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Trapping energy of a spherical particle on a curved liquid interface

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ABSTRACT

We derive the trapping energy of a colloidal particle at a liquid interface with contact angle θ and principal curvatures c_1 and c_2. The boundary conditions at the particle surface are significantly simplified by introducing the shift ε of its vertical position. We discuss the undulating contact line and the curvature-induced lateral forces for a single particle and a pair of nearby particles. The single-particle trapping energy is found to decrease with the square of both the total curvature $c_1 + c_2$ and the anisotropy $c_1 - c_2$. In the case of non-uniform curvatures, the resulting lateral force pushes particles toward more strongly curved regions.

1. Introduction

Colloidal particles trapped at a liquid phase boundary are subject to capillary forces which induce pattern formation and directed motion [1–3], and contribute to stabilize Pickering emulsions and particle aggregates [4,5]. Such microstructures affect the mechanical and flow behavior of liquid and gel phases [6], which in turn are relevant for material properties and biotechnological applications [7]. In many instances, the particles are trapped at curved liquid interfaces; rather surprisingly, even for spherical particles the influence of curvature on capillary forces is not fully understood at present.

At a flat interface, capillary phenomena arise from normal forces induced by the particle's weight or charge, or from geometrical constraints due to its shape [8,9]. As a simple example, an oat grain floating on a cup of milk is surrounded by a meniscus that results from the its weight and buoyancy; the superposition of the dimples of nearby grains reduces the surface energy and thus causes aggregation. Charged beads exert electric stress on the interface. The meniscus overlap of nearby particles causes a repulsive electrocapillary potential [10,11], whereas beyond the superposition approximation, a significantly larger attractive term is found [12–14]. In the absence of gravity and electric forces, capillary phenomena still occur for non-spherical particles: a capillary quadrupole may arise from surface irregularities [15,16], pinning of the contact line [17], and for ellipsoids [18–21], and favors the formation of clusters with strong orientational order.

A more complex situation occurs for interfaces with principal curvatures c_1 and c_2. The superposition of the weight-induced meniscus and the intrinsic curvature results in a coupling energy that is linear in the total curvature $H = c_1 + c_2$. Its spatial variation gives rise to a lateral force that drags a colloidal sphere along the curvature gradient [22,23]. Non-spherical particles interact through their capillary quadrupole with the curvature difference $\delta c = c_1 - c_2$, and thus experience both a torque and lateral force [24]. The latter is well known from the locomotion of meniscus-climbing insects and larvae, which bend their body according to the local curvature such that the capillary energy overcomes gravity [25,26]; through a similar effect, ellipsoidal particles prevent ring formation of drying coffee stains [27,28]. A recent experiment on micro-rods trapped at a water–oil meniscus illustrates both rotational and translational motion driven by curvature [3].

In this paper, we evaluate the geometrical part of the trapping energy of a spherical particle on a curved interface; thus we consider only terms that arise from the interface profile but are independent of body forces such as weight and buoyancy. Previous papers considered limiting cases such as a minimal surface ($H = 0$) [29], a spherical droplet ($\delta c = 0$) [30,31], or a cylindrical interface ($H = \delta c$) [32]; yet a comprehensive picture is missing so far. Here we treat the general case illustrated in Fig. 1, where both H and δc are finite, and obtain the trapping energy in a controlled approximation to quadratic order in the curvature parameters. We resort to the usual assumptions of constant contact angle θ, curvature radius much larger than the particle size, and small meniscus gradient.

As an original feature of the formal apparatus, we introduce the curvature-induced shift ε of the vertical particle position as an adjustable parameter, in addition to the amplitude ξ_2 of the quadrupolar interface deformation. As a main advantage, the boundary conditions at the contact line separate in two independent equations for ε and ξ_2, which are readily solved and provide a simple physical picture for the effects of the two curvature parameters.

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Fig. 1. Three-phase boundary of a spherical particle at a liquid interface with curvatures $c_2 = -\frac{1}{2}c_1$. The contact line is not a circle but undulates in space.

The paper is organized as follows. Section 2 gives a detailed derivation of the energy functional and the deformation field $\xi(\mathbf{r})$. From the usual variational procedure we find in Section 3 the energy as a function of the curvature parameters and the unknowns ε and ξ_2; then the energy is minimized with respect to the unknowns ε and ξ_2. In Section 4 we show that the solution satisfies Young's law at the three-phase boundary. In Section 5 we compare the trapping energy with previous work, and discuss the contact line and curvature-induced forces. Section 6 contains a brief summary.

2. Trapping energy

Here we derive the expression for the trapping energy and then evaluate it explicitly to quadratic order in the curvatures. It consists of the surface energies of all phase boundaries and the work done by the Laplace pressure both on the liquid interface and on the area occupied by the particle.

First consider a particle dispersed in the liquid phase with the smaller surface tension $\gamma_m = \min(\gamma_1, \gamma_2)$. The total energy

$$\gamma S_0 + W_0 + \gamma_m 4\pi a^2,$$

accounts for the interface area S_0, the work W_0, and for the particle surface $4\pi a^2$, as illustrated in Fig. 3a.

A particle approaching the interface gets trapped if the surface tensions satisfy the inequality $|\gamma_1 - \gamma_2| < \gamma$. The situation shown in Fig. 3 corresponds to $\gamma_m = \gamma_2$. The total energy

$$\gamma S + W + \gamma_1 S_1 + \gamma_2 S_2,$$

consists of a term γS proportional to the area of the liquid interface, the work W, and the particle segments in contact with the two phases, $\gamma_1 S_1 + \gamma_2 S_2$.

The trapping potential is given by the energy difference of these two situations,

$$E = \gamma(S - S_0) + W - W_0 + \gamma_1 S_1 + \gamma_2 S_2 - \gamma_m 4\pi a^2. \quad (1)$$

As illustrated in Fig. 2b, S is smaller than the unperturbed area S_0. Since Young's law needs to be satisfied everywhere along the three-phase contact line, S may show a significantly more complex profile than S_0.

In this section we evaluate the trapping energy to second order in the curvature. There are two issues requiring particular care. First, both the particle surface and the liquid interface contribute linear terms which, however, cancel each other. Second, at quadratic order, there are various contributions from the liquid interface, the area occupied by the particle, and the work done by the Laplace pressure; these terms carry comparable prefactors but opposite sign. The main result is given in Eq. (18) below.

2.1. Flat interface $H = 0 = \delta c$

We briefly recall the well-known results for zero curvature $w_0 = 0$, where both S_0 and S are flat [1]. Imposing local mechanical equilibrium relates the surface tension parameters to the contact angle θ at the three-phase line in terms of Young's law

$$\gamma_1 - \gamma_2 = \gamma \cos\theta. \quad (2)$$

Then the area of the liquid interface is reduced by

$$S - S_0 = -\pi r_0^2,$$

and the segments of the particle surface read

$$S_1 = 2\pi a^2 - 2\pi a z_0, \quad S_2 = 2\pi a^2 + 2\pi a z_0.$$

Here and in the following we use the vertical and radial coordinates of the contact line,

$$z_0 = a\cos\theta, \quad r_0 = a\sin\theta,$$

as illustrated in the left panel of Fig. 2. With Young's law one finds for a flat interface [1],

$$E_F = -\pi a^2 \gamma (1 - |\cos\theta|)^2. \quad (3)$$

The trapping energy vanishes for contact angles $\theta = 0$ and $\theta = \pi$. For $|\gamma_1 - \gamma_2| > \gamma$ Young's law has no solution, meaning that there is no stable trapped state. In the remainder of this section we consider corrections to E_F that arise at a curved interface.

2.2. Curved interface without particles

Now we consider the case of finite curvature. In Monge representation, $w_0(u, v)$ gives the interface height with respect to a tangent plane with coordinates u and v. The energy consists of two terms,

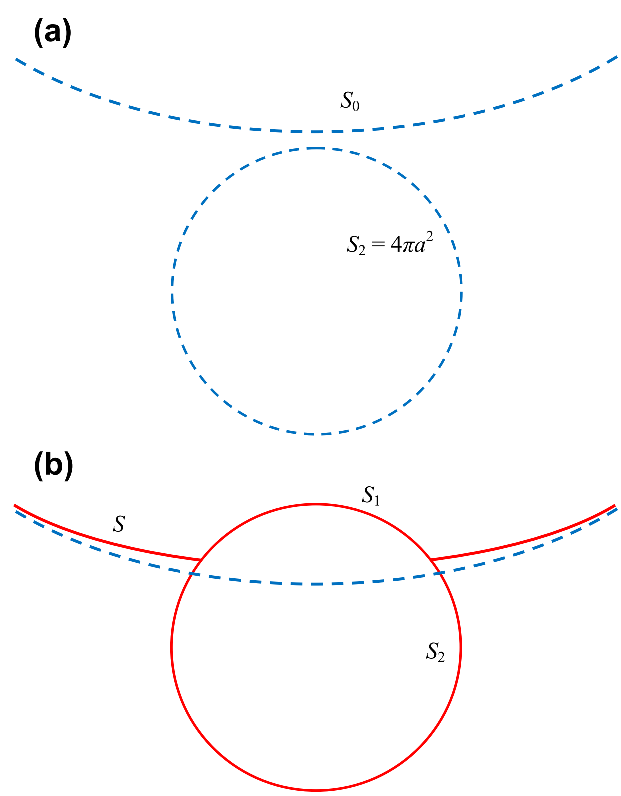

Fig. 2. Surface and interface areas contributing to the trapping energy in Eq. (1). The upper liquid is labeled "1" and the lower "2". (a) The particle is in the phase of lower surface energy (here $\gamma_2 < \gamma_1$); the liquid interface of area S_0 is described by (6). (b) Trapped state. The presence of the particle reduces the area of the liquid phase boundary to the value S and deforms its profile. The surface areas S_1 and S_2 are in contact with the two liquid phases. Note that the figure shows one vertical section of the interface; both S_0 and S undulate when rotating about the vertical axis.