COLLOIDS AT INTERFACES

Pinned down

A colloidal particle straddling an air/water interface experiences an unexpectedly large viscous drag.

Vinothan N. Manoharan

In 1903 Walter Ramsden found that an air bubble placed in a liquid suspension of microscopic particles "can be seen to pick up the particles […] and to retain them obstinately […]"[1]. Ramsden had discovered the strong affinity of colloidal particles to fluid interfaces, an affinity that a century later can be harnessed to make microstructured materials such as Pickering emulsions, colloidosomes and bijels[2]. The production of these materials relies not only on the particles obstinately sticking to the interface, but also on their ability to move about and self-assemble. In this regard, Maurizio Nobili and colleagues[3] show in Nature Materials that the motion of a colloidal particle confined to lie at an air/water interface is, surprisingly, slower than the motion of the particle in the bulk of the fluid.

To understand this finding, one ought to consider the classical picture of how a colloidal particle sticks to an air/water interface (Fig. 1a)[4]. If the particle is a smooth sphere, and small enough so that its weight can be neglected, its equilibrium position with respect to the fluid interface can be determined by minimizing the sum of three interfacial energies (those corresponding to the water/air, water/particle, and air/particle interfaces). For typical values of the interfacial tensions, a micrometre-sized particle that adsorbs to the interface lowers the total interfacial energy by 10^3–10^6 times the thermal energy. This energetic argument explains why the interface can so 'obstinately' retain the particles. In the lowest-energy configuration, the interface remains flat, and the top of the particle protrudes into the upper phase by an amount determined by the contact angle (as described by Young's equation). However, the equilibrium state is not a static situation: a colloidal particle is always in motion owing to the constant and random bombardment of solvent molecules. As Einstein showed, the diffusion coefficient that characterizes this Brownian motion in the bulk varies inversely with the drag force on the particle, which is proportional to the fluid's dynamic viscosity. Hence, one expects that the diffusion coefficient of a particle sitting at the air/liquid interface should increase with the contact angle, because the larger its magnitude the more the particle protrudes into the less viscous air phase. The same prediction follows from more rigorous hydrodynamic arguments[5].

Yet by measuring the particle's Brownian motion in the plane of the interface (and avoiding any contamination that might affect its properties), Nobili and co-authors found exactly the opposite trend: as they increased the contact angle (that is, by using progressively more hydrophobic particles), the particles diffused more slowly. They observed this same trend for a variety of different particles, which suggests that the phenomenon originates from some common feature of the particles. The authors propose that this common feature is nanoscale heterogeneity. At some small scale, all solid surfaces are irregular, because of the presence of surface functional groups or topographical features (or both). These 'defects' can pin a contact line. If the pinning is much stronger than the thermal energy, the local contact angle might fluctuate as thermal capillary waves lap at the boundary of the particle; if the pinning is weak, the position of the contact line might hop randomly from defect to defect, driven by the thermal energy. In either case, the fluctuation–dissipation theorem predicts that these fluctuations must couple to a dissipative or drag force. Such additional dissipation adds to the usual drag force on a particle in a viscous fluid, which leads to a reduced diffusion coefficient.

At present, this explanation is supported only by indirect evidence. Nobili and colleagues show that the length scale between defects, determined by fitting two different pinning models to the data, is on the order of a nanometre, and hence comparable to the expected distance between functional groups on the particle's surface. But such small defects have never been seen directly, and there is no evidence that the functional groups are capable of pinning the contact line. Nevertheless, the results are consistent with a growing body of work showing — in the same, indirect way — that nanoscale heterogeneities do exist in colloids and are important for understanding their behaviour at fluid interfaces. In fact, recent experiments have shown that the attractive interactions between particles at interfaces[6], as well as the relaxation rates of particles that breach an interface[7,8], appear to be governed by surface defects. And because colloids typically have surface groups that keep the particles from aggregating, surface defects and contact-line pinning may be inherent features of colloidal systems. The effects of heterogeneities on the wetting dynamics of macroscopic surfaces (which offer easier control over heterogeneities than colloids do) have been extensively studied, but the molecular origins remain a point of discussion[9].

Nobili and co-authors suggest that future work could look for similar "ultraslow diffusion" in other systems, such as proteins on membranes, or colloidal particles at liquid/liquid interfaces. Yet the characterization of the observed slow diffusion as 'ultraslow' is debatable: although the measured diffusion coefficients at the air/water interface are indeed much smaller than those predicted by hydrodynamic theories[5], they are comparable to those in bulk water. So one shouldn't expect the enhanced drag to significantly slow down the self-assembly of particles at interfaces, except possibly when the contact angle is large.

What could more significantly affect the assembly of particles at interfaces are interparticle capillary interactions, which arise because the interface must be rippled, not flat, when the particle surfaces are heterogeneous[6] (Fig. 1b). Although this is not a new argument, it assumes the existence of pinning sites. Nobili and co-workers' findings provide the most compelling evidence to date that such sites may be a general feature of colloids. Furthermore, their elegant experiment is a straightforward assay for surface heterogeneities.

Much work remains to be done to understand what the heterogeneities are and how strongly they pin the contact line. But there is strong impetus to find out: as recently shown, nanoscale heterogeneities can cause a particle to migrate on a curved surface[10]. So if pinning could be understood, it could be harnessed to create new dynamics and new assembly pathways. The experiments of Nobili and co-workers point the way toward getting these 'obstinately' sticky systems to further yield to our control.

Vinothan N. Manoharan is at the Harvard John A. Paulson School of Engineering and Applied Sciences and at the Department of Physics, Harvard University, Cambridge, MA 02138, USA.
e-mail: vnm@seas.harvard.edu

References

1. Ramsden, W. *Proc. R. Soc. Lond.* **72,** 156–164 (1903).
2. McGorty, R., Fung, J., Kaz, D. & Manoharan, V. N. *Mater. Today* **13,** 34–42 (2010).
3. Boniello, G. *et al. Nature Mater.* **14,** XXX–YYY (2015).
4. Binks, B. P. & Horozov, T. S. *Colloidal particles at liquid interfaces*. (Cambridge University Press, 2006).
5. Fischer, T. M., Dhar, P. & Heinig, P. *J. Fluid Mech.* **558,** 451–475 (2006).
6. Park, B. J. & Furst, E. M. *Soft Matter* **7,** 7676–7682 (2011).
7. Kaz, D. M., McGorty, R., Mani, M., Brenner, M. P. & Manoharan, V. N. *Nature Mater.* **11,** 138–142 (2012).
8. Chen, L., Heim, L.-O., Golovko, D. S. & Bonaccurso, E. *Appl. Phys. Lett.* **101,** 031601 (2012).
9. Bonn, D., Eggers, J., Indekeu, J., Meunier, J. & Rolley, E. *Rev. Mod. Phys.* **81,** 739 (2009).
10. Sharifi-Mood, N., Liu, I. B. & Stebe, K. J. *Soft Matter* (2015). doi:10.1039/C5SM00310E
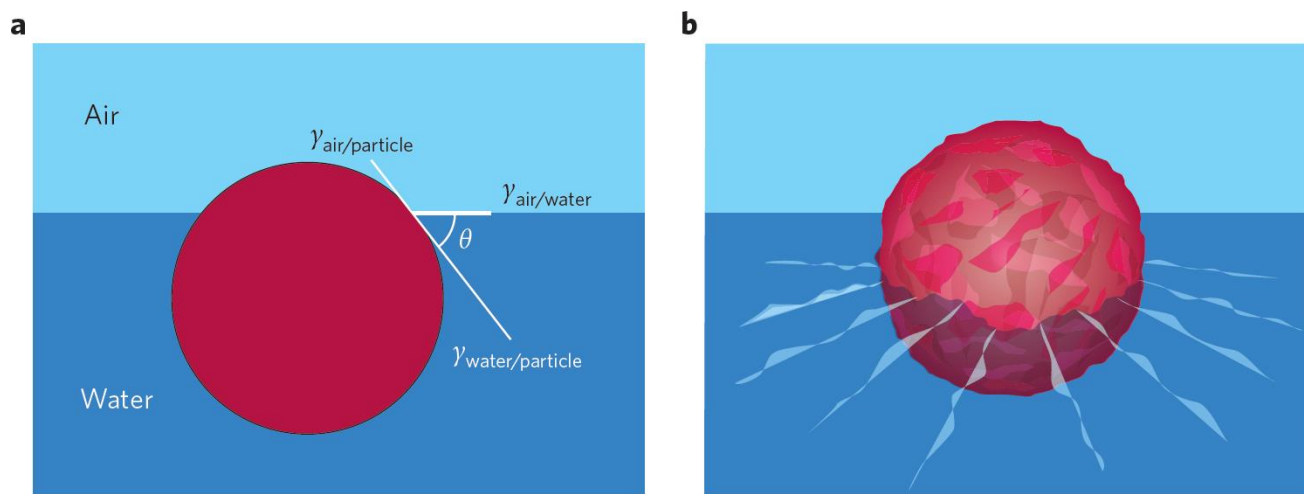
Figure 1 | Increased drag of a colloidal particle straddling a fluid/fluid interface. **a**, At equilibrium, colloidal particles 'stick' to fluid/fluid interfaces (here, an air/water interface) because this configuration minimizes the total interfacial energy of the system (the major contribution typically being the decrease in fluid/fluid interfacial energy, $\pi R^2 \sin^2\theta\, \gamma_{air\text{-}water}$, where γ is the surface tension of the air/water interface, R the particle's radius, and θ its contact angle). The position of the particle at the interface depends solely on its contact angle θ. **b**, The unexpected higher viscous drag of a colloidal particle at a fluid/fluid interface is attributed to the pinning of the particle/fluid-interface contact line by nanoscale heterogeneities on the particle's surface[3], which also cause ripples on the nearby fluid/fluid interface. Fluctuations in the contact angle or in the position of the contact line give rise to an additional drag force on the particle. Surface heterogeneities and interface ripples are not depicted at scale.