COMMUNICATIONS ARISING

Capillary attraction

Like-charged particles at liquid interfaces

ikolaides *et al.*¹ propose that the puzzling attraction that occurs between micrometre-sized particles adsorbed at an aqueous interface is caused by a distortion of the liquid interface that is due to the dipolar electric field of the particles and which induces a capillary attraction. Here we argue that this effect cannot account for the observed attraction, on the fundamental grounds that it is inconsistent with force balance.

To estimate the influence of the surface deformation, the authors assume that the sum total of the electrostatic pressure acting on the liquid interface is equivalent to an external force, F, pushing the particle into the water. The resulting deformation of the interface would give rise to a long-range interparticle interaction energy

$$U(r) = (F^2/2\pi\gamma) \ln(r/r_0)$$
 (1)

where γ is the surface tension, r is the distance between particles, and r_0 is an arbitrary constant. However, the electrostatic force acts on the particle and the liquid interface simultaneously, so equation (1) does not apply.

The force *F* on the sphere is balanced by surface tension, creating a dimple in the water surface. The shape of the dimple is governed by the Young–Laplace equation

$$[(1/R_1) + (1/R_2)]\gamma = \Delta p \tag{2}$$

If the force acts only on the particle, then the pressure difference across the interface $\Delta p \approx 0$ and the radii of curvature R_1 and R_2 of the surface are equal but opposite (Fig. 1). The resulting water level around an isolated sphere would be $h(r) = F/(2\pi\gamma) \ln(r/r_0)$ for small surface slopes, such that $F \approx 2\pi r_c \gamma h'(r_c)$, where $2\pi r_c$ is the length of the contact line. Owing to the long range of the logarithm, the force on the sphere is

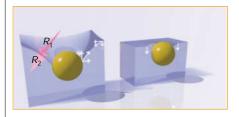


Figure 1 Pushing a sphere into water creates a dimple (left) in the surface, caused by the force on the particle being balanced by the surface tension. But if the electrostatic force pushing the sphere into the liquid is balanced by the electrostatic pressure on the liquid interface, there is no force on the rim and the surface is flattened again (right), inhibiting capillary attraction. R_1 , R_2 are the radii of curvature of the surface.

passed on to the rim of the vessel containing the liquid (Fig. 1, left).

The situation changes fundamentally when the force F is not external but originates from a surface pressure $\Delta p \propto 1/r^6$, as stated in ref. 1. Now the meniscus profile is $h(r) = -F/(8\pi\gamma) (r_c/r)^4$ —that is, very short range. The electrostatic force F pushing the sphere into the liquid is balanced by the sum total of electrostatic pressure on the liquid interface and there is no force on the rim of the vessel (Fig. 1, right). In contrast, by unquestioningly applying equation (1), one implicitly admits that there is also a force on the vessel, a force not balanced by any other force. This is inconsistent with Newton's third law.

Capillary attraction between spheres is caused by the overlap of their dimples, which reduces the total surface area of the water². The resulting attraction energy is

$$U(r) = -(F^2/\pi\gamma)(r_c/r)^6$$
 (3)

for large r. This interaction has a much shorter range than that shown in equation (1), even a shorter range than the dipoledipole repulsion between like-charged particles that is proportional to $1/r^3$, so overall there is no attraction at all. The capillary deformation of the interface contributes a mere $1.8 \times 10^{-5} \ kT$ to the interaction potential, so it is insignificant thermodynamically. Thus, the mechanism proposed by Nikolaides et al. does not account for the observations, and the origin of the observed attraction remains enigmatic.

Mischa Megens*, Joanna Aizenberg†

- *Philips Research, 5656 AA Eindhoven, The Netherlands e-mail: mischa.megens@philips.com †Bell Laboratories/Lucent Technologies, Murray Hill. New Jersey 07974-2008. USA
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Nikolaides et al. reply — Our experiment¹ provides a clear measure of the interactions between charged particles at fluid–fluid interfaces and demonstrates that there can be a long-range attractive interaction between such particles.

However, Megens and Aizenberg raise important points about our interpretation of these results. Our calculations account for the electrostatic stresses acting on the fluid–fluid interface, but neglect the force that the electric field exerts on the particle itself. A detailed evaluation of this force, obtained by calculating the change in electrostatic energy as the particle is pushed into the fluid, shows that the interfacial force pulling the particle out of the fluid is exactly cancelled by the electrical force pushing the particle into the fluid, in agreement with the suggestion of Megens and Aizenberg.

This creates a puzzle: the data show unambiguously that there is a long-range attraction, but what is its origin? The particles have a long-range repulsive interaction, owing to their charges; this is dipolar in character, with the electrostatic energy decaying as $1/r^3$. The attractive interaction must balance this electrostatic repulsion, so, if it decays as a power law, the attractive interaction energy must decay more slowly than $1/r^3$ to create the stable energy minimum observed experimentally. This eliminates possibilities such as asymmetries in the contact line or fluctuation-induced forces, all of which have a power-law decay that is more rapid than $1/\hat{r}^3$. The most likely interaction that has sufficient range therefore remains capillary distortion of the interface.

Capillary distortion can occur only if there is an imbalance between the force pulling the particle into the water and the force pushing the interface outwards towards the oil. However, it is sufficient for these forces to be imbalanced only up to distances comparable to the interparticle separation: this would still lead to distortion of the interface between the particles, causing the attractive force. The resolution of the puzzle could lie in charges on the particles on the oil side, rather than on the water side². As the density of free charges in oil is much lower than that in water, the screening length is correspondingly larger; this significantly extends the range of the force imbalance and can account for our experimental observations. The origin of the capillary distortion therefore remains electrostatic in nature.

We have since confirmed that the particles do have a measurable charge, even when immersed in oil. Measurements of the electrophoretic mobility and pair correlation functions of these particles indicate that their charge can be as high as 200e in oil. In the absence of additional solubilized charges, this would result in a screening length of the order of 20 µm for the particle volume fraction of about 10⁻⁴ used in our experiments. This is larger than the particle separation, allowing the force imbalance between the particle and the interface to persist far enough for significant interfacial distortion to exist at scales comparable to the interparticle separation. We therefore believe that electric-field-induced capillary distortion remains the likely culprit for the attractive interactions between like-charged interfacial particles.

M. G. Nikolaides, A. R. Bausch, M. F. Hsu, A. D. Dinsmore, M. P. Brenner, C. Gay, D. A. Weitz*

*Department of Physics, and Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA e-mail: weitz@deas.harvard.edu

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