

Anisotropic capillary interactions and jamming of colloidal particles trapped at a liquid-fluid interface

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We determine the capillary attraction and equilibrium configurations of particles trapped at a liquid-fluid interface due to the pinning of their contact line. We calculate analytically the asymptotic interaction energy between two particles and, numerically, the multibody energy landscape for up to four contacting particles. Our results are consistent with recent experiments. We show that a system composed of a large number of such particles behaves as a jammed system.

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Capillary interactions arise whenever particles that are floating between a liquid and a fluid distort the interface. These interactions originate from the dependence of the energy stored in the interface on the distance between the particles. More generally, interactions mediated by the elasticity of the medium in which particles are embedded occur in, e.g., phase-separating binary mixtures [1], critical fluids [2], bilayer membranes [3,4], and liquid crystals [5,6]. Capillary interactions play significant roles in several important technologies [7], including ore flotation [8], foam stabilization [9], and solid surface nanostructuring by deposition of two-dimensional colloidal crystal or aggregates [10–12].

The interaction between floating objects is well understood only when the contact lines can freely adjust their shape at the surfaces of particles: the weight of the particles induces an interfacial distortion that relaxes by capillarity, thereby mediating the interaction. However, exact numerical results are only available for the simplest case of two parallel cylinders [13]. Various approximations, e.g., Nicolson's superposition approximation [14], have been devised for spheres and cylinders [15–17].

Recently, strong capillary aggregations of floating colloidal spheres have been reported in a regime where the above gravity-induced interaction is negligible, due to the smallness of the particles [18]. This effect has been attributed to a *pinning* of the contact line at the surfaces of particles. The corresponding long-range interfacial distortion has a quadrupolar shape, which mediates a very strong interaction in units of $k_B T$. Similar behaviors were recently observed in experiments involving photolithography-fabricated curved discs having one hydrophobic and one hydrophilic side. It is then the edge of the curved disc that effectively pins the contact line [19].

In this paper, we model both experiments in a unified way and we produce exact results for the interaction between such “trapped” particles. We obtain the asymptotic interaction *analytically* without using uncontrolled superposition

approximations. We then compute numerically the exact interaction between two particles, and the *many-body* interaction between three and four particles, in order to understand collective behaviors. We finally attempt to connect our results with the *jammed-fluidized* transition for attractive particles under external stress [20,21], thereby proposing these systems as models for microrheological studies.

For definiteness, we consider floating particles that possess a fixed, nonplanar line that *pins* the fluid's interface (as in the above examples [18,19]). When such particles interact, their contact lines rise, tilt, and rotate rigidly with the particles; however, each line remains fixed in the local frame attached to its particle. For simplicity, and in agreement with Ref. [19], we assume that the contact lines depart weakly from a circle, thus excluding elongated particles. We also assume weak distortions of the interface height $h(x,y)$ relative to the plane (x,y) . This implies that the projection of each contact line onto this plane can be approximated by a circle, even when the particle is tilted. We describe the i th particle's contact line by the height function $\zeta_i(\phi_i)$ (see Fig. 1), that we expand in Fourier harmonics: $\zeta_i(\phi_i) = C_{0i} + \sum_n [C_{ni} \cos(n\phi_i) + S_{ni} \sin(n\phi_i)]$. Due to the fixed shape of the contact line in the particle's frame, some of the above coefficients are constrained while others are free. C_{0i} , which describes how the particle rises, is free (Fig. 1). The dipolar coefficients C_{1i} and S_{1i} , which parametrize the tilts of the contact line relative to the z axis, are also free. The lowest-order multipole bearing the information concerning the shape of the contact line is, therefore, the *quadrupole* [18]. We assume explicitly

$$\zeta_i(\phi_i) = C_{0i} + C_{1i} \cos \phi_i + S_{1i} \sin \phi_i + H_{2i} \cos[2(\phi_i - \beta_i)] + H_{4i} \cos[4(\phi_i - \beta_i)]. \quad (1)$$

The quadrupolar coefficient H_{2i} is a *constant*, associated with the shape of the contact line, and β_i is the free variable that represents the *rotation* of the particle about its normal \mathbf{n} (Fig. 1). For the sake of completeness we have added the lowest-order multipole that does not break mirror symmetry, $H_{4i} \cos[4(\phi_i - \beta_i)]$. The octupolar coefficient H_{4i} is a *constant* that describes how the contact lines depart from a

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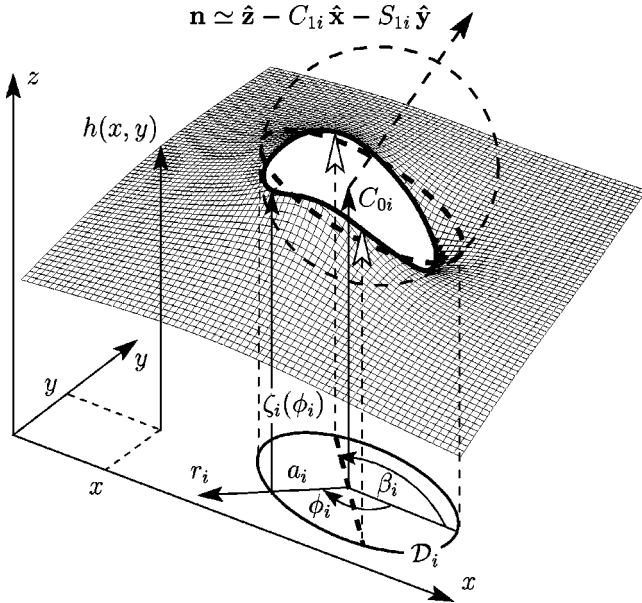


FIG. 1. Representation of the contact line of the i th particle and of its projection onto the reference plane.

purely quadrupolar shape. The two points where the height modulation of the contact line relative to its average plane is the largest define an *axis*, evidenced by the dashed line in the figures. For small deformations, the excess free energy associated with the surface tension γ of the interface is given by

$$F = \frac{\gamma}{2} \int d^2r (\nabla h)^2, \quad (2)$$

where $\mathbf{r} = (x, y)$. For micron-sized particles as we consider here, gravity is negligible [18]. At equilibrium, the first variation of F vanishes, which yields (see Fig. 1)

$$\int d^2r (\nabla^2 h) \delta h + \sum_i \oint_{\mathcal{D}_i} ds_i \frac{\partial h}{\partial r_i} \delta \zeta_i = 0, \quad (3)$$

where $ds_i = a_i d\phi_i$. Thus $\nabla^2 h = 0$. For fixed projected positions and rotations β_i of the particles, $\delta \zeta_i$ reduces to $\delta C_{0i} + \delta C_{1i} \cos \phi_i + \delta S_{1i} \sin \phi_i$, since the β_i 's and the coefficients H_{2i} and H_{4i} in Eq. (1) are constant. Hence the boundary equilibrium (freedom of the particles to rise and tilt) is expressed by the vanishing of the zeroth and first-order Fourier harmonics of $\partial h / \partial r_i$ on \mathcal{D}_i , which implies that the expansion of $\partial h / \partial r_i$ starts at $n = 2$,

$$\frac{\partial h}{\partial r_i}(r_i = a_i, \phi_i) = \sum_{n=2}^{\infty} c_{ni} \cos(n\phi_i) + s_{ni} \sin(n\phi_i). \quad (4)$$

The condition $\nabla^2 h = 0$ implies the integral equation

$$h(\mathbf{r}') = \sum_i \oint_{\mathcal{D}_i} \left[\frac{\partial h(\mathbf{r})}{\partial r_i} G(\mathbf{r}, \mathbf{r}') - h(\mathbf{r}) \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial r_i} \right] ds_i, \quad (5)$$

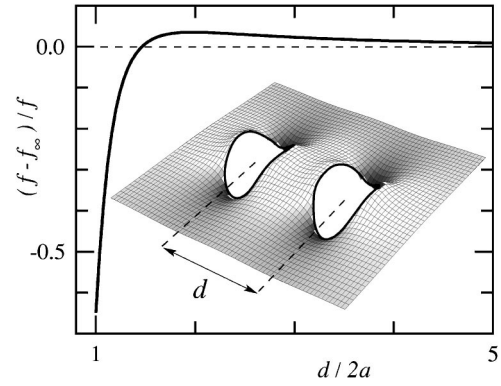


FIG. 2. Universal relative error between the exact force f and the asymptotic force f_∞ for two identical, purely quadrupolar particles ($H_{4i} = 0$) of size $a_i = a$, as a function of their reduced separation. Inset: calculated interface profile for β_i 's equal to zero.

known as the second Green identity [22], where $G(\mathbf{r}, \mathbf{r}') = \ln |\mathbf{r} - \mathbf{r}'| / 2\pi$ is ∇^2 's Green function. Evaluating Eq. (5) for \mathbf{r}' on the \mathcal{D}_i 's with the Fourier series (1) and (4), and with the multipolar expansion:

$$G(\mathbf{r}, \mathbf{r}') = \frac{1}{2\pi} \left[\ln r' - \sum_{n=1}^{\infty} \frac{r^n}{nr'^n} \cos[n(\phi - \phi')] \right], \quad (6)$$

we obtain a linear set of equations for the unknown variables C_{0i}, C_{1i}, S_{1i} , and c_{ni}, s_{ni} for $n \geq 2$. Given β_i, H_{2i} , and H_{4i} , these variables determine completely both h and $\partial h / \partial r_i$ on the \mathcal{D}_i 's. Finally, Eq. (5) determines $h(\mathbf{r})$ everywhere. The corresponding free energy is obtained by integrating Eq. (2) by parts and using $\nabla^2 h = 0$

$$\begin{aligned} F &= \frac{\gamma}{2} \int d^2r \nabla \cdot (h \nabla h) \\ &= -\frac{\gamma}{2} \sum_i a_i \int_0^{2\pi} d\phi_i \zeta_i \frac{\partial h}{\partial r_i} \\ &= -\frac{\pi\gamma}{2} \sum_{i,k=2,4} a_i [H_{ki} \{c_{ki} \cos(k\beta_i) + s_{ki} \sin(k\beta_i)\}]. \end{aligned} \quad (7)$$

Two particles. Consider two particles ($i = \ell, r$) separated by a distance d (Fig. 2). Solving analytically the linear system determining the unknown profile coefficients for $d \rightarrow \infty$ yields $F(d) = F_0 + F_4(d) + O(d^{-6})$, where the leading-order interaction is

$$F_4 = -12\pi\gamma \frac{a_\ell^2 a_r^2}{d^4} H_{2\ell} H_{2r} \cos[2(\beta_\ell + \beta_r)]. \quad (8)$$

It coincides with the result found in Ref. [18] from a superposition approximation in the spirit of Nicolson [14]. Note that it does *not* depend on the H_{4i} 's. At fixed d , the particles interaction is minimized when the axes of the particles are symmetrically rotated with respect to the line joining them

($\beta_\ell = -\beta_r$), as if the particles were geared. Then, the force acting between them is attractive, and is asymptotically given by

$$f_\infty(d) = -48\pi\gamma \frac{a_\ell^2 a_r^2 H_2 / H_{2r}}{d^5}. \quad (9)$$

The exact interaction energy $\Delta F(d, \beta_\ell, \beta_r)$ can be obtained for any distance by solving numerically the set of equations for the profile coefficients after truncating the Fourier expansions at a large but finite order, and checking for convergence. f_∞ turns to be a very good approximation for a wide range of separations, as evidenced in Fig. 2, for two identical particles with $H_{4i} = 0$. The corresponding force at contact is, however, $\approx 65\%$ weaker than f_∞ . The associated interaction energy is $-2.0\gamma H_2^2$, $\approx 20\%$ weaker than the approximation given by F_4 . For $\gamma \approx 70$ erg/cm² (water), $a \approx 1$ μm , and $H_2/a \approx 0.1$, this gives $\approx -1.4 \times 10^{-8}$ erg ($\approx -3 \times 10^5 k_B T$). Note that the contact force actually depends on the details of the higher Fourier components. When the H_{4i} 's are zero (purely quadrupolar particles), the numerically determined interaction turns out to be proportional to $\cos[2(\beta_\ell + \beta_r)]$ at any separation: the energy minimum is *degenerate*, corresponding to $\beta_\ell = -\beta_r$. Physically, this “gearing” condition is favored because it allows the heights ζ_i of the contact lines of particles to match, thereby preventing a strong local interfacial distortion [19]. Our exact calculations further showed that the presence of nonzero octupolar corrections H_{4i} actually *lifts* this degeneracy: the minimum energy is attained when $\beta_\ell = \beta_r = 0$ (axes of particles parallel to the separation vector), as intuited in Ref. [19]. Indeed, it is best to match the heights where the contact lines have a sharper distortion, i.e., at the tips of the axes.

Three particles. Owing to the strength of the above attraction ($\approx 10^5 k_B T$), we study the equilibrium states of three particles by assuming: (i) that each particle contacts at least another particle, (ii) that the particles can rotate around each other, in agreement with the experiments of Ref. [19]. We consider generic particles, i.e., $H_{4i} \neq 0$. Without loss of generality, we fix two particles at contact, and we explore the energy landscape as a function of the position of the third particle, described by the angle ψ (Fig. 3). For each ψ we minimize the energy with respect to the rotations β_i of the three particles.

We obtain two distinct branches exhibiting three metastable minima (see Fig. 3). The latter almost perfectly satisfy the above-mentioned “gearing” rule. The *curved-line* configuration A suggests a *three-body effect*, since the axes of the particles are not parallel to one another, contrary to the pairwise case. Indeed, repeating the calculation with pairwise interactions instead of the exact many-body interaction yields a straight line. The most stable, packed configuration is the triangle C with a radial orientation of the particles. One might argue that it best relaxes the strong interfacial distortion located at the facing tips of the axes of particles. The orthoradial triangle B is also very stable.

Four particles. To determine the equilibrium states of four contacting particles, we explore the energy landscape by fix-

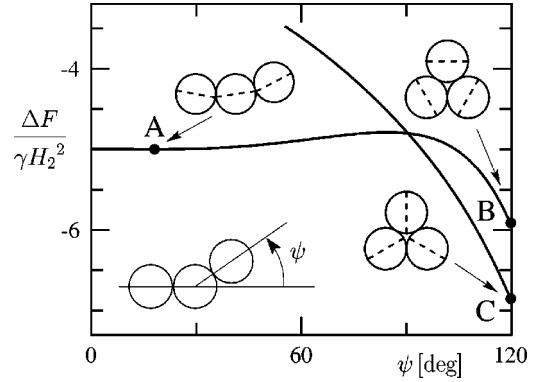


FIG. 3. Normalized interaction energy $\Delta F/\gamma H_2^2$ for three identical particles with $H_4 = 0.25H_2$ as a function of the configuration angle ψ . The two branches come from the minimization with respect to the angles β_i . The barrier associated with the minimum A is $\approx 3.6 \times 10^4 k_B T$ for $H_2 = 0.1$ μm .

ing the positions of three particles through the angle ψ_r , and minimizing with respect to both the position ψ_ℓ of the fourth one and all the rotation angles β_i (see Fig. 4). We obtain three branches and six equilibrium states.

As a new indication of a many-body effect, the “gearing” rule is strongly violated in configuration D and slightly violated in C. Contrary to the three-particle case, the *orthoradial* square B is more stable than the *radial* square E. One might suspect that since the gap between the particles is larger than in the triangular case, it is more important to relax the distortion stored at the tips of the axes on the sides of the square rather than in its center. Note, however, that such reasonings become more and more delicate as the number of particles increases. The fact that B and E are the most stable configurations suggests, as proposed in Ref. [19], that the ground state for many particles should be a square lattice with B, or equivalently E, as unit cell. We find again the curved-line A and different triangular arrangements with a fourth attached particle (C, D, F). Our results do successfully reproduce the various structures that can be locally seen in the experimental pictures of Ref. [19].

Such floating particles can be considered as a model system to study *jamming* phenomena in complex fluids. Jam-

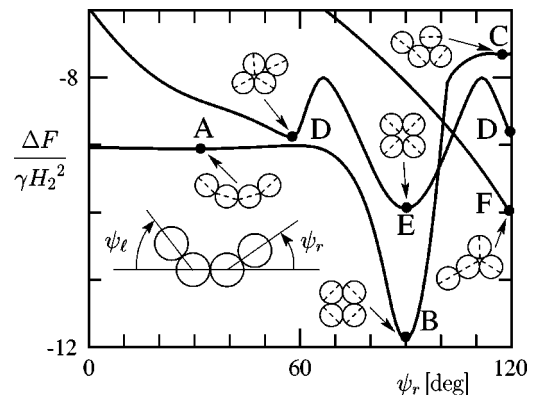


FIG. 4. Normalized interaction energy $\Delta F/\gamma H_2^2$ for four identical particles with $H_4 = 0.4H_2$ as a function of the angle ψ_r , specifying the position of the rightmost particle.

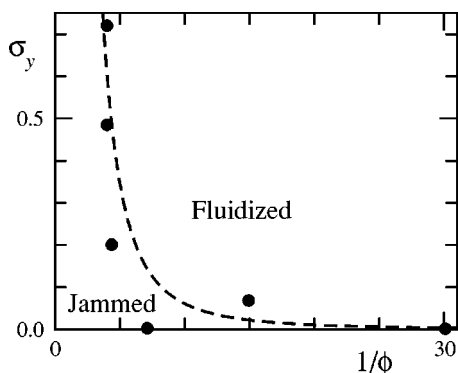


FIG. 5. Tentative jamming phase diagram extrapolated from the results for four particles. The dashed line is the power law $\sigma_y \sim \phi^{2.5}$.

ming occurs in the presence of either repulsive or attractive forces [21], when a disordered system gets trapped in phase space, for kinetic or energetical reasons, and thus exhibits a yield stress [20]. Aggregates of a large number of the “trapped” particles discussed in this paper should form by accretion of individual particles or small clusters. In the absence of irreversible sticking, at each accretion the particles

will rearrange until they fall in one of the many metastable configurations. They will thereby form a disordered structure with a yield stress. Such colloidal aggregates are, therefore, more akin to a foam [23] than to a collection of sticky spheres [24].

To test the relevance of this description in terms of jamming, we estimate the dependence of the yield stress σ_y on the volume fraction ϕ , from the energetical landscape for four particles (Fig. 4). For each metastable state, we set $\phi \propto 1/L^2$, where L is the distance between the farthest particles, and we estimate $\sigma_y \approx E_b/aL$, where E_b is the energy barrier towards the nearest minimum, and $\approx E_b/a$ the force required to rearrange a given state. This yields the diagram of Fig. 5, which is quite reminiscent of the phase diagram for attractive athermal systems proposed in Ref. [21], with a characteristic power law $\sigma_y \sim \phi^\mu$.

It should thus be very interesting to experimentally study the microrheological behavior of such particles’ aggregates. Indeed, direct observations would be possible because the system is two dimensional; furthermore, as we have shown, this is one of the few systems where exact many-body calculations are possible.

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