

Figure 1 Molecular model of a lipid bilayer–water interface. The lipid bilayer is dipalmitoylphosphatidylcholine. Bulk water molecules are green, whereas the molecules most involved in solvation — forming favourable interactions with neighbouring hydrophilic lipid atoms — are blue. The hydrophilic lipid atoms are highlighted in black ($\text{N}(\text{CH}_3)_3$ groups and phosphate phosphorus) and red (phosphate oxygen and carbonyl oxygen). The structure of the interface is distinct from that of bulk water or an air–water interface, in that the hydrophilic groups are well mixed with the water molecules. In their experiment, Benderskii and Eissenthal¹ observe the behaviour of a solute at a similar interface between a lipid-like monolayer and water. (Courtesy of D. Tobias, Univ. California, Irvine, and M. L. Klein, Univ. Pennsylvania.)

Benderskii and Eissenthal are particularly interested in what happens at the interface when the water surface is covered with a lipid-like monolayer of protonated fatty acid. This membrane-like layer contains both hydrophobic and hydrophilic regions, pointing towards the air and water respectively. The effect of the lipid-like layer on the properties of the interface can be monitored in two ways. First, the strength of equilibrium solvation of the dye at the interface can be measured from the size of the frequency shift in the dye absorption spectrum. Second, the solvation dynamics can be tracked using ultrashort laser pulses. Benderskii and Eissenthal find that both the equilibrium solvation and the solvation dynamics are sensitive to the presence of the lipid-like layer.

Structurally, the hydrophilic (protonated acid) ends of the lipid-like layer are densely clustered at the interface with water, so one might expect this interface to be uniquely organized. Indeed, Benderskii and Eissenthal show that the equilibrium solvation of the dye molecules at the lipid interface is of intermediate strength between bulk water and an air–water interface. Figure 1 shows a ‘snapshot’ from a molecular simulation of a similar environment — a lipid bilayer interface with water². In this membrane-like configuration, the interface with water has a mixed molecular character, with hydrophilic groups (black and red) interspersed with neighbouring water molecules (blue).

The lipid-like layer can also have an effect on solvation dynamics. At a bare air–water

interface, solvation dynamics are similar to those in bulk¹. But Benderskii and Eissenthal show that solvation occurs roughly twice as fast at the interface with the lipid-like layer as it does in bulk water or at an air–water interface.

The response time of the solvent is not simply considerably faster with the lipid-like layer — it is also different. The diffusive response time of bulk water can be described by two components: a faster solvation component (of around 250 femtoseconds) and a slower component (around 1,200 femtoseconds). With the lipid-like layer, the faster component actually increases to about 400 femtoseconds, but the slower component is suppressed. The net result is a shorter overall solvation time. The faster component seen at the air–water interface or in bulk water is mostly associated with molecular reorientation, whereas the slower component is more associated with collective diffusion of the solvent. The authors explain the suppression of this slower component by the lipid-like layer as the result of interfacial interactions that break up the extended network of water hydrogen bonds close to the interface. This would reduce the tendency of the solvent to respond collectively, reducing the importance of the slower collective motion.

The hydrophilic groups in the lipid-like molecules can themselves act as a solvent, so it is best to think of the lipid–water interface as an alternative solvent, rather than as a perturbed water environment. The change in solvation dynamics, relative to bulk water or the air–water interface, is consistent with this point of view. The authors note that the sol-

Materials science

Turbulent creep

Applying long-term, constant stress to ice causes it to deform like a plastic, meaning that it won't spring back to its original shape. The deformation has typically been thought to be a smooth dynamical process similar to the laminar flow of fluids. But on page 667 of this issue, M.-C. Miguel and co-workers show that the way ice flows under stress is actually turbulent.

Miguel *et al.* use a technique called acoustic emission — recording of acoustic waves emitted during plastic deformation — to measure the internal dynamics of squeezed ice. They find that one-dimensional defects in the crystalline lattice, known as dislocations, move in intermittent bursts. And from the particular statistical distribution of the

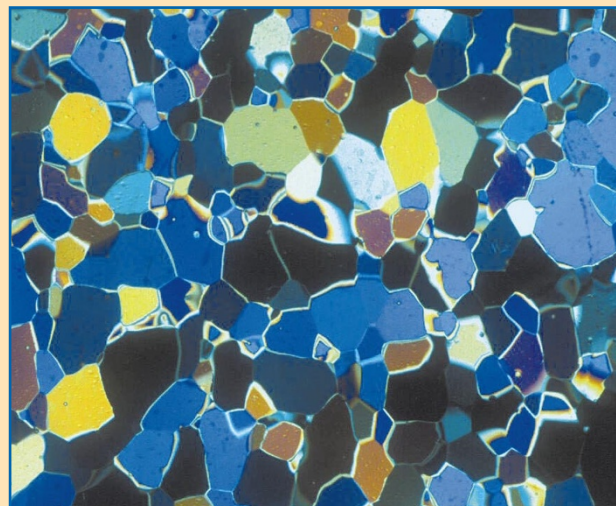
energies associated with each acoustic burst (it follows a power law) they conclude that plastic deformation in ice is more akin to turbulent flow than laminar flow.

The textbook view of plastic deformation is that the dislocations glide and slip along smoothly. But this is true only of average behaviour over large length scales. A close look at artificial granular ice reveals a complex and unpredictable structure, as the image on the right illustrates. These crystals are enhanced by polarized light and the average grain size is about 1.2 micrometres.

To confirm that the effect they have identified is not specific to ice, Miguel and co-workers have done numerical simulations; what they have found is that turbulence should

be considered a general feature of creep flow. These results should have implications for our understanding of plastic

deformation more generally, and have practical bearing on problems in materials science and engineering. **Josette Chen**



M.-C. MIGUEL ET AL.