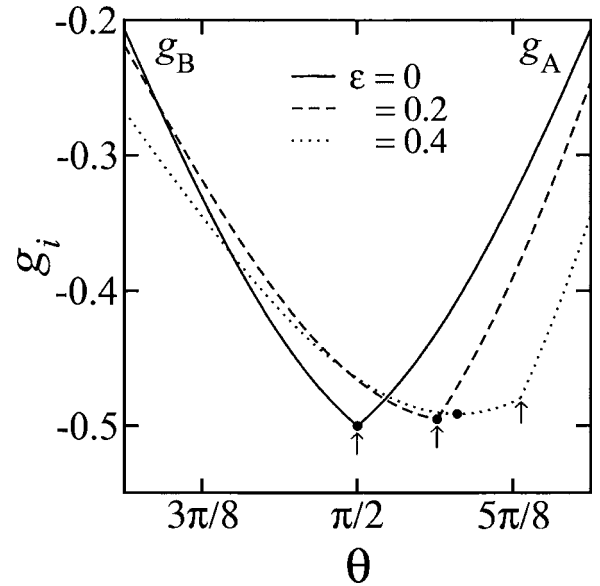


FIG. 3. The dimensionless adsorption energy g_i as a function of the contact angle θ for $\epsilon = 0$ (solid line), $\epsilon = 0.2$ (dashed line), and $\epsilon = 0.4$ (dotted line). The other parameters are $\alpha = \pi/2$, $\gamma_A = -0.25$, and $\gamma_B = 0.25$. The minimum denoted by the filled circle coincides with the anchoring angle (indicated by an arrow) when $\epsilon = 0$ and 0.2 , while it is given by Young's equation for $\epsilon = 0.4$.

while they differ when $\epsilon = 0.4$ due to the curvature effect. When the curvature is relatively large, the high internal pressure prevents the particle from anchoring at the borderline. For general curvatures, we can obtain the equilibrium contact angle θ_{eq} as

$$\theta_{\text{eq}} = \begin{cases} \theta_B & \text{when } \theta_B \leq \theta_{\text{an}} \\ \theta_{\text{an}} & \text{when } \theta_A \leq \theta_{\text{an}} \leq \theta_B \\ \theta_A & \text{when } \theta_{\text{an}} \leq \theta_A, \end{cases} \quad (19)$$

where $\theta_B \equiv \arccos(-\gamma_B) \geq \pi/2$ and $\theta_A \equiv \arccos(-\gamma_A) \leq \pi/2$. Again this result reduces to that for a flat interface when $\epsilon \rightarrow 0$.^{1,2,10} The cases which give Young's equation ($\theta_{\text{eq}} = \theta_B$ and θ_A) are obtained from the condition $(\partial g_i / \partial \theta)_{\epsilon=0} = 0$. An analogous calculation to obtain Young's equation was explained in our previous paper.¹⁴ To represent the above result, we show in Fig. 4 the equilibrium contact angle θ_{eq} as a function of the curvature ϵ for various values of γ_A and γ_B (taken as $|\gamma_A| = |\gamma_B|$ for simplicity) when α is fixed to $\pi/2$. It should be noticed that the particle surface is homogeneous when $\gamma_A = \gamma_B = 0$ for which there is no ϵ dependence (solid line). For finite values of γ_A and γ_B , the equilibrium angle θ_{eq} depends on the curvature when the particle is anchored. The curvature-dependent region of θ_{eq} becomes larger as $|\gamma_i|$ is increased.

Whether the equilibrium contact angle θ_{eq} is determined by the anchoring angle or Young's relation depends on α , ϵ , γ_A , or γ_B , as discussed above. It is important to note that the equilibrium contact angle θ_{eq} is independent of the interfacial curvature ϵ when Young's equation holds, while it does depend on ϵ when $\theta_{\text{eq}} = \theta_{\text{an}}$. Such a property of the Janus particle is in sharp contrast compared to a homogeneous surface particle for which the equilibrium contact angle is always determined by Young's equation.¹⁴ A similar result using a

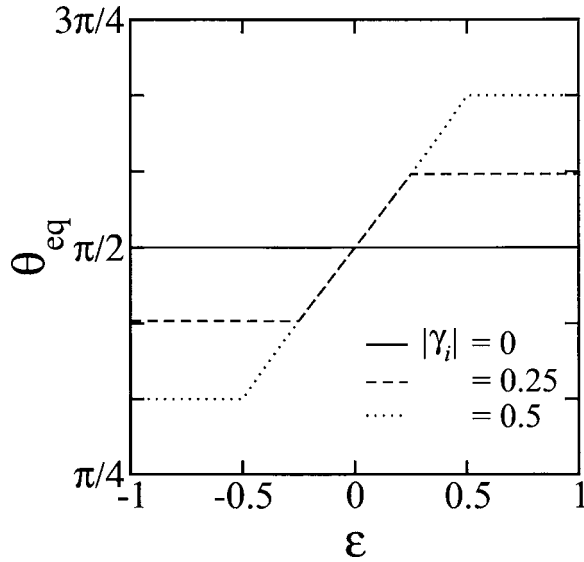


FIG. 4. The equilibrium contact angle θ_{eq} as a function of the interfacial curvature ϵ for different values of $|\gamma_i|$ ($i=A, B$) when $\alpha=\pi/2$. The particle is homogeneous when $|\gamma_i|=0$, and θ_{eq} does not depend on ϵ (solid line). However, θ_{eq} depends on ϵ when $|\gamma_i|\neq 0$ when the particle is anchored.

different approach was given before by di Meglio and Raphaël.¹⁶ However, they did not consider the volume energy which becomes important in the following argument.

We now substitute back the equilibrium contact angle θ_{eq} into g_i , and obtain the adsorption energy which is a function of ϵ only. Then we have

$$g(\epsilon) = -\frac{1}{3\epsilon^2} [1 + 3\epsilon^2 \gamma_B \cos \alpha - (1 - 2\epsilon^2 + \epsilon \gamma_B) \times (1 + \epsilon^2 - 2\epsilon \gamma_B)^{1/2}], \quad (20)$$

when $\theta_B \leq \theta_{\text{an}}$,

$$g(\epsilon) = -\frac{1}{3\epsilon^2} [1 - (1 - \epsilon^2 \sin^2 \alpha)^{3/2}] - \frac{\epsilon}{3} (3 \cos \alpha - \cos^3 \alpha), \quad (21)$$

when $\theta_A \leq \theta_{\text{an}} \leq \theta_B$, and

$$g(\epsilon) = -\frac{1}{3\epsilon^2} [1 + 3\epsilon^2 \gamma_A \cos \alpha - (1 - 2\epsilon^2 + \epsilon \gamma_A) \times (1 + \epsilon^2 - 2\epsilon \gamma_A)^{1/2}], \quad (22)$$

when $\theta_{\text{an}} \leq \theta_A$. Note that these different cases correspond to those in Eq. (19). In Fig. 5, we have plotted the minimized adsorption energy $g(\epsilon)$ as a function of ϵ for $\alpha=\pi/2$ (solid line), $\alpha=31\pi/60$ (dashed line), and $\alpha=8\pi/15$ (dotted line). For all the cases plotted here, $g(\epsilon)$ is downside convex when the particle is anchored. As marked by the filled circles, the minimum of $g(\epsilon)$ appears for $\alpha=\pi/2$ and $31\pi/60$. The curvature ϵ_{min} which gives the minimum of g depends on the surface geometry α . On the other hand, the minimum no longer exists for $\alpha=8\pi/15$. For larger curvature, $g(\epsilon)$ takes a maximum value and then decreases. This is due to the fact that the equilibrium contact angle θ_{eq} changes from the anchoring angle to that given by Young's equation.

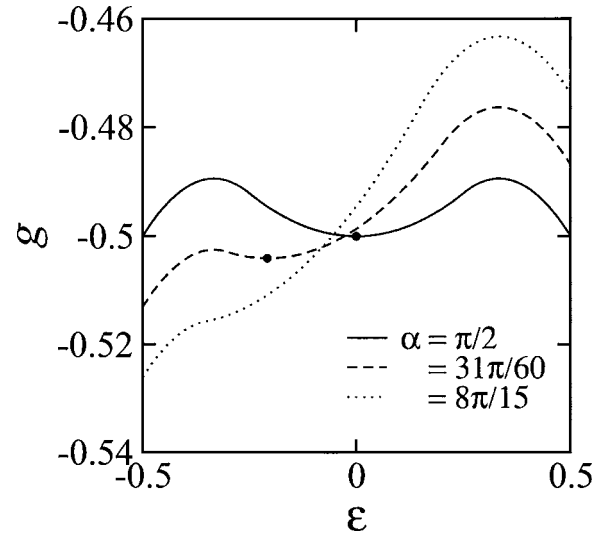


FIG. 5. The minimized adsorption energy g as a function of the interfacial curvature ϵ for $\alpha=\pi/2$ (solid line), $\alpha=31\pi/60$ (dashed line), and $\alpha=8\pi/15$ (dotted line). The parameters are $\gamma_A=-0.25$ and $\gamma_B=0.25$ for all the cases. Filled circles correspond to the minimum points.

From the minimization of $g(\epsilon)$, we have numerically calculated ϵ_{min} as a function of α which is plotted in Fig. 6. Notice again that the minimum appears only when α is close to $\pi/2$. The range of α for which ϵ_{min} exists is dependent on the values of γ_i . When $|\gamma_i|$ becomes larger, α can deviate from $\pi/2$ in order that $g(\epsilon)$ has a minimum. The preferred curvature ϵ_{min} is an odd function of α and vanishes when $\alpha=\pi/2$. Hence the flat interface is stable for a Janus particle characterized by $\alpha=\pi/2$. Such a behavior is completely different from that of the homogeneous particle for which the interface is always unstable.¹⁴ By assuming $\epsilon \ll 1$, we expand $g(\epsilon)$ in terms of ϵ to obtain

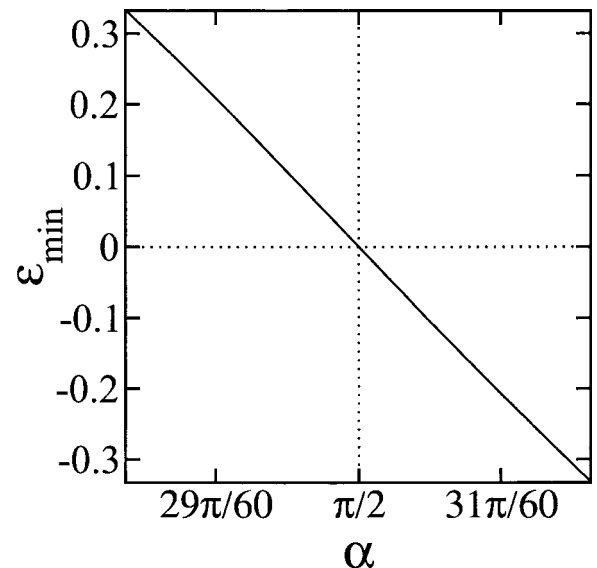


FIG. 6. The minimum curvature ϵ_{min} as a function of the angle α . The other parameters are $\gamma_A=-0.25$ and $\gamma_B=0.25$. The minimum does not exist for α outside the range of the present plot.

$$g(\epsilon) \approx -\frac{\sin^2 \alpha}{2} + \epsilon \cos \alpha \left(\frac{\cos^2 \alpha}{3} - 1 \right) + \frac{\epsilon^2}{8} \sin^4 \alpha + \dots \quad (23)$$

Then ϵ_{\min} can be approximately obtained as

$$\epsilon_{\min} \approx \frac{4 \cos \alpha}{\sin^4 \alpha} \left(1 - \frac{\cos^2 \alpha}{3} \right). \quad (24)$$

The existence of such a preferred curvature is a unique character of the Janus particle. Notice that $\epsilon_{\min} > 0$ and the interface is curved toward liquid 1 when $\alpha < \pi/2$.

Quite generally, Helfrich proposed an elastic model applicable for biological membranes, microemulsions, and other self-assembled molecular films.^{15,17} The corresponding curvature elasticity energy per unit area of the interface is given by

$$f_c(c_1, c_2) = \frac{\kappa}{2}(c_1 + c_2 - 2c_0)^2 + \bar{\kappa}c_1c_2, \quad (25)$$

where c_1 and c_2 are two principle curvatures, κ and $\bar{\kappa}$ are the bending and Gaussian moduli, respectively, and c_0 is the spontaneous curvature. Using the expansion Eq. (23), we calculate the sum and the difference of $g(\epsilon)$ and $g(-\epsilon)$ to obtain

$$\kappa c_0 = \pi \sigma_{12} a \cos \alpha \left(1 - \frac{\cos^2 \alpha}{3} \right), \quad (26)$$

$$2\kappa + \bar{\kappa} = \frac{\pi}{4} \sigma_{12} a^2 \sin^4 \alpha. \quad (27)$$

The sum of the elastic moduli $2\kappa + \bar{\kappa}$ is proportional to $\sigma_{12} a^2$ which is in contrast with an interface saturated with amphiphilic molecules. In the latter case, the bending modulus is proportional to the cube of the molecular size.¹⁸

In order to give a value for the derived κ , we consider a system in which $\sigma_{12} = 5 \times 10^{-2} \text{ J/m}^2$ and $a = 10^{-7} \text{ m}$. We then have $\kappa \approx 4.7 \times 10^4 k_B T$ for $\alpha = \pi/2$ at room temperature (we have neglected $\bar{\kappa}$). Hence the bending modulus can be much larger than that of the interface made of surfactants, and the effect of thermal fluctuations can be neglected. This result suggests that emulsions made of Janus particles are quite stable against the coalescence of the droplets since the en-

ergy barrier to break a droplet is primarily determined by the curvature energy of the interface. A liquid droplet coated by Janus particles may be rather stable and behaves like a soft solid.

To summarize, we have discussed the adsorption of a Janus particle to a spherically curved liquid-liquid interface. We showed that the equilibrium contact angle depends on the geometry of the particle, its wettability, and also the interfacial curvature. Furthermore, there exists a preferred interfacial curvature due to the presence of a Janus particle.

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