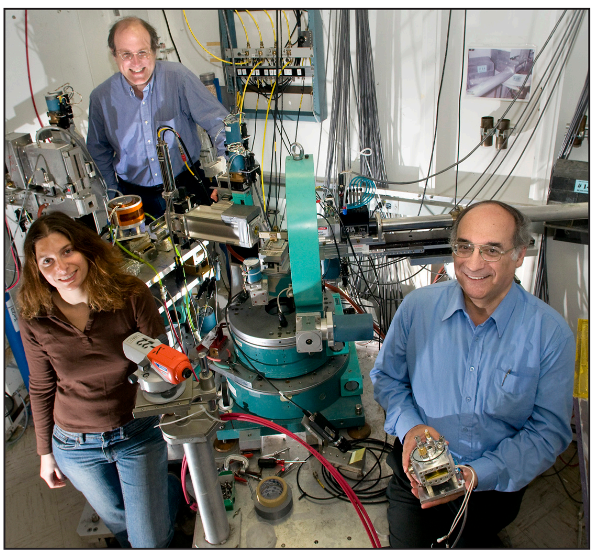
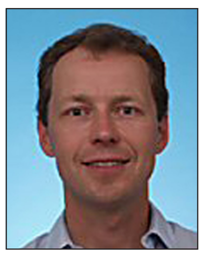
Spreading and Surface Freezing of Nanometer-Thick Oil Films on Water

Most kindergarteners can tell you that no matter how hard you try to mix them, a droplet of oil won't spread on water. However, things are different in the nano world. Recently, a team of researchers from Durham and Oxford universities in the United Kingdom, Bar-Ilan University in Israel, and BNL used x-ray experiments at the NSLS to show that a nanometer-thick layer of oil can be induced to spread on the surface of water by a minute amount of an additive called surfactant. More intriguing, these layers exhibit a very peculiar behavior known as the surface freezing effect.

"Surface freezing is unusual because in most situations, the bulk of a material freezes before the surface," said Bar-Ilan physicist Moshe Deutsch. "You can think of it as a crowd of people standing at a concert. The people in the center are more limited in movement than the people positioned on the outside, and therefore, they'll order first. Yet, if you replace the people with molecules, the surface freezing we've observed in liquids is exactly the opposite: the molecules at the boundary order (or freeze) first while the bulk remains liquid."


Authors (from left) Lilach Tamam, Ben Ocko, and Moshe Deutsch


Colin Bain


Eli Sloutskin

Among other applications, understanding surface freezing could be valuable to improving the function of diesel engines, which at cold climates, might be effected by the way oil is injected into the motor.

"It's such an unusual effect, and we still don't fully understand how it happens," said researcher and Durham University chemist Colin Bain.

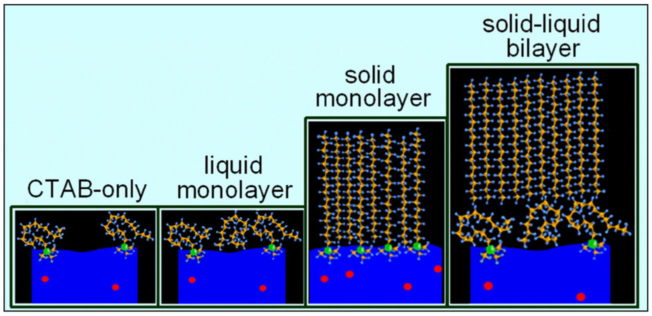
To gain a better understanding of this phenomenon, the researchers put a drop of a liquid oil called alkane onto the surface of water containing a minute concentration of the surfactant cetyltrimethylammonium bromide (CTAB). This is not so different than making salad dressing by adding oil to vinegar – two liquids that don't naturally mix.

"If you take an oily plate and fill it with water, you'll notice these little droplets of oil on the surface," said Harvard physicist Eli Sloutskin, who took part in the study as a graduate student at Bar-Ilan. "The oil droplets won't spread. But the moment you drop a little bit of soap, which is a surfactant, on the plate, the oil droplets vanish: they spread out on the water's surface and also mix with the bulk."

On a much smaller scale than the kitchen sink, the research group determined that while an alkane won't naturally spread on water, a small amount of CTAB causes it to form a single liquid alkane layer on the surface. After the material is cooled past a certain point, the liquid layer turns crystalline. The type of crystal formed depends on whether the alkane chain is longer or shorter than the CTAB molecule's hydrocarbon tail. Using surface x-ray scattering techniques at NSLS beamline X22B, the researchers determined that if the alkane chain is shorter than the surfactant's tail, the liquid surface monolayer becomes a solid monolayer. If the alkane chain is longer, two layers form: an upper crystalline layer on top of a lower liquid one. Until now, this type of behavior has not been observed in any system.

Their results were published in the September 28, 2007 edition of *Physical Review Letters*.

"In forming these phases, spreading the oil on water and causing it to freeze as a monolayer or a double layer, we are doing nothing but self-assembly: we 'encourage' the molecules to self-organize by creating an environment that favors a particular phase," said Brookhaven physicist Ben Ocko. "We can fine tune the structure through the type of oil and surfactant used, and of course, the temperature. This is an exciting new system that certainly holds more secrets to be discovered and surprises to stumble upon. We are working hard to uncover the former, and keeping our eyes open for the latter"



Molecular interpretations of the different phases of the alkane film on the CTAB-decorated water surface.

Other researchers involved included Zvi Sapir and Lilach Tamam (Bar Ilan), and Qunfang Lei and Katharine Wilkinson (Oxford). Funding was provided by the U.S. Department of Energy and the U.S.-Israel Binational Science Foundation.

E. Sloutskin, Z. Sapir, C. Bain, Q. Lei, K. Wilkinson, L. Tamam, M. Deutsch, B. Ocko, "Wetting, Mixing and Phase Transitions in Langmuir-Gibbs Films," Phys. Rev. Lett., **99**, *136102 (2007).*

— Kendra Snyder