

either by changing the ice sheet's basal thermal regime or by introducing water into the path of the ice stream through periodic drainage events.

If this proves to be the case, it would substantially change our understanding of the effect of subglacial lakes on ice-sheet stability. It indicates that basal hydrology needs to be accounted for in numerical models of ice-sheet motion because it has the potential to rapidly induce fast flow. The recent sudden acceleration of ice streams in Greenland<sup>6,7</sup>, and its resultant effect on the mass balance of the Greenland ice sheet<sup>8</sup>, underscores the importance of understanding the dynamics of ice-sheet response to climatic change.

Might the geographical coincidence of the Recovery lakes and the start of fast flow be just that, a coincidence? So far we have not seen any other large subglacial lakes at the heads of ice streams. But Antarctica remains one of the most poorly mapped parts of our planet — we know more about the surface of the dark side of the Moon than we do about the bedrock or even the surface topography of Antarctica. Antarctica's surface is being mapped at ever higher resolution with remote-sensing satellites such as NASA's ICESat or the planned European Space Agency mission CryoSat-2, but radar imaging of the bedrock is not keeping pace. Proposed missions to put ice-sounding radar instruments on board a satellite, with the goal of mapping the bed in Greenland and Antarctica, have yet to be approved. For now, continued airborne and ground-based geophysical exploration is the only way forward for imaging the ice sheet's base.

During the forthcoming International Polar Year, a number of land traverses and aerial campaigns are planned for Antarctica. In 2008, a Norwegian–US traverse will survey the Recovery lakes area. This was last visited by the US–UK traverse from the South Pole to Dronning Maud Land in 1965–66. Interestingly, that early expedition, which was equipped with one



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**Figure 2 | Scenes from above the shores of the Recovery lakes.** The 1965–66 US–UK South Pole–Queen Maud Land traverse, showing a Sno-Cat tractor and, in the background, a ‘rolly’ tyre set containing fuel, and the ice-sounding radar antennae. The tractor is just crossing a crevasse at the edge of the Recovery ice stream, near where Bell *et al.*<sup>2</sup> have now discovered four subglacial lakes.

of the first radars, also crossed over the lakes discovered by Bell and colleagues (Fig. 2). The radar equipment was relatively primitive and used only intermittently, so the lakes were not identified in the field. But a logbook duly noted that Gordon de Q. Robin, then head of the Scott Polar Research Institute in Cambridge, UK, and one of the pioneers of radar glaciology, had suggested the existence of a “... possible melt-layer at the bottom of ice cap”.

The implications of this early prediction for ice flow are just starting to be appreciated, as Bell *et al.*<sup>2</sup> make the link between subglacial lakes and the onset of one of the largest ice streams in Antarctica. ■

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## PHYSICAL CHEMISTRY

# Oil on troubled waters

David Chandler

**The nature of the boundary between water and oil is crucial to many nanometre-scale assembly processes, including protein folding. But until now, what the interface really looks like remained in dispute.**

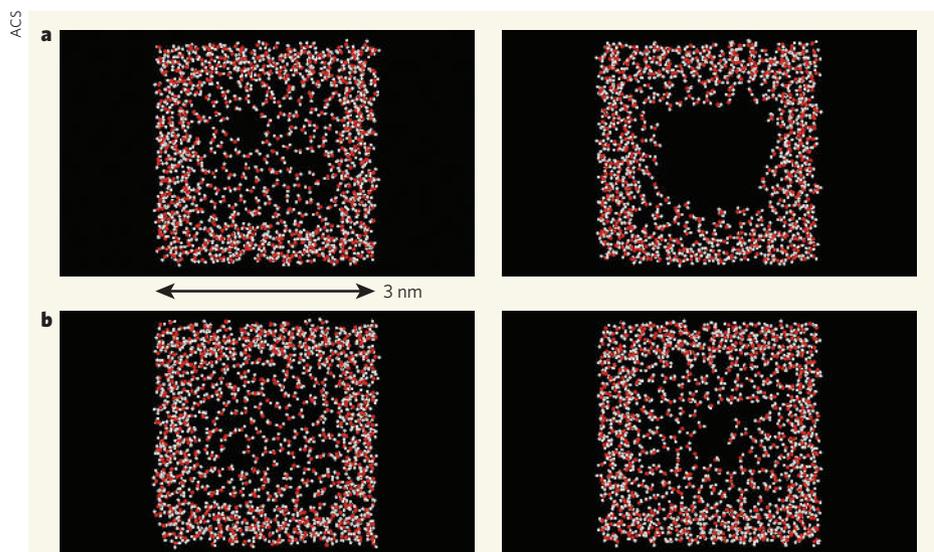
At the boundary between liquid water and water vapour, an interface forms that is marked by an area of lower-than-average density. The same sort of ‘depletion layer’ also occurs when water comes into contact with a sufficiently large hydrophobic surface — oil, in the most notorious instance, and various other organic molecules. According to theory, this happens because

hydrophobic surfaces provide no opportunity for water molecules to establish their usual hydrogen bonds. Without this adhesive force, the molecules move away from the surface to seek such bonds in the bulk of the liquid.

As lucid as this explanation might seem, experimental confirmation has so far been surprisingly elusive. But at last two independent

groups of researchers — Poynor *et al.*<sup>1</sup>, writing in *Physical Review Letters*, and Mezger *et al.*<sup>2</sup>, writing in *Proceedings of the National Academy of Sciences* — provide experimental confirmation of a depletion layer at the interface between water and a hydrophobic surface. And calculations of the molecular dynamics of water confined by two surfaces with nanometre-scale patterns of hydrophobic and hydrophilic regions, described by Giovambattista *et al.*<sup>3</sup> in the *Journal of Physical Chemistry C*, provide further grist to the mill.

The prediction that liquid water borders with oil in the same way it does with vapour was first made more than 30 years ago<sup>4</sup>. Since then, the idea has been bolstered by further theoretical analysis<sup>5</sup>, and has helped in understanding the forces that stabilize the assembly of hydrophobic molecules, among them the



**Figure 1 | Depletion in action.** In Giovambattista and colleagues' simulations<sup>3</sup>, water molecules from a large bath of water are confined between two parallel, hydrophobic square plates of side 3 nanometres (to be imagined in front of and behind the plane of the image) separated by 0.6 nanometres. **a**, In this case, one layer of hydrophilic groups is added to ring the outer edges of the otherwise hydrophobic plates. The two images show states between which the system fluctuates; depletion is visible in both, but is most apparent in a large central area in the right-hand image. **b**, If two hydrophilic layers ring the plates, the hydrophobic domain is reduced to a disc less than 2 nanometres in diameter. The degree of density fluctuation is sharply reduced. (Figure adapted from ref. 3.)

building-blocks of proteins, on nanometre and larger length scales<sup>5,6</sup>. Yet despite these successes, the depletion layer has been such a slippery customer experimentally that its existence has even been called into question<sup>7</sup>.

The reason for this is that, under standard conditions of room temperature and atmospheric pressure, liquid water and vapour very nearly coexist: the free-energy difference per molecule between the two phases is just a fraction of the uncertainty in a molecule's energy that results from ubiquitous thermal fluctuations. An oily surface that is capable of nucleating vapour-like interfaces in water can therefore also nucleate large, metastable vapour bubbles. Such bubbles are transient, non-equilibrium structures, but the density fluctuations that they cause are sufficiently long-lived to confuse observations of the equilibrium interface structure. Furthermore, the interface can wander in space at little free-energy cost. Van der Waals forces between hydrophobic molecules and water limit this translation, but by pulling the interface close to the oily surface, they make the boundary difficult to see.

Poynor *et al.*<sup>1</sup> and Mezger *et al.*<sup>2</sup> get around the bubble problem by meticulous preparation of their respective hydrophobic organic surfaces. They resolve the interface, which is only a few molecules thick, using synchrotron radiation sources that produce brilliant X-ray beams. The measurements clearly show a layer of depleted average water density that runs along an extended hydrophobic surface — just as the average density of water within a few tenths of a nanometre of its intrinsic liquid–vapour interface is depleted relative to that of the bulk liquid.

Large density fluctuations such as those that

make X-ray measurements difficult are intrinsic to hydrophobic forces that guide molecular assembly. Bulk liquids are almost incompressible and strongly resist density fluctuations needed to accommodate solvation — the reorganization of solvent molecules that occurs when a solute molecule is introduced. The associated high free-energy cost can be balanced if there are very strong attractive forces between solvent and solute. Hydrophobic species have no such forces to compete with the hydrogen bonding between water molecules, so their solvation is generally costly.

Nevertheless, if a large enough cluster of a hydrophobic species does manage to become hydrated, a hydrophobic surface of low curvature may extend over a nanometre or more. In this case, the nucleation of a soft, vapour-like interface with the liquid is energetically favoured. Unlike in bulk liquids or at solid surfaces, the resulting fluid interfaces can be deformed by forces as weak as those produced by typical thermal fluctuations. The mechanism of hydrophobic assembly so important to protein structuring is thus apparent: the reorganization of the solvent required to accommodate small, separated hydrophobic species is more costly than is the accommodation of the clustered species, provided the cluster is nanometre-scale or larger.

In measuring a depleted water density where water meets an extended hydrophobic surface, the new experiments<sup>1,2</sup> have verified the existence of interfacial fluctuations indirectly. If the average density is, say, half that of bulk water, this can only mean that the instantaneous density is as often at the bulk value as it is at the vapour value. Further experimental work is required to see the fluctuations explicitly.

In computer simulations of liquid water with large hydrophobic solutes<sup>8</sup>, fluctuations were noted as long ago as 1995. They were further inferred from the observation several years later of huge fluctuations in forces required to trap a film of water between hydrophobic and hydrophilic solid surfaces<sup>9</sup>. A simulation of a hydrated carbon nanotube provides another case in point<sup>10</sup>: in this example slight adjustment of parameters proves sufficient to move the system from a regime in which the tube is mostly filled with water, to another in which the tube is mostly empty. The dynamics of the transformation involve collective motion of many water molecules, suggesting the possibility of nanometre-scale steam engines that are perhaps already harnessed in some biomolecular motors.

Giovambattista and colleagues<sup>3</sup> add illustrations of an aspect related to these nanometre-scale manifestations of fluctuations and liquid–vapour coexistence. Altering the hydrophobic surface, for example by the inclusion of hydrophilic units, should bring significant changes to the interface. Natural hydrophobic systems such as proteins generally have heterogeneity of this sort: it is their 'amphiphilic' character that allows them to be solvated at reasonable cost. Giovambattista *et al.* perform simulations of water confined between patterned hydrophilic and hydrophobic surfaces, and record collective fluctuations evocative of dynamic equilibrium between liquid and vapour (Fig. 1). Hydrophilic heterogeneities tend to pin the soft fluid interface to the otherwise oily surface, and a large enough hydrophilic region removes it altogether. Increasing pressure moves water away from phase coexistence, and the authors show that enough pressure removes the interface, and the mean depletion associated with it.

Such computational work throws the gauntlet back to the experimentalists, to see whether they can observe such behaviour in the laboratory. Much could ride on the answer, as knowing the timescales and energetics of interface fluctuations, as well as their sensitivity to hydrophilic inhomogeneities, could be central to understanding kinetics of self-assembly. One only hopes that this time we will not have to wait another 30 years for experimental validation. ■ David Chandler is in the Department of Chemistry, University of California, Berkeley, California 94720, USA. e-mail: chandler@cchem.berkeley.edu

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