

Putting the squeeze on liquid films

Squeezing a liquid into a tight space, such as the narrow gap between two plates, strongly affects its physical properties. Indeed, recent experiments show that in some instances, a thin, confined film behaves more like a solid than a liquid. "We don't know what structure we're forming here," says Steve Granick of the University of Illinois in Urbana-Champaign. "But the liquid appears to be capable of taking on long-range order." The question of what surfaces do to the structure of liquids is an important issue in studies of how liquids behave in porous materials and how lubrication works.

To study the resistance of liquid films to sliding, Granick and colleague John Van Alsten use a custom-built apparatus (SN: 4/30/88, p.283) to squeeze a liquid between two extremely smooth, curved mica surfaces. Under sufficient pressure, the cylindrical surfaces flatten over a small area yet retain enough liquid between them to create a film only a few molecules thick. The top mica surface is mounted on a "boat" that slowly oscillates back and forth in response to an electrical signal. By comparing the boat's actual displacement with the input signal, the researchers can calculate how much the liquid film resists the motion, providing a measure of the film's apparent dynamic viscosity and its rate of energy dissipation.

For liquids such as hexadecane, which consists of long, flexible chains of carbon and hydrogen atoms, Granick and Van Alsten find that a confined liquid's dynamic viscosity is at least 100 times greater than that of the bulk liquid. The viscosity also depends very strongly on the pressure between the plates. For instance, doubling the pressure causes a fivefold increase in the viscosity, whereas the film's thickness changes by less than an angstrom. Details in the pattern of the film's response to pressure suggest that, rather than moving about at random, molecules in a confined liquid somehow coordinate their movements to accommodate the applied stress.

In liquids such as octamethylcyclo-tetrasiloxane, made up of compact, globular molecules, the researchers sometimes see an abrupt transition from a liquid-like to a solid-like response. In other words, at a sufficiently high pressure between the plates, the film somehow locks together. The transition is also reversible: Lowering the pressure brings back the liquid-like response. "This was the kind of [observation] that we didn't know whether to believe when we first saw it," Granick says.

The results suggest the liquid's molecules may be settling into an arrangement resembling a glass. "As we squeeze on these liquids harder and harder, we're freezing out more and more modes of motion until the molecules just sit there," Granick says. However, it's still difficult to account for the rapidity and reversibility of the transition. Adds Granick, "The results raise many questions concerning the packing and crowding of fluid molecules in constricted geometries."

Electron superconductors and more

The recent discovery of a new family of high-temperature superconductors in which electrons carry the superconducting current (SN: 3/4/89, p.143) has prompted a flurry of research activity. Some of this work aims at finding materials that lose their resistance to the flow of electrical current at temperatures higher than the 24 kelvins (-416°F) achieved in the initially discovered compounds. Now, Allen M. Hermann of the University of Arkansas in Fayetteville reports a formulation that may boost the transition temperature for an electron superconductor to 85 kelvins.

The new compound consists of thallium, barium, cerium, copper and oxygen. "It's quite reproducible and easy to make," Hermann says. However, his samples contain a mixture of components, or phases, in which the proportion of each element may vary. Because the superconducting phase hasn't

been isolated and identified yet, Hermann can't tell whether the observed electron current is in the superconducting part of the material or in some other, nonsuperconducting phase. "The results are very preliminary but intriguing," he says.

To study the role oxygen plays in high-temperature superconductors, James E. Schirber of the Sandia National Laboratories in Albuquerque, N.M., and his collaborators have gone back to lanthanum copper oxide, a relatively simple compound that becomes a superconductor with the substitution of barium for some of the lanthanum. Schirber and his colleagues use high pressure to force oxygen into a heated sample of lanthanum copper oxide. They find that raising the amount of oxygen in the sample by less than 1 percent turns the material into a superconductor with a transition temperature of 40 kelvins. They want to get a better sense of where the oxygen goes and what it does to the copper lanthanum oxide's crystal structure.

"This is a very important material to try to understand," Schirber says. "It's a very simple copper-oxide system. We feel we can get a handle on what the oxygen is doing, how it turns the antiferromagnetic insulator into a 40-degree superconductor with a very, very small amount of oxygen."

The sounds of particles

When a particle absorbs laser light, it heats up. That heating causes the particle to expand, which in turn generates a sound wave or pulse in the surrounding liquid or gas. According to Gerald J. Diebold of Brown University in Providence, R.I., that signal, if detected, may be distinctive enough to provide useful information about the particle's geometry and acoustic properties. Diebold's theoretical calculations show that objects such as spheres, slabs and cylinders have characteristic acoustic signatures that depend on the source's shape and how the object interacts acoustically with the surrounding fluid. "I believe that in the long run, it may be possible to go backwards from the photoacoustic waveforms to determine some of the properties of unknown particles," Diebold says. Initial, "primitive" experimental tests, using a laser to heat droplets of xylene in water, show the idea is worth pursuing.

Bombardment versus quick cooling

Does rapidly cooling a liquid to form a glass produce the same kind of disorder as that produced by bombarding the crystal form of the same substance with ions? In other words, what is the relationship between the microscopic structure of an amorphous, or disordered, material and the method used to produce it? A research team at the Oak Ridge (Tenn.) National Laboratory has now determined for the first time that for at least one material, the method used to create disorder makes a difference.

The researchers studied lead pyrophosphate, which contains chains of phosphate ions. In one case, they bombarded the surface of a single crystal of the material with lead ions. The ions did enough damage to the surface to make it appear amorphous in X-ray diffraction measurements. In the other case, they cooled the molten form of the material rapidly to produce a homogeneous glass. The researchers used a technique known as high-performance liquid chromatography to determine the length of phosphate chains in both the ion-damaged material and the glass. They discovered that no matter how high the dose of lead ions, the ion-damaged amorphous structure differed significantly from the glass form.

The results contradict what some researchers have argued in the past. The Oak Ridge experiments show that for some materials, the ion-damage process isn't always equivalent to melting followed by rapid cooling of the same material.