Nano Focus

## Molecular ordering phenomenon found at interface between liquids and solids

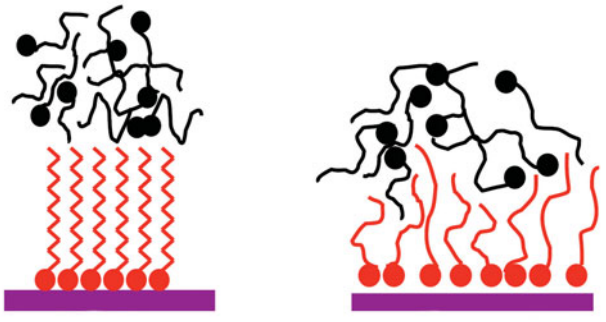
As part of the quest to form perfectly smooth single-molecule layers of materials for advanced energy, electronic, and medical devices, researchers at Brookhaven National Laboratory have discovered that the molecules in thin films remain frozen at a temperature where the bulk material is molten. Thin molecular films have a range of applications extending from organic solar cells to biosensors, and understanding the fundamental aspects of these films could lead to improved devices.

The study, which appears in the April 1st issue of *Physical Review Letters* (DOI: 10.1103/PhysRevLett.106.137801), is the first to directly observe "surface freezing" at the buried interface between bulk liquids and solid surfaces.

"In most materials, you expect that the surface will start to disorder and eventually melt at a temperature where the bulk remains solid," said physicist Ben Ocko, who collaborated on the research with scientists from the European Synchrotron Radiation Facility (ESRF), in France, and Bar-Ilan University, in Israel. "This is because the molecules on the outside are less confined than those packed in the deeper layers and much more able to move around. But surface freezing contradicts this basic idea. In surface freezing, the interfacial layers freeze before the bulk."

In the early 1990s, two independent teams made the first observations of surface freezing at the vapor interface of bulk alkanes, organic molecules similar to those in candle wax that contain only carbon and hydrogen atoms. Surface freezing has since been observed in a range of simple chain molecules and at various interfaces between them.

"The mechanics of surface freezing are still a mystery," said Bar Ilan scientist Moshe Deutsch. "It's puzzling why alkanes and their derivatives show this unusual effect, while virtually all other materials exhibit the opposite, surface melting, effect."




Schematic representation of the alkanol monolayer when frozen (left) and melted (right).

In the most recent study, the researchers discovered that surface freezing also occurs at the interface between a liquid and a solid surface. In a temperature-controlled environment at Brookhaven's National Synchrotron Light Source and the ESRF, the research group made contact between a piece of highly polished sapphire surface and a puddle of liquid alkanol. The researchers shot a beam of high-intensity x-rays through the interface and by measuring how the x-rays reflected off the sample, the group revealed that the alkanol molecules at the sapphire surface behave very differently from those in the bulk liquid.

According to ESRF scientist Diego Pontoni, "Surprisingly, the alkanol molecules form a perfect frozen monolayer at the sapphire interface at temperatures where the bulk is still liquid." At sufficiently high temperatures, about 30°C above the melting temperature of the bulk alkanol, the monolayer also melts.

The temperature range over which this frozen monolayer exists is about 10 times greater than what is observed at the liquid-vapor interfaces of similar materials. According to Alexei Tkachenko, a theoretical physicist who works at Brookhaven's Center for Functional Nanomaterials, "The temperature range of the surface-frozen layer and its temperature-dependent thickness can be described by a very simple model that we developed. What is remarkable is that the surface layer does not freeze abruptly as in the case of ice, or any other crystal. Rather, a smooth transition occurs over a temperature range of several degrees."

Ocko said, "These films are better ordered and smoother than all other organic monolayer films created to date."

Deutsch said, "The results of this study and the theoretical framework which it provides may lead to new ideas on how to make defect-free, single molecule-thick films."

Energy Focus

## Why strongly photoluminescent polymers make poor solar cells

At first glance, the semiconducting polymers used in organic light-emitting diodes and photovoltaics may seem to require similar properties, and yet materials which work well for one application are often unsuitable for the other. Highly photoluminescent polymers such as polyfluorenes have long exciton lifetimes which should aid charge separation in an organic solar cell, but instead tend to give poor efficiencies. Recent work by Y.W. Soon and J.R. Durrant of Imperial College London and their co-workers suggests that one cause of this discrepancy may be a fast energy transfer mechanism which competes with electron transfer to the acceptor material.

The group's article in the online edition of *Chemical Science* (DOI: 10.1039/c0sc00606h) compares the photophysics of photovoltaic devices made from blends of the electron acceptor [6,6]-phenyl C61 butyric acid methyl ester (PCBM) and either of two indenofluorene-based poly-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