

Janus balance of amphiphilic colloidal particles

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We introduce the notion of “Janus balance” (J), defined as the dimensionless ratio of work to transfer an amphiphilic colloidal particle (a “Janus particle”) from the oil-water interface into the oil phase, normalized by the work needed to move it into the water phase. The J value can be calculated simply from the interfacial contact angle and the geometry of Janus particles, without the need to know the interfacial energy. It is demonstrated that Janus particles of the same chemical composition but different geometries will have the highest adsorption energy when $J=1$. Even for particles of homogeneous chemical makeup, the Janus balance concept can be applied when considering the contact angle hysteresis in desorbing the particle from equilibrium into the water or oil phase. The Janus balance concept may enable predictions of how a Janus particle behaves with respect to efficiency and function as a solid surfactant, as the Janus balance of solid surfactants is the analog of the classical hydrophile-lipophile balance of small surfactant molecules. © 2007 American Institute of Physics. [DOI: 10.1063/1.2803420]

INTRODUCTION

Colloidal particles—larger than molecules but small enough to sustain Brownian motion—are fundamental in nature and technology. A traditional goal in colloid and nanoparticle science was to obtain particles that are homogeneous in their chemical composition. This has numerous applications (for example, in areas such as painting, ceramics, and photonic materials¹) and on the scientific side is driven by the desire to use colloids to emulate atomic systems where homogeneous chemical makeup of the elements in the system is essential.² At the same time, of emerging interest is the alternative idea of obtaining particles whose surface chemical composition differs on two sides of the particle (“Janus” as suggested by de Gennes³). To date, an impressive number of methods have been developed to fabricate Janus particles.⁴ New methods demonstrated the possibility to synthesize Janus particles with different geometries in large quantity.⁵ This field of experimental study now appears poised to implement the vision of “molecular colloids” whose patchy surface chemical makeup governs their assembly into superstructures.⁶ Indeed, the assembly of larger (non-Brownian) objects has already been implemented.⁷

We are concerned here with amphiphilic Janus particles because amphiphilicity, which is to possess hydrophobic and hydrophilic elements in the same object, drives molecules to self-assemble into superstructures that are integral to many of the most useful and complex features of soft materials. Among synthetic amphiphiles, prominent examples include not only surfactants and detergents⁸ but also the burgeoning use of block copolymers in technology.⁹ In biology, self-assembly of phospholipids into biological membranes follows similar elemental principles, although those systems present the added complexity of containing mixtures of

many different sorts of amphiphilic molecules.¹⁰ Colloids have hardly been studied from this perspective.

The balance between hydrophilic and hydrophobic elements on Janus particles is analogous to the hydrophilic-lipophilic balance (HLB) of molecular-sized surfactants. The self-assembly in a bulk liquid phase¹¹ of amphiphilic Janus particles, hydrophilic in one region and lipophilic in another, and their adsorption at interfaces¹² has already been considered phenomenologically. It has been shown that the adsorption energy of amphiphilic Janus particles at an oil-water interface can be up to three times higher than that for a homogeneous particle—a substantial number when one considers that, unlike the case when a molecular-sized surfactant adsorbs, the adsorption energy for a homogeneous colloidal-sized particle is typically orders of magnitude larger than $k_B T$.¹³ The aim of this paper, inspired by the well-known concept of HLB of surfactant molecules,¹⁴ is to present a strict definition of the Janus balance concept for solid surfactants and illustrate it for the example of Janus spheres.

This communication introduces the concept of “Janus balance” (J), defined as the dimensionless ratio of work to transfer an amphiphilic colloidal particle (a “Janus particle”) from the oil-water interface into the oil phase, normalized by the work needed to move it into the water phase. The value of J can be calculated simply from the interfacial contact angle and the geometry of Janus particles, without the need to know interfacial energy. It is demonstrated that Janus particles of the same chemical composition but different geometries will have the highest adsorption energy when $J=1$. As has been the case for the classical HLB of conventional surfactant molecules, the Janus balance concept may be useful for predicting the efficiency and functions of solid (particulate) surfactants.

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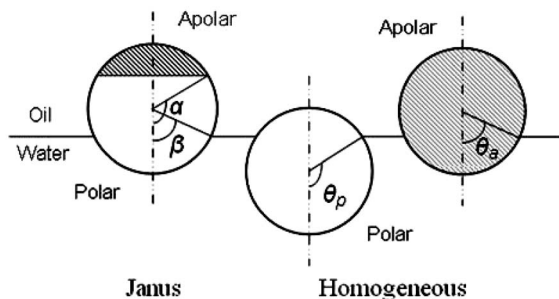


FIG. 1. The geometry of a Janus particle at the oil-water interface and the contact angle at its hydrophilic and hydrophobic sides. The relative areas of the polar and apolar particle surface regions are parametrized by angle α and the contact angle of the Janus particle at interface β . The contact angle of the hydrophilic side is θ_p . The contact angle of the hydrophobic side is θ_a .

QUANTIFICATION OF THE JANUS BALANCE CONCEPT

The calculations presented below can simply be extended to Janus particles whose shape is not spherical but for simplicity, and without loss of generality, we consider a single Janus sphere of radius R sitting at a flat oil-water interface.

The interfacial energies (γ), referring to interface of polar (P) side, apolar (A) side against the oil (O) side, and the water (W) side are $\gamma(PO)$, $\gamma(PW)$, $\gamma(AO)$, $\gamma(AW)$, respectively. For clarity, we follow the nomenclature of Binks and Fletcher.¹³ Figure 1 shows that the geometry of the Janus particle is quantified by the angle α , which determines the position of the boundary dividing the apolar (hydrophobic) and polar (hydrophilic) regions on the particle. Hydrophobicity is characterized by the angles θ_p (hydrophilic side) and θ_a (hydrophobic side), corresponding to the three-phase contact angle at the oil-water interface of a homogeneous particle consisting of this same hydrophilic or hydrophobic surface chemical makeup. For consistency, this angle is always measured starting from the center line pointing toward the water phase. In this way, θ_p is necessarily larger than 90° , while θ_a is necessarily smaller than 90° . For perfect hydrophilic and hydrophobic surfaces, $\theta_p=180^\circ$ and $\theta_a=0^\circ$.

The first step in the following argument is to find the contact angle β of the Janus particle, determined by minimizing the free energy of the Janus particle at the oil-water interface. As shown in Fig. 2, when $\alpha < \theta_a < 90^\circ < \theta_p$, the contact angle of the Janus particle equals the contact angle of a hypothetical homogeneous particle that possesses the same surface chemical makeup as the hydrophobic side of the Janus particle, that is, $\beta = \theta_a$. The physical meaning is evident when one considers the free energy change. Whenever the particle is moved up or down to lower the free energy, the change of free energy is the same as long as the entire hydrophilic moiety is immersed in the water phase, no matter what the size of the hydrophilic moiety is. In fact, this statement holds even when the surface area of the hydrophilic moiety is zero, i.e., if the particle is homogeneously hydrophobic. This means that the contact angle of this Janus particle is the same as that of a hypothetical homogeneous particle with the same hydrophobic surface.

However, when $\theta_a < \alpha < \theta_p$, the result is different: β

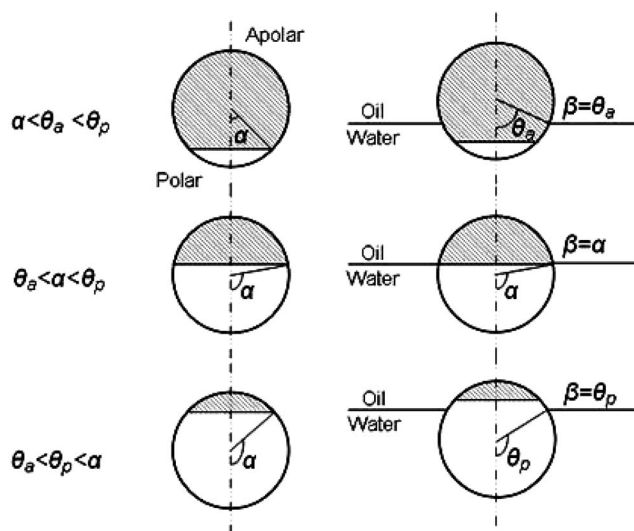


FIG. 2. The contact angle for a Janus particle at the oil-water interface, with parameters defined in the caption of Fig. 1.

$= \alpha$. The physical meaning is that moving the particle up or down necessarily increases the free energy, either by increasing the amount of polar surface area in contact with oil or the amount of apolar surface area in contact with water. In the same spirit, in the case where $\theta_a < 90^\circ < \theta_p < \alpha$, it follows that $\beta = \theta_p$. The physical meaning is that moving the particle up or down necessarily increases the free energy by the same reasoning.

For simplicity, we first discuss the case if $\theta_a < \alpha < \theta_p$. It is worth pointing out that when the particle is moved away from the interface, the water-oil surface area increases. The energy to desorb this particle from equilibrium into the oil (water) phase follows considering the surface areas induced or eliminated by this process, as quantified below:

$$\frac{E(\alpha)_{\text{oil}}}{2\pi R^2} = \frac{1}{2} \gamma(OW) \sin^2 \alpha + [\gamma(PO) - \gamma(PW)](1 - \cos \alpha), \quad (1)$$

$$\frac{E(\alpha)_{\text{water}}}{2\pi R^2} = \frac{1}{2} \gamma(OW) \sin^2 \alpha + [\gamma(AW) - \gamma(AO)](1 + \cos \alpha). \quad (2)$$

Here, $E(\alpha)_{\text{oil}}$ is the energy to desorb particle from equilibrium into the oil phase and $E(\alpha)_{\text{water}}$ is the energy to desorb particle from equilibrium into the water phase. Substituting the contact angles θ_a and θ_p specified by Young's equations, Eqs. (3) and (4), Eqs. (5) and (6) will result to

$$\gamma(OW) \cos \theta_p = \gamma(PW) - \gamma(PO), \quad (3)$$

$$\gamma(OW) \cos \theta_a = \gamma(AW) - \gamma(AO), \quad (4)$$

$$\frac{E(\alpha)_{\text{oil}}}{2\pi R^2} = \gamma(OW) \left[\frac{\sin^2 \alpha}{2} + \cos \theta_p (\cos \alpha - 1) \right], \quad (5)$$

$$\frac{E(\alpha)_{\text{water}}}{2\pi R^2} = \gamma(OW) \left[\frac{\sin^2 \alpha}{2} + \cos \theta_a (\cos \alpha + 1) \right]. \quad (6)$$

This gives the Janus balance (J), defined as the energy needed to desorb the particle from equilibrium into the oil phase, normalized by the energy needed to desorb it from equilibrium into the water phase,

$$J = \frac{\sin^2 \alpha + 2 \cos \theta_p (\cos \alpha - 1)}{\sin^2 \alpha + 2 \cos \theta_a (\cos \alpha + 1)}. \quad (7)$$

Equation (7) shows that Janus balance depends not just on the respective areas of hydrophilic and hydrophobic chemical makeup, quantified by α but also on the hydrophobicity of the two sides, quantified by θ_a and θ_p . Janus balance defined this way considers all factors that affect thermodynamics of the particle's adsorption.

If θ_a and θ_p are fixed, J increases as α increases (since $\cos \theta_p < 0$), which corresponds to larger hydrophilic area. If α is fixed, J increases when θ_a or θ_p increases, which corresponds to the hydrophilic part becoming more hydrophilic or the hydrophobic part becoming less hydrophobic. The larger the magnitude of J , the more hydrophilic is the solid surfactant. The same trend holds for the HLB value of surfactant molecules: surfactants with larger HLB have more affinity for water.

What about the extreme limits of these parameters? If a particle has a homogeneous chemical makeup ($\alpha = \theta_p = \theta_a$, where α refers simply to the contact angle of the homogeneous particle at oil-water interface), it results to the following equation (for clarity, β substitutes α by symmetry):

$$J = \frac{(1 - \cos \beta)^2}{(1 + \cos \beta)^2}. \quad (8)$$

Here, β is the contact angle of the homogeneous particle at oil-water interface. Some years ago, in a visionary book, Kruglyukov¹⁵ already defined the HLB value of a homogeneous particle at the oil-water interface, deriving an expression equivalent to Eq. (8).

Similarly, Eqs. (9) and (10) yield expressions for the Janus balance for the other two cases. When $\alpha < \theta_a < \theta_p$,

$$J = \frac{\sin^2 \theta_a + 2 \cos \theta_p (\cos \alpha - 1) + 2 \cos \theta_a (\cos \theta_a - \cos \alpha)}{\sin^2 \theta_a + 2 \cos \theta_a (\cos \theta_a + 1)}, \quad (9)$$

and when $\theta_a < \theta_p < \alpha$,

$$J = \frac{\sin^2 \theta_p + 2 \cos \theta_p (\cos \theta_p - 1)}{\sin^2 \theta_p + 2 \cos \theta_a (1 + \cos \alpha) + 2 \cos \theta_p (\cos \theta_p - \cos \alpha)}. \quad (10)$$

EXAMPLES

Homogeneous particles

We first use data from the literature to calculate the Janus balance of a homogeneous particle. In the literature, silica particles of various hydrophobicity (modified by silanes) have been used to stabilize water-toluene emulsions¹⁶ and the interfacial contact angles of silica particles at the water-toluene interface have been estimated, although without considering contact angle hysteresis.¹⁷ It is found that emulsions stabilized by either very hydrophilic [surface cov-

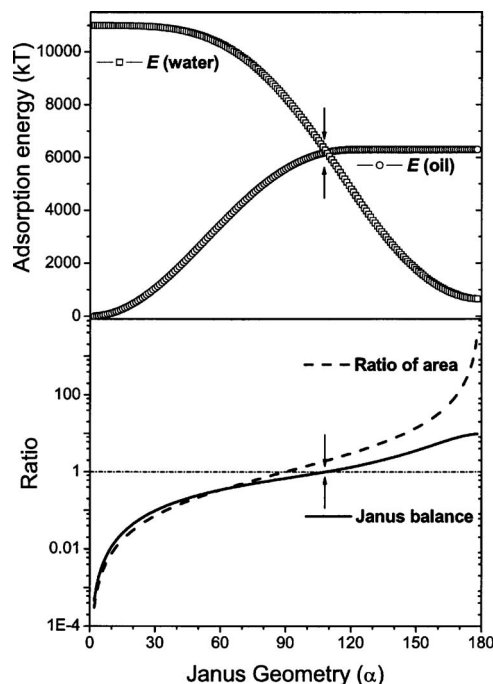


FIG. 3. A typical example. The adsorption energy and Janus balance for a 10 nm Janus particle with hydrophilic ($\theta_p=121^\circ$) and hydrophobic ($\theta_a=0^\circ$) areas at room temperature ($T=298$ K). The value $J=1$ occurs for this example when $\alpha=109^\circ$, as indicated by the arrows, corresponding to maximum adsorption energy. The dashed line, drawn for reference, is the ratio of hydrophilic to hydrophobic surface area on the Janus particle.

ered with 100% Si-OH groups, contact angle $\beta=121^\circ$, hence, $J=9.8$ from Eq. (8)] and very hydrophobic (surface covered with 20% Si-OH groups, contact angle $\beta < 68^\circ$, hence, $J < 0.2$) were unstable to coalescence. Note that in the convention used in this paper, introduced in the previous section, β equals 180° minus the literature value of contact angle. However, emulsions with particles of intermediate hydrophobicity (surfaces covered with 50% and 76% Si-OH groups, contact angles $\beta=90^\circ$ and 106° , respectively, hence, $J=1.0$ and 3.1) were stable to coalescence.¹⁶ The results agree well with our definition and the physical meaning of Janus balance: the emulsion will be more stable when J is closer to 1.

Janus particles

As silica is commonly used as a platform from which to construct Janus colloidal particles,⁵ the Janus balance concept is now illustrated with numbers that are realistic for this system. As a demonstration of calculation, now we consider a 10 nm Janus particle made from silica particles, with bare silica surface as the hydrophilic surface and silane modified surface as the hydrophobic surface. Particle size will only affect the absolute values but not the shape of the curve. For this example, the emulsion system is the widely used toluene-water system. According to the literature,¹⁷ values of θ_a and θ_p in this system are close to 0° and 121° , respectively.

Figure 3 shows the desorption energy and the Janus balance value plotted as functions of the Janus geometry (α). If the adsorption energy is defined as the minimum of E_{oil} and

E_{water} , then $J=1$ corresponds to the point of maximum of the adsorption energy. Here, $J=1$ when $\alpha \approx 109^\circ$. This is a counterexample to the naive thought that a Janus particle, half hydrophilic and half hydrophobic in area, gives the highest adsorption energy. Instead, it is necessary to weight physical area by interfacial energy.

We also notice that the emulsion type can differ even for the same Janus balance. Also our calculation did not take into account the effect of the curvature. These issues are discussed in the next section.

OUTLOOK AND POTENTIAL IMPLICATIONS

It has been shown by both experiment and calculation that for the same surface, the contact angle depends on the oil involved.¹⁷ Therefore, even for the same Janus particle, Janus balance can differ according to the oil. The same arises concerning the determination of HLB value for small surfactant molecules: standard oil must be used for calibration or else the HLB value depends on the oil. It is necessary to calculate the Janus balance value for a specific system in order to design the best geometry of Janus particles to stabilize the emulsion. Then, α should be chosen to ensure that J is as close to unity as possible.

Even for particles of homogeneous chemical makeup, the Janus balance concept can be applied when considering the contact angle hysteresis to desorb the particle from equilibrium into the water or oil phase. In this case of homogeneous particle makeup, θ_a and θ_p become the advancing or receding angles.

The Janus balance concept also applies when particles coexist together with the surfactants. Recently, synergy between surfactants and particles to stabilize emulsions has been studied.¹⁸ Since how much adsorbs depends on the phase from which it adsorbs, it is natural to expect that, according to the HLB balance, more surfactant will adsorb from the oil phase and less from the water phase, or else vice versa. However, as surfactant molecules adsorb less strongly than particles, their amount adsorbed may change in response to the presence of adsorbed particles. This projected situation is complex and requires more modeling and calculation to quantify the overall adsorption energy.

Finally, we take note of several factors, ignored in this paper, that might potentially affect the emulsion stability and emulsion type under certain conditions. Particle-particle interaction and bending energy at a curved oil-water interface were not considered¹⁹ but the calculation presented here can be extended to the situation of having a curved interface.²⁰ Line tension was not considered, though it becomes increasingly important as particle size becomes smaller, since the theoretical estimate is on the order of 10^{-10} N.²¹ Gravity and roughness of the particle also were ignored.²² Gravitational forces can deform the interface and affect the location of the contact line. However, gravity is negligible for particles of submicron size; for example, the gravity force of a $1 \mu\text{m}$ silica particle is on the order of 10^{-14} N, negligible since the force induced by surface tension is on the order of 10^{-7} N.

In analogy to the usefulness of the classical HLB of surfactant molecules, the concept of Janus balance may be

useful in facilitating design of Janus particles as emulsifiers, in predicting their self-assembly behavior, and in building a bridge between theory and practical applications, but no quantitative predictions are offered at this time.

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