

1

Colloidal Particles at Liquid Interfaces: An Introduction

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1.1 Some Basic Concepts

Colloidal particles are an intrinsic part of systems in which finely divided matter (particles) is dispersed in a liquid or gas. Their size usually ranges from 1 nm to several tens of micrometres, thus covering a broad size domain.^{1–3} They are not necessarily solid and examples of “soft” colloidal particles (microgels and bacteria) will be briefly considered later in this chapter. Colloidal particles, similar to surfactant molecules, can spontaneously accumulate at the interface between two immiscible fluids (liquid–gas or liquid–liquid); they are therefore surface active.⁴ This fact was realised in the beginning of the last century by Ramsden⁵ and Pickering⁶ whose merit for instigating the field of particles at liquid interfaces will be discussed later. It is important to emphasise that the surface activity of these particles is not necessarily due to their amphiphilic nature. Solid particles with homogeneous chemical composition and properties everywhere on their surface (Figure 1.1(a)) can strongly attach to liquid interfaces and the reason for their surface activity is made clear below. There is, however, another class of particles with two distinct surface regions

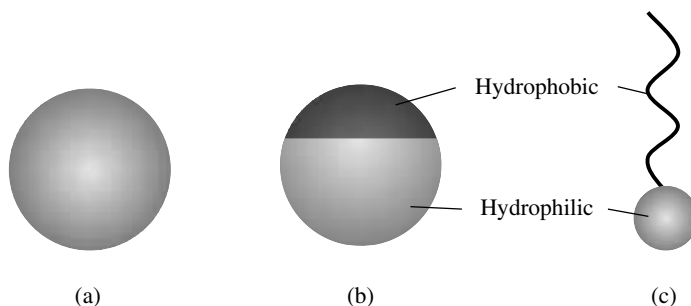


Figure 1.1 Schematic of (a) homogeneous, (b) heterogeneous or amphiphilic (Janus) colloidal particles and (c) a surfactant molecule.

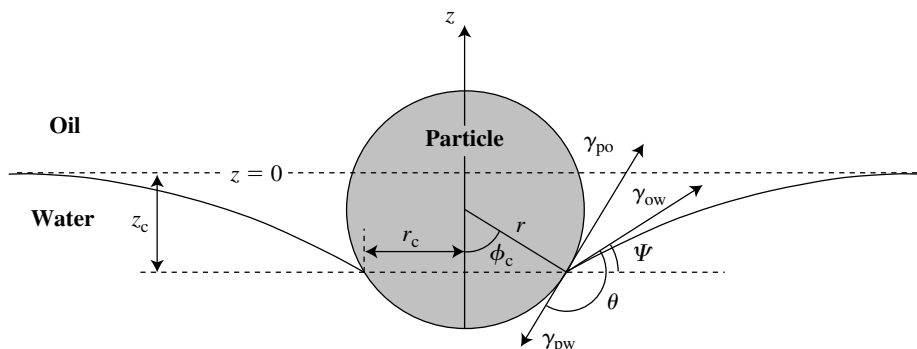


Figure 1.2 Heavy solid spherical particle with radius r and contact angle θ in equilibrium at the oil–water interface levelled at $z = 0$ far from the particle. The three-phase contact line with radius r_c is depressed at depth z_c below the zero level. Other symbols are defined in the text.

with different chemical composition and wetting properties (Figure 1.1(b)). These so-called “Janus” particles are both surface active and amphiphilic⁷ which makes them very similar to surfactant molecules (Figure 1.1(c)). This class of amphiphilic particles will not be considered here. Information about Janus particle design, synthesis and properties can be found in a recent review.⁸

A key parameter when dealing with solid particles at fluid interfaces is the three-phase contact angle θ . This is the angle between the tangents to the solid surface and the liquid–liquid (or liquid–gas) interface measured through one of the liquids in each point of the three-phase contact line where the solid and two fluids meet. An example for a spherical particle at the oil–water interface is shown in Figure 1.2. We use the convention to measure θ through the more polar liquid (water). The contact angle depends on the surface free energies (interfacial tensions) at the particle–water, γ_{pw} , particle–oil, γ_{po} , and oil–water, γ_{ow} , interface according to Young’s equation⁹

$$\cos\theta = \frac{\gamma_{po} - \gamma_{pw}}{\gamma_{ow}} \quad (1.1)$$

Particles equally wet by both liquids ($\gamma_{po} = \gamma_{pw}$) have a contact angle of 90° . Hydrophilic particles are preferentially wet by water ($\gamma_{po} > \gamma_{pw}$), therefore $0^\circ \leq \theta < 90^\circ$, while hydrophobic particles are preferentially wet by oil ($\gamma_{po} < \gamma_{pw}$), hence $90^\circ < \theta \leq 180^\circ$.

When particles are very small the contact angle will be influenced by the excess free energy associated with the three-phase contact line (so-called line tension effect). Bearing in mind that the theoretical and experimental aspects of the line tension are well discussed in the literature,^{10–16} including books^{12,13} and a recent review,¹⁴ it will be excluded from our considerations for simplicity. The rest of the

chapter is organised as follows. In the next section, without being exhaustive, some key issues about the equilibrium position of a single colloidal particle at a planar fluid interface and the free energy of its detachment to the bulk liquids are presented. The effect of particle shape is considered in the case of rod- and disk-like particles. This is followed by a summary of some very recent developments in the experimental research of particle monolayers at horizontal and vertical fluid interfaces and in thin liquid films. The second section, concentrating on particles adsorbed at curved liquid interfaces, details the important findings on the stabilisation of emulsions and foams by particles alone, and draws examples from a wide range of industrially important products and processes.

1.2 Single Particle at a Fluid Interface

1.2.1 *Equilibrium position of a solid particle at a horizontal fluid interface*

It is very important in many technological processes (see Chapters 6, 8 and 9) to know the conditions at which a solid particle can stay attached in equilibrium at the liquid–liquid or liquid–gas interface. The problem for the equilibrium of a solid particle at a fluid interface has been extensively treated in the literature^{10,12,13,17–21} often in relation to the lateral capillary inter-particle forces caused by the deformation of the fluid interface around two or more floating particles (*e.g.* see Ref. [13] and references therein). This problem can be very difficult in the case of a particle with complex shape and inhomogeneous surface. Solutions have been obtained for particles with simple shape and smooth surface (*e.g.* spheres^{12,17–21} and cylinders parallel to the fluid interface^{12,17,18}) or sharp edges (*e.g.* disks²¹ and long prismatic particles¹⁷ parallel to the fluid interface). In the latter case the three-phase contact line is pinned at the edges and the angle of contact between the fluid and solid interface is not directly defined by equation (1.1). This problem needs a slightly different treatment^{17,21} and will not be considered here. The equilibrium position of a particle at a fluid interface can be found either by minimising the free energy of the system^{12,18,19,22} or by means of a force analysis^{17–21} setting the net force (and the net torque) acting on the particle to zero. The advantage of the first approach is that complex cases (*e.g.* non-uniform particle wetting, line tension effect, *etc.*) can be tackled.^{12,18,22} In the case of a smooth homogeneous spherical particle considered below, the force balance approach is equally applicable.^{17,19–21}

For clarity we will consider a solid spherical particle with radius r in equilibrium at the oil–water interface when the particle density ρ_p is larger than that of water, ρ_w , and oil ρ_o ($\rho_p > \rho_w > \rho_o$, Figure 1.2). In this situation the oil–water interfacial tension is decisive for keeping the particle attached at the fluid interface. The general case for arbitrary fluids and densities was considered by Princen.¹⁷ Far from the particle the liquid interface is flat and levelled at $z = 0$; the z -axis points

upwards (against gravity) normal to the flat liquid interface. The three-phase contact line (a circle with radius r_c) is located at a distance z_c below the zero level, while its position with respect to the particle centre is measured by the angle ϕ_c , hence $r_c = r \sin \phi_c$. The deformed fluid interface (the meniscus) meets the particle surface at angle $\psi = \phi_c + \theta - 180^\circ$ measured to the horizontal level. At equilibrium the net force acting on the particle must be equal to zero. Due to the symmetry the net torque is zero. For the same reason only the vertical force balance (in the z -direction) has to be considered. There are three forces which are involved: the particle weight, mg (m is the particle mass, g is the acceleration due to gravity) acting downwards, the vertical capillary force F_γ due to the vertical component of the oil–water interfacial tension, $\gamma_{ow} \sin(\phi_c + \theta)$ acting upwards at the contact line with length $2\pi r \sin \phi_c$ and the vertical resultant of the hydrostatic pressure distribution around the entire particle, F_p , acting also upwards. The other two interfacial tension forces (γ_{po} and γ_{pw}) depicted in Figure 1.2 must not be included in the force balance because they cannot be considered as external to the particle forces (*e.g.* see Ref. [13, p. 92]). At equilibrium we have

$$F_\gamma + F_p = mg \quad (1.2)$$

The vertical capillary force is

$$F_\gamma = -2\pi r \gamma_{ow} \sin \phi_c \sin(\phi_c + \theta) \quad (1.3)$$

F_p can be obtained by integrating the hydrostatic pressure distribution around the entire particle surface. The result can be written in the form²⁰

$$F_p = \rho_w V_{pw} g + \rho_o V_{po} g - (\rho_w - \rho_o) g z_c A_c \quad (1.4)$$

where $V_{pw} = \pi r^3 (2 - 3 \cos \phi_c + \cos^3 \phi_c) / 3$ and $V_{po} = 4\pi r^3 / 3 - V_{pw}$ are the particle volumes immersed in water and in oil, respectively and $A_c = \pi (r \sin \phi_c)^2$ is the area of the contact line circle. The first two terms on the right hand side of equation (1.4) are the buoyancy (Archimedes) forces, while the last term accounts for the additional hydrostatic pressure due to depression of the liquid interface below the zero level ($z_c < 0$). The mass of a spherical particle is $m = \rho_p 4\pi r^3 / 3$. Bearing this in mind, substitution of equations (1.3) and (1.4) in the force balance equation (1.2) after some rearrangement yields^{17,19–21}

$$\sin \phi_c \sin(\phi_c + \theta) = -\frac{B}{6} \left[4 \frac{\rho_p - \rho_o}{\rho_w - \rho_o} - (1 - \cos \phi_c)^2 (2 - \cos \phi_c) + 3 \frac{z_c}{r} \sin^2 \phi_c \right] \quad (1.5)$$

where $B = (\rho_w - \rho_o) r^2 g / \gamma_{ow}$ is a dimensionless parameter (the Bond number). In the considered case of a heavy particle ($\rho_p > \rho_w > \rho_o$), F_γ must always act upwards,

therefore $\phi_c + \theta \geq 180^\circ$, $\phi_c \leq 180^\circ$. Hence, the left hand side of equation (1.5) is restricted in the range $-1 \leq \sin \phi_c \sin(\phi_c + \theta) \leq 0$. The same should apply to the right hand side of equation (1.5). Obviously, equation (1.5) cannot be solved if B is too large, *i.e.* the particle is too big or too dense. In this case the particle cannot be supported by the fluid interface and will sink in water. To find the critical particle size and density below which the particle can stay attached to the fluid interface at given θ , γ_{ow} , ρ_w and ρ_o is very important for the flotation of minerals considered in Chapter 9. This can be done by solving equation (1.5) if the dependence of z_c on B , ϕ_c and θ is known. The latter can be found by solving the Laplace equation of capillarity

$$\gamma_{ow} \left[z''(1 + z'^2)^{-3/2} + z'(1 + z'^2)^{-1/2} l^{-1} \right] = (\rho_w - \rho_o)gz \quad (1.6)$$

where $z' \equiv dz/dl$ and $z'' \equiv d^2z/dl^2$ are the first and second derivatives with respect to the radial distance $l \geq r_c$ measured from the particle centre in the plane $z = 0$. The two terms in the square brackets are the reciprocals of the principle radii of curvature of the fluid interface, while the right hand side of the equation is the pressure difference across the interface. In the considered case of a circular contact line equation (1.6) has no closed analytical solution and has to be solved numerically^{12,13,19} but approximate analytical solutions are available (see Chapter 2 in Ref. [13]). It is worth noting that the deformation of the fluid interface extends to a distance comparable to the capillary length $1/\sqrt{(\rho_w - \rho_o)g/\gamma_{ow}}$ which is usually much larger than the particle size (the capillary length for the pure water–air surface is ~ 2.7 mm). Therefore when two or more particles are attached to the fluid interface and their menisci overlap a long-range lateral capillary force between particles appears^{13,23,24} and can be attractive (when both menisci are depressed or elevated) or repulsive (when depressed and elevated menisci overlap). Directed self assembly of particles at fluid interfaces due to these type of forces is considered in Chapter 7.

When B tends to zero the left hand side of equation (1.5) must also approach zero and $\phi_c + \theta \approx 180^\circ$, thus $\psi \approx 0^\circ$. Hence, for a sufficiently small particle, the deformation of the fluid interface caused by the gravity is very small and can be neglected. In this case the fluid interface can be considered as flat up to the three-phase contact line as shown in Figure 1.3(a). In the case of the air–water surface this is fulfilled for floating particles with radius smaller than $\sim 5 \mu\text{m}$ when the lateral capillary force is negligible.¹³ Deformation of the fluid interface around small spherical particles could exist, however, for reasons different to gravity such as non-uniform wetting of the particle surface.^{25,26} The asymmetric electric field around a charged particle at the interface between fluids with very different relative permittivities, ϵ , *e.g.* water ($\epsilon \approx 80$) and air ($\epsilon \approx 1$) or oil ($\epsilon \approx 2$ for alkanes), could

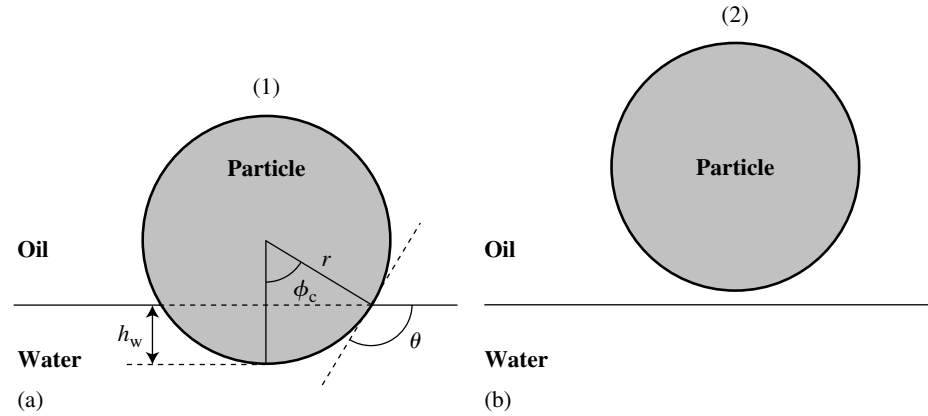


Figure 1.3 Small solid spherical particle with radius r and contact angle θ (a) attached to a planar oil–water interface in its equilibrium state “1” and (b) after its detachment into oil in state “2”.

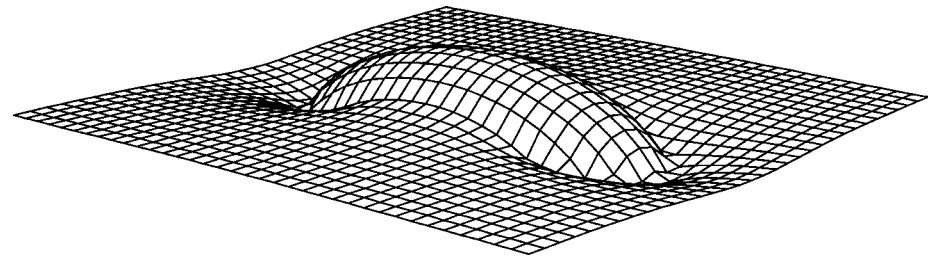


Figure 1.4 Possible interfacial profile around an ellipsoidal particle with contact angle 45° , aspect ratio $a/b = 4$ and both short axes equal to $2.52\text{ }\mu\text{m}$ oriented with its long axis parallel to the fluid interface. Taken from Ref. [30]; with permission of the American Physical Society.

also generate a deformation of the fluid interface as suggested recently.^{27,28} The role of these deformations in particle interactions at fluid interfaces is discussed in Chapter 3. Deformation of the fluid interface may also arise around a non-spherical small particle.^{29,30} An example for such a deformation around an ellipsoidal particle at a fluid interface is shown in Figure 1.4.

1.2.2 Free energy of particle detachment from a planar fluid interface

When a small spherical particle at a planar undeformed oil–water interface is in its equilibrium state “1” (Figure 1.3(a)) the surface free energy of the system, $G^{(1)}$ is minimum and is given by the equation

$$G^{(1)} = \gamma_{ow}A_{ow}^{(1)} + \gamma_{pw}A_{pw}^{(1)} + \gamma_{po}A_{po}^{(1)} \tag{1.7}$$

where $A_{ow}^{(1)}$ is the area of the oil–water interface, $A_{pw}^{(1)}$ and $A_{po}^{(1)}$ are the respective areas of the particle–water and particle–oil interfaces whose sum equals the total surface area of the particle A_p

$$A_{pw}^{(1)} + A_{po}^{(1)} = A_p \quad (1.8)$$

In this state the depth of immersion of the particle in water, h_w (thereby the depth of immersion in oil, $h_o = 2r - h_w$) is directly related to the contact angle by the expression

$$h_w = r(1 + \cos \theta) \quad (1.9)$$

Therefore this equation can be used for calculating the particle contact angle from the measured value of h_w if r is known.^{31–33} If we move the particle from its equilibrium position towards either of the bulk phases by applying some small external force, equation (1.9) will be violated since Young's equation must be satisfied (θ is fixed). Hence, the fluid interface in the new position of the particle after its movement will be deformed. To calculate the change of the surface free energy, ΔG , in this case is not an easy task, since the Laplace equation of capillarity (equation (1.6)) has to be solved, and the approach used by Rapacchietta and Neumann¹⁹ has to be followed. However, if the particle in its final state is detached from the fluid interface and is fully immersed in one of the liquids (Figure 1.3(b)) the calculation of ΔG is straightforward. If the particle after its detachment is in the oil, the surface free energy of the system $G_o^{(2)}$ corresponding to the final state “2” is

$$G_o^{(2)} = \gamma_{ow}A_{ow}^{(2)} + \gamma_{po}A_{po}^{(2)} \quad (1.10)$$

where $A_{ow}^{(2)}$ is the area of the flat oil–water interface after the detachment and $A_{po}^{(2)} = A_p$. Subtracting equation (1.7) from equation (1.10) and taking into account equations (1.1) and (1.8), the following expression for the free energy of particle detachment into oil, ΔG_{do} is obtained

$$\Delta G_{do} = \gamma_{ow}(A_c + A_{pw}^{(1)} \cos \theta) \quad (1.11)$$

where $A_c = A_{ow}^{(2)} - A_{ow}^{(1)}$ is the area of the oil–water interface occupied by the particle when it is attached at the fluid interface. A similar derivation leads to the following expression for the free energy of particle detachment into water ΔG_{dw}

$$\Delta G_{dw} = \gamma_{ow}(A_c - A_{po}^{(1)} \cos \theta) \quad (1.12)$$

By means of equations (1.8) and (1.12), equation (1.11) can be expressed in the form

$$\Delta G_{do} = \Delta G_{dw} + \gamma_{ow}A_p \cos \theta \quad (1.13)$$

that gives the relation between the two free energies of particle detachment. It is obvious that the detachment of a hydrophilic particle ($\cos \theta > 0$) into oil needs more energy than into water ($\Delta G_{\text{do}} > \Delta G_{\text{dw}}$), while for the detachment of a hydrophobic particle ($\cos \theta < 0$) the opposite is true ($\Delta G_{\text{do}} < \Delta G_{\text{dw}}$). This is important for understanding the stabilisation of emulsions by solid particles (see Chapter 6). It is also seen that at $\theta = 90^\circ$ both energies are equal to each other. The minimum energy required for particle detachment irrespective into which of the bulk phases, ΔG_d (called simply the free energy of particle detachment) can be written as

$$\Delta G_d = \begin{cases} \Delta G_{\text{dw}} & \text{for } 0 \leq \theta \leq 90^\circ \\ \Delta G_{\text{do}} & \text{for } 90^\circ \leq \theta \leq 180^\circ \end{cases} \quad (1.14)$$

where ΔG_{dw} and ΔG_{do} are given by equations (1.12) and (1.13) (or (1.11)), respectively. The respective free energies of particle attachment to the fluid interface are given by the same equations taken with the opposite sign. The above equations ((1.8), (1.10)–(1.14)) are written in a rather general form. They depend on the particle shape implicitly through the respective areas. Therefore they are valid for any shape of the particle if the fluid interface can be considered flat up to the particle surface. Some special cases which satisfy the latter requirement are considered below.

1.2.2.1 Spherical particle

In this case the three-phase contact line is a circle with radius $r_c = r \sin \theta$ dividing the particle surface (with area $A_p = 4\pi r^2$) into two spherical caps, so that $A_c = \pi(r \sin \theta)^2$ and $A_{\text{pw}}^{(1)} = 2\pi r^2(1 + \cos \theta)$. With these expressions equations (1.12) and (1.13) yield

$$\Delta G_{\text{dw}} = \pi r^2 \gamma_{\text{ow}} (1 - \cos \theta)^2 \quad (1.15a)$$

$$\Delta G_{\text{do}} = \pi r^2 \gamma_{\text{ow}} (1 + \cos \theta)^2 \quad (1.15b)$$

These equations were derived by Koretsky and Kruglyakov³⁴ and later by others.^{35,36} In view of equation (1.14) they can be combined to give

$$\Delta G_d = \pi r^2 \gamma_{\text{ow}} (1 - |\cos \theta|)^2 \quad (1.16)$$

Therefore, the minimum energy needed to detach a spherical particle from the oil–water interface rapidly increases with particle size (as r^2). The free energies of particle detachment calculated by equations (1.15) and (1.16) with $r = 10 \text{ nm}$ and $\gamma_{\text{ow}} = 50 \text{ mN m}^{-1}$ are plotted against the contact angle in Figure 1.5. It is seen that the free energy of particle detachment into water (squares) is smaller than that into oil (circles) for hydrophilic particles ($\theta < 90^\circ$). The opposite is true for hydrophobic particles ($\theta > 90^\circ$). The (minimum) energy of particle detachment, ΔG_d (the line) increases from zero with an increase of the contact angle, reaches its

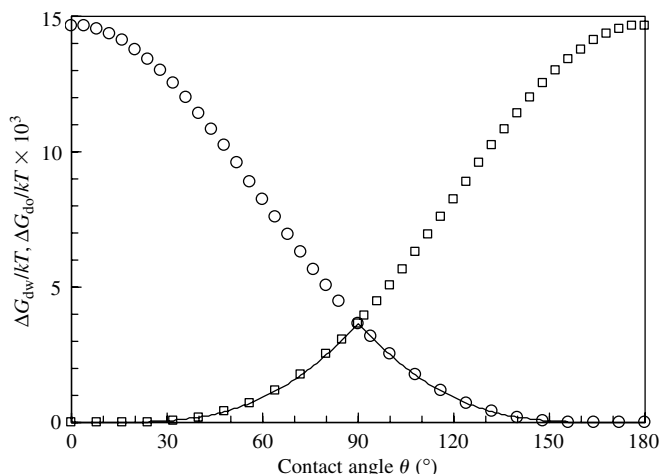


Figure 1.5 Free energy of detachment of a spherical particle into water (squares) and into oil (circles) calculated by equations (1.15) (a) and (b) with $r = 10$ nm and $\gamma_{ow} = 50$ mN m⁻¹ versus particle contact angle θ . The line is drawn according to equation (1.16).

maximum at $\theta = 90^\circ$ and then decreases to zero at $\theta = 180^\circ$. Except for very small and very large contact angles, ΔG_d is much greater than the thermal energy kT (the Boltzmann constant, k times the temperature, T). At contact angles around 90° even nanoparticles can be trapped at the fluid interface with energy which is several orders of magnitude greater than kT and sufficient to make their attachment irreversible. This is in sharp contrast to surfactant molecules, which can adsorb and desorb,⁴ and makes certain particles superior stabilisers of emulsions (Chapter 6) and foams (see later in this chapter).

The energy of particle attachment to the fluid interface, $\Delta G_a = -\Delta G_d$, is negative for all contact angles (except for the extremes), hence the particle attachment is thermodynamically favourable (this might not be true in the case of small particles and positive line tension acting to contract the contact line^{10,11}). Therefore colloidal particles with chemically homogeneous surfaces can spontaneously attach to fluid interfaces and are surface active. The reason is that part of the fluid interface with area A_c is removed (see equations (1.11) and (1.12)). ΔG_a and ΔG_d for nanoparticles with contact angles close to 0° or 180° can be comparable to the thermal energy. Such particles can exhibit a reversible attachment–detachment behaviour (similar to surfactants) which has been demonstrated by elegant experiments described later.

The above equations are also applicable for particles at spherically curved oil–water interfaces (drops), if the particle radius is much smaller than the drop radius. This case,

which is relevant to particle-stabilised emulsions, has been considered in Refs. [37] and [38] where more precise equations are obtained.

1.2.2.2 Non-spherical particles

In the case of non-spherical particles, the respective areas involved in equations (1.8), (1.10)–(1.14) will depend on at least two geometrical parameters characterising the particle dimensions (*e.g.* for rods these are the rod radius and length). Therefore the detachment energy will depend on the particle orientation and at least two characteristic sizes. This opens up the question of how to compare the free energies of detachment of particles with different shapes. The comparison can be done in different ways (*e.g.* by keeping constant one of the particle sizes or the total particle area¹⁵). A suitable way of comparison seems to be at constant particle volume. This makes sense because it is related to the answer to the question: *how will the free energy of detachment of a particle with contact angle θ change if we re-shape it keeping its volume constant?* This question is answered below in the case of two smooth bodies: a rod-like particle with rounded hemispherical ends and a rounded disk-like particle (Figure 1.6). They are both shapes of revolution with long and short semi-axes a and b , respectively. We will assume that the particles

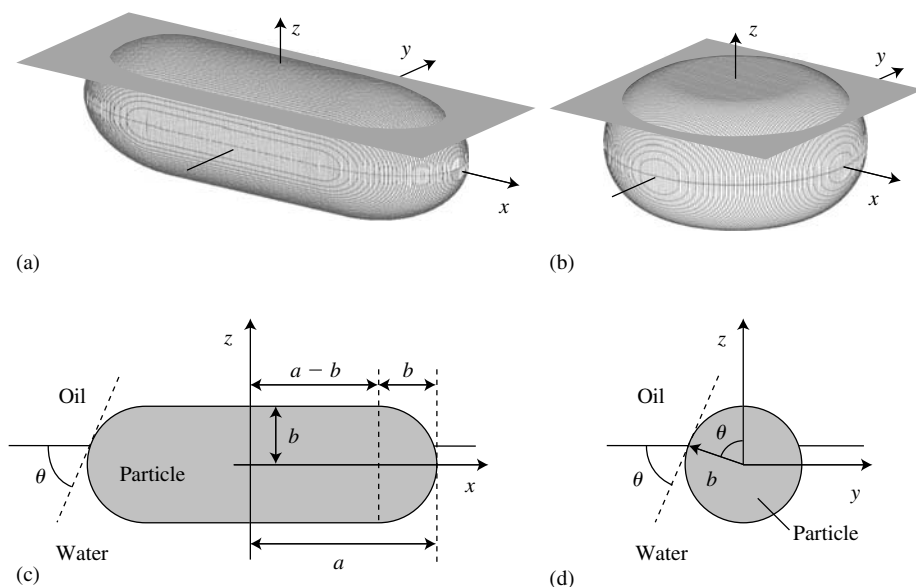


Figure 1.6 Non-spherical particles with contact angle $\theta = 45^\circ$ attached to a planar oil–water interface in the case of (a) a rod-like particle with hemispherical ends and (b) a rounded disk-like particle; (c) cross section along their long semi-axis, a ; (d) cross section of the rod-like particle along its short semi-axis, b .