Probing Interfaces Involving Liquids

Last month in Washington, D.C., the National Academy of Sciences held the first of what it hopes will be a series of seminars in forefront fields of science, technology, and medicine. The idea is to bring the academy closer to the frontlines of research and to help spread the word to federal science policy-makers. The subject of the 23 and 24 March seminar was interfaces and thin films, and the talks, though tutorial in nature, contained a pleasantly large number of still unpublished results. Interfaces, such as the surface of a solid exposed to a liquid or gas, and thin films, whose properties are heavily influenced by interfaces, have long been of considerable technological importance and have always been so in biological processes, but researchers are now getting access to the experimental and theoretical tools needed to explore these complex physical systems that are neither ideally two-dimensional nor fully three-dimensional. The briefings that follow give a peek at three ways to probe interfaces involving liquids.

Images of Solid Surfaces in Liquids

In the real worlds of technology and biology, many surfaces are solid-liquid interfaces. The scanning tunneling microscope (STM), which was invented only a few years ago but has already won its developers a Nobel Prize in Physics, gives atomic-resolution surface contour maps of solid surfaces in a vacuum. But researchers have also shown that it retains its image-making capability even for samples immersed in water and in cryogenic fluids, such as liquid nitrogen and liquid helium.

At the seminar, Paul Hansma reviewed several STM experiments carried out by his group at the University of California at Santa Barbara in collaboration with Robert Coleman and his co-workers at the University of Virginia that extend the imaging of the STM to a wider variety of liquids. The most recent results demonstrate that the instrument can generate high- but not quite atomic-resolution images of surfaces under various oils and greases. Another experiment revealed the evolution at intervals of 5 seconds of the corrosion of iron in salt water, thereby showing that the STM can take snapshots of dynamic processes.

As Hansma explained, surface scientists have preferred to work with specimens under ultrahigh vacuum for three reasons: (i) a clean surface under vacuum poses the simplest problem for theorists; (ii) the vacuum protects a clean surface from contamination; and (iii) many of the standard surface-science techniques, such as low-energy electron diffraction and photoelectron spectroscopy, work only in a vacuum.

Chemists, if not physicists, have long understood that a liquid protects the integrity of the surface as well as a vacuum. Hansma began his presentation by showing some STM images of the surface of tantalum disulfide in liquid nitrogen and liquid helium. The contours at the higher temperature clearly show individual atoms and even sites where atoms are missing, whereas those at the lower temperature show the charge density wave phenomenon for which the material is well known. To get the same images in an ultrahigh vacuum would have been a considerably more expensive and time-consuming proposition.

Immersing samples in oil or grease, although it sounds messy, also can be a surface-protecting strategy during STM imaging, particularly for surfaces of freshly etched materials, such as the semiconductor gallium arsenide that oxidizes quickly in air. Hansma showed several images of the surface of a gold film bathed in microscope immersion oil, silicone oil, paraffin oil, fluorocarbon grease, glycerol, and silicone vacuum grease. The lateral resolution in most of these images was about 10 angstroms, rather than the 2 angstroms possible for many surfaces in ultrahigh vacuum.

Because the STM works by means of the tiny electric current that tunnels through the gap between the surface under investigation and a scanning metal tip that may be only one atom wide at the very end, it cannot be used with highly insulating surfaces. A variation of the STM called an atomic force microscope (AFM) overcomes this limitation. Hansma also reported on the use of the AFM to image freshly cleaved surfaces of graphite, which is not insulating, and sodium chloride in paraffin oil.

To register the time evolution of dynamic processes, researchers can use something as simple as a videocassette recorder to store digital STM images as they are generated by a computer. In an experiment with an iron film immersed in salt water, the STM images taken at intervals over a period of 2.5 minutes show the initial smoothing of the surface, followed by a roughening characterized by the emergence over time of progressively smaller crystalline grains, some with lateral dimensions less than 50 angstroms.

For an STM operating in a vacuum, the tunneling current decreases exponentially with the gap distance, so that the contour map of a surface across which the tip scans is generated by recording the vertical tip position while the tunneling current and hence the gap is held constant. An interesting question is, Why does the STM work in a medium such as an oil? Would not the oil molecules interfere with the tunneling process? Hansma offered a tentative but unverified explanation. The scanning tip is only a few angstroms from the surface being imaged, so that there is no room for the oil molecule, which is squeezed out, and the local environment is effectively a vacuum.

Forces Between Two Surfaces in Liquids

Before railroads got up steam in the 19th century, there was considerable debate whether the smooth driving wheels of a locomotive would be able to pull a train or would just spin on the rails, moving the train nowhere. From the modern point of view, the debate reflects the importance of understanding what forces act between two surfaces that are very close together. Countless examples of the same issue of intermolecular forces between surfaces in multicomponent systems involving liquids arise in rather mundane industrial processes, such as the manufacture of paints, in more high-tech enterprises, such as the fabrication of advanced ceramics that retain their strength at high temperatures, and in the biological world, as in the interactions between membranes.

For the last decade, Jacob Israelachvili, who is also at the University of California at Santa Barbara, has been building a series of instruments to measure forces between surfaces (the surface forces apparatus). The latest version is sensitive to forces whose strengths range over six orders of magnitude starting at 10 nanonewtons (1 microgram) and has a distance resolution of better than 1 angstrom. The atomic force microscope mentioned in the previous briefing, which is sensitive to much smaller forces of 0.1 nanonewton or less (depending on the mass of the spring), is a complementary more than a competitive instrument. It can measure forces between individual atoms at very close separations for example, whereas the surface force apparatus can sense a variety of both repulsive and attractive interactions between rather complicated molecules at "longer" distances of many angstroms. It also is beginning to see use as an instrument to measure dynamic properties, such as the viscosities of liquids near surfaces.

The guts of the surface forces apparatus at Santa Barbara consist of two cylindrically curved mica sheets whose axes are perpendicular, so that there is saddle-shaped volume where the surfaces are closest together. With a system comprising a micrometer, a differential cantilevered spring, and a piezoelectric drive, the spacing between the surfaces can be controlled to less than 1 angstrom. An optical interference technique that uses the light reflected from a silver coating on the back surface of the mica allows measurement of the separation to the same accuracy. The apparatus is filled with any of a wide range of liquids.

At the seminar, Israelachvili reviewed the types of intermolecular interactions that the surface forces apparatus has been used to probe. For example, the results of experiments on several systems suggest that there are two general types of interactions active in solvation (the clustering of liquid molecules around a simple atomic ion or some more complex chemical group attached to the mica surfaces).

The first, which shows up as a force that oscillates with an exponentially decaying amplitude as the distance between the mica surfaces increases, is due to the tendency of the liquid molecules to pack into layers near the surface. It shows up by itself in the surface forces apparatus when the mica surfaces are bare. The period of the oscillations is equal to the diameter of the molecule. The second force, which is superimposed on the first when coated mica surfaces are immersed in water or one of a few related liquids, also decays with distance, but the decay is monotonic and can be either attractive or repulsive, depending on the surface coating. Hydrophilic surfaces experience a repulsive force, whereas hydrophobic surfaces attract one another strongly.

Israelachvili noted that the attachment to the mica surfaces of groups whose free ends are mobile can override these interactions and give a simple monotonic, exponentially decaying repulsive force, although the precise mechanism depends on the length and hence the mobility of the molecule. This is no surprise because polymer additives have long been added to paints as dispersion agents to prevent the aggregation of the suspended colloidal particles.

In this same spirit, Matthew Tirrell of the University of Minnesota reported on the use of block copolymers to attach long molecules firmly to the mica surface. In a block copolymer, the polymer components are segregated in blocks along the molecule. To accomplish the bonding, researchers at Minnesota chose the components of a di-block copolymer, so that one polymer, poly(2-vinyl pyridine), prefers to adsorb on the mica, while the other, polystyrene, prefers the liquid.

The long range and other details of the measured repulsive force between these surfaces suggest that the polystyrene end of the molecule actually uncoils to a considerable extent in the liquid, a useful property for a dispersion agent. The length of the poly(2-vinyl pyridine) end affects both the packing density of the molecules on the surface and the degree to which the polystyrene uncoils. Moreover, the investigators have found that the bonding to the surface is strong enough to allow measuring forces between dissimilar surfaces without the disrupting exchange of molecules between surfaces that usually occurs in an attempt to maintain chemical equilibrium.

The Structure of Liquid Surfaces

The layering of liquid molecules near a solid surface that was revealed by the surface forces apparatus (see briefing above) suggests that liquids are far from uniform, but have a rich structure of their own. At the seminar, Stuart Rice reviewed work by his group at the University of Chicago, as well as that of others, that demonstrated stratification in liquid metal surfaces when the liquid is in contact with a vapor. The Chicago group relied mainly on computer (Monte Carlo) simulations, but also made use of surface x-ray scattering to obtain experimental confirmation of its findings. In a separate presentation, Peter Pershan of Harvard University gave a more detailed overview of a particular kind of surface scattering, specular reflection, and its use in studying surface structure in liquids and liquid crystals.

Rice made a strong distinction between liquids in which the interatomic forces are independent of the density of atoms, which is the case for dielectric liquids, and those, such as liquid metals, in which the they are not. In the former case, researchers generally agree that the interface between the liquid and vapor is smooth and characterized by a monotonic decrease in the density over a distance of about two molecular diameters.

Interatomic forces that depend on the density make the calculation of the surface structure considerably more difficult, and most early attempts to do so reached the conclusion, now regarded as erroneous, that the interface between liquid metal and vapor was very sharp, less than one atomic diameter. A few years ago, the Chicago group adopted the alternative approach of computer simulation, using what they called a generalized self-consistent Monte Carlo procedure to account for the circular relation that the surface configuration of atoms fixes the density, which affects the forces between atoms, which determines the surface configuration.

The original simulations and more recent ones of liquid cesium based on less restrictive assumptions agree that the atomic density at the surface is strongly stratified over a distance of about three atomic diameters; that is, the density oscillates before dropping off to the value appropriate for the vapor. New simulations also address the questions of the effect of the stratification on the distribution of atoms in the lateral direction (not much) and on statification effects in liquid metal alloys. In an alloy, the interatomic forces depend on composition, as well as density. Simulations of a cesium-sodium alloy, for example, predict that the outermost layer of the stratified surface is almost completely cesium, the second layer is only slightly cesium deficient, and succeeding layers tend toward the average composition of the liquid.

Surface x-ray scattering is one way for experimentalists to look for these and other aspects of surface structure. To obtain a high sensitivity to the surface, the x-rays must come in at a grazing angle near the critical angle for total external reflection, the x-ray analog of total internal reflection in optics. In the last few years, several different ways to use grazing-incidence x-rays on solid surfaces have been developed. Pershan discussed one of the conceptually simplest, specular reflection, in the context of the problem arising because liquid surfaces are not ideally flat at the molecular level.

The basic technique is to measure the reflectivity over a range of angles just above the critical angle. The high x-ray flux available from a synchrotron light source makes the experiment practical. From the deviation between the measured values and the calculated (Fresnel) reflectivity for a flat surface, it is possible to extract information about the surface roughness. For example, from reflectivity measurements on water, carbon tetrachloride, and methanol, Pershan and co-workers at Harvard and the Risø National Laboratory in Denmark have extracted the root-mean-square roughness. The 3.2 angstroms measured for water was in good agreement with a theoretical roughness for so-called thermally excited capillary waves that are dominated by surface tension. ■

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