

## WITH NANOPARTICLES, A LITTLE WATER ON THE OUTSIDE CAN REARRANGE THE ATOMS ON THE INSIDE

Sometimes, it is what's on the outside that counts. Within a nanometer-sized particle of a given material, the arrangement of atoms may depend on the particle size and the conditions during growth. But that internal organization can change when a nanoparticle is coated with a little water, a team from the University of California, Berkeley, recently found in experiments at the APS. The observation suggests that the structure of nanoparticles can be controllably altered after the particles are synthesized and that their behavior may depend on the chemistry of their surroundings.

Thermodynamically, a nanoparticle is distinct from a tiny dollop of a bulk material. The free energy of a nanoparticle includes a hefty surface term, and that term can determine the arrangement of atoms within the nanoparticle as it minimizes its free energy. Moreover, chemical interactions on the surface can alter the free-energy balance and, hence, the internal structure of the particle.

That is what the Berkeley team demonstrated in work at the BESSRC/XOR beamline 11 ID-C. The researchers synthesized nanoparticles of zinc sulfide in anhydrous methanol in a special vial compatible with x-ray scattering experiments. Using wide-angle x-ray scattering (WAXS), they studied *in situ* the structure of the nanoparticles, both before and after seasoning the methanol with a soupçon of water, which was anticipated to interact strongly with the nanoparticles. The high energies available at the beamline—up to 115 keV—enabled the researchers to probe a wide range in x-ray diffraction vector. With this high-quality diffraction data, they then deduced the real-space pair distribution function for atoms within the nanoparticles.

The WAXS data clearly showed that the water caused the atoms within the nanoparticles to rearrange. Additional measurements showed that the water changed the structure of the nanoparticles but did not make them grow or shrink. According to transmission electron microscopy and ultraviolet light absorption studies, the average nanoparticle diameter was 3 nm both before and after the addition of water.

To obtain detailed views of the nanoparticle structures, the team employed molecular dynamics simulations. For the nanoparticles in pure methanol, the simulations indicated that the zinc and sulfur atoms were highly disordered; only near the very center of the nanoparticle did they form a regular cubic zinc blende structure. When the simulation included a sub-monolayer coating of water molecules, however, the cubic phase filled the entire particle, and only the surface remained disordered. The simulated structures were in good agreement with the experimental observations, reinforcing the conclusion that the transformation was caused by the interaction of water molecules with the nanoparticle surface.

The researchers were not able to remove the water because it bonded too tightly to the zinc sulfide. However, other experiments by the team indicate that such structural transitions are reversible. X-ray absorption fine structure measurements at

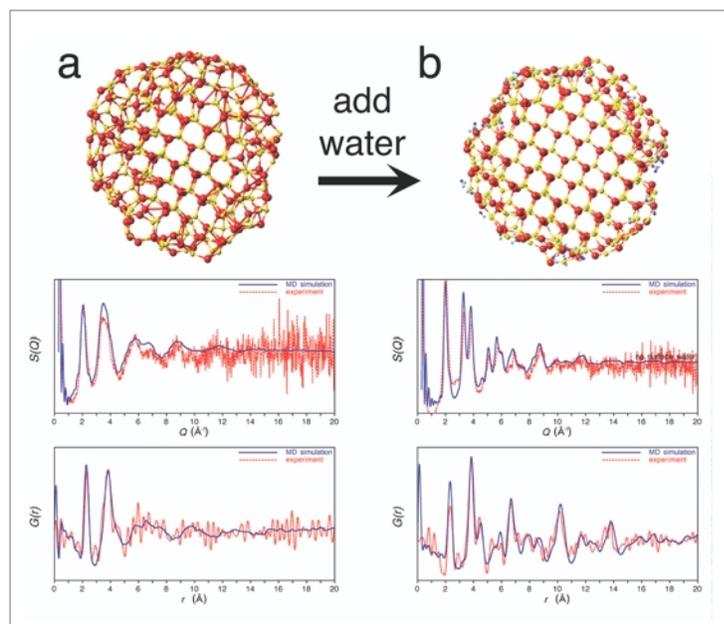


Fig. 1 Water binds to the surface of zinc sulfide nanoparticles in methanol and drives a transition from structural disorder (a) to order (b). From wide angle x-ray scattering data acquired versus diffraction vector,  $Q$ , the researchers calculate the structure factors,  $S(Q)$ , and the real-space pair distribution functions,  $G(r)$  of the nanoparticles before and after the transformation. Molecular dynamics simulations reproduce the x-ray scattering data and provide specific predictions of the nanoparticle structure.

the DCM beamline of the University of Wisconsin-Madison's Synchrotron Radiation Center (SRC) in Stoughton showed that dried zinc sulfide nanoparticles changed structure when they were heated to drive off residual methanol. The structure reverted to its original form when the methanol was replaced.

The results demonstrate that nanoparticles are not kinetically trapped in one structure or another but can respond to environmental changes and surface interactions. They suggest that coatings might induce and stabilize uncommon structures even after the particles are synthesized. Moreover, the findings indicate that the properties of nanoparticles depend not just on what the particles are made of and how they're created, but on their surroundings as well. As with people, nanoparticles will be judged by the company they keep. ○

**See:** Z.H. Zhang, B. Gilbert, F. Huang, and J.F. Banfield, "Water-driven transformation of nanoparticle structure at room temperature," *Nature* **424**, 1025-1029 (23 August 2003)

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## REVEALING THE MICROSCOPIC TRANSPORT PROPERTIES OF MOLTEN ALUMINUM OXIDE



Levitated liquid-aluminum-oxide sample in a super-cooled state at  $\sim 1800^\circ\text{C}$ . The sample is levitated by an oxygen gas stream and heated by a 270-W  $\text{CO}_2$  laser. The article reports on inelastic x-ray measurements performed on this sample.

The transport properties of high-temperature oxide melts are of considerable interest for a variety of applications, including modeling the Earth's mantle, optimizing aluminum production, confining nuclear waste, and investigating the use of aluminum in aerospace propulsion. Information on melt viscosities and the speed of sound through liquid oxides is essential for testing the validity of theories used in predicting the geophysical behavior of the Earth's mantle as well as mathematical models of aluminum combustion. The experimental techniques described here supply fundamental insights into the behavior of liquid oxides that help provide a basis for these and other advanced applications.

Kinematic restrictions on neutron scattering make it impossible to reach acoustic modes in liquid oxides, and the high-temperature regime is inaccessible by light scattering because of black body radiation. Another factor making it difficult to obtain data on microscopic transport properties with conventional techniques is the chemical reactivity of oxide melts at high temperatures. Aluminum oxide, for example, melts at about 2327K and is an exceptionally aggressive material in the liquid state, which precludes the use of traditional containers for the material while measurements are being made.

Researchers from three French research centers, Centre de la Recherche sur la Matière Divisée, Institut de Science et

de Génie des Matériaux et Procédés, and Centre de la Recherche sur la Matériaux à Haute Température; Spain's University of the Basque Country; and from Argonne National Laboratory sought to circumvent these limitations by studying molten aluminum oxide using high-resolution inelastic x-ray scattering (IXS) at XOR beamline 3-ID-C at the APS. The measurements were performed in a containerless environment. Aluminum oxide spheres 3 to 4 mm in diameter were suspended in an oxygen gas jet and heated with a 270-W  $\text{CO}_2$  laser beam to temperatures between 2300 and 3100K. A carefully adjusted gas flow through a conical nozzle maintained the levitated sample at a position that was stable to within  $\pm 20\ \mu\text{m}$  above the plane of the top edge of the nozzle, allowing a clear path for the incident and diffracted x-ray beams. Sample temperature was measured by a pyrometer directed at the point illuminated by the x-ray beam.

The x-ray energy was 21.657 keV, and the energy resolution was determined to be 1.8 meV, full width at half maximum. Data were collected at six values of the wave vector  $Q$  (over the energy transfer range of  $-30$  to  $60$  meV), covering the  $Q$  value range of  $1.09$  to  $6.09\ \text{nm}^{-1}$ , and over a more restricted range ( $-30$  to  $30$  meV), covering values of  $Q$  out to  $28\ \text{nm}^{-1}$ .

The excitation spectra showed a well-defined triplet peak structure at lower  $Q$  values ( $1$  to  $6\ \text{nm}^{-1}$ ) (Fig. 1), and a single quasi-elastic peak at higher  $Q$ . The high- $Q$  spectra were well described by kinetic theory, but the low- $Q$  spectra diverged significantly from predictions based on hydrodynamic theory.

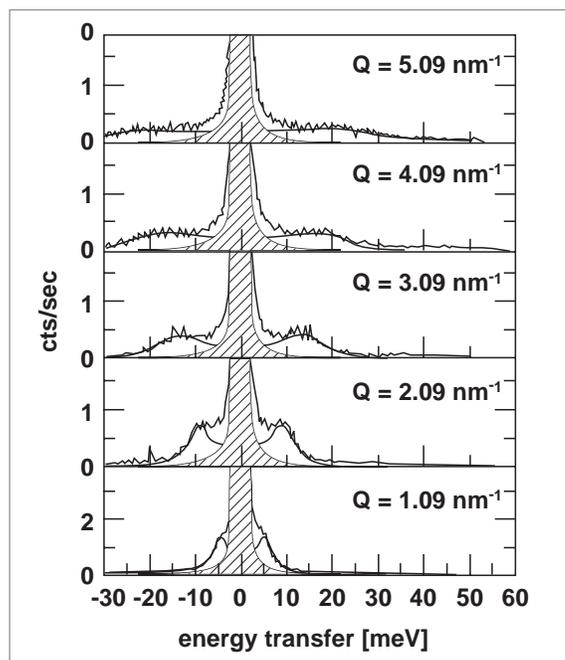


Fig. 1. Excitation spectra in liquid aluminum oxide at 2323K measured with inelastic x-ray scattering for different  $Q$ .

When the IXS spectra measured at the lowest six wave vectors at 2323K were fit to the hydrodynamic equation for the scattering function, it was found unexpectedly that the Brillouin modes remained underdamped out to  $Q=6 \text{ nm}^{-1}$  (Fig. 2). Furthermore, the observed Brillouin line width increased with temperature, whereas it was expected that the viscosity would decrease in the hydrodynamic limit. Other discrepancies were discovered as well. The researchers found that an extension of hydrodynamic theory that allows for frequency dependence of the transport coefficients, such as the viscosity, yielded reasonable fits to the low- $Q$  data up to  $6.09 \text{ nm}^{-1}$ . This provides a description of the liquid dynamics in the relatively uncharted regions between hydrodynamics and kinetic theory (Fig. 3). ○

**See:** H. Sinn<sup>1</sup>, B. Glorieux<sup>2</sup>, L. Hennet<sup>3</sup>, A. Alatas<sup>1</sup>, M. Hu<sup>1</sup>, E.E. Alp<sup>1</sup>, F.J. Bermejo<sup>4</sup>, D.L. Price<sup>3</sup>, and M.-L. Saboungi<sup>5</sup>, *Science* **299**, 2047-2049 (28 March 2003).

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## DEMONSTRATION OF THE INFLUENCE OF LOCAL ICOSAHEDRAL ORDER ON THE NUCLEATION BARRIER OF METALLIC LIQUIDS

For over 50 years, it has been known that, under carefully controlled conditions, metallic liquids can be cooled far below their equilibrium melting temperatures (undercooled) before crystallization takes place. This suggests that the homogeneous nucleation mechanism responsible for formation of the solid phase must present a large barrier to phase change. To explain this surprising result, F. C. Frank [1] theorized that as metallic liquids cool, (1) local structures develop in the liquid phase containing icosahedral short-range order (ISRO), which is incompatible with the long-range periodicity of the crystalline phase, and that (2) this incompatibility creates a barrier to the formation of the crystalline phase.

Several experimental studies have supported this hypothesis, but have shopped short of providing direct proof of it. It has been found, for example, that an increase in the maximum undercooling before crystallization is associated with decreasing ISRO of the crystallized phases of Al-Cu-Fe, Al-Cu-Co, and Ti-Zr-Ni liquids. Direct observations of ISRO in the undercooled liquids, however, were not made. Similarly, ISRO was recently found in undercooled Ni, Fe, and Zr liquids, but these results did not establish a link between the ISRO and the nucleation barrier for the solid phase.

The first direct experimental confirmation of Frank's hypothesis took place at the MU-CAT 6-ID-D beamline at the APS [2]. Using the recently developed Beamline Electrostatic Levitation technique, which allows *in situ* x-ray diffraction experiments on electrostatically levitated droplets (Fig. 1), researchers from Washington University, NASA Marshall

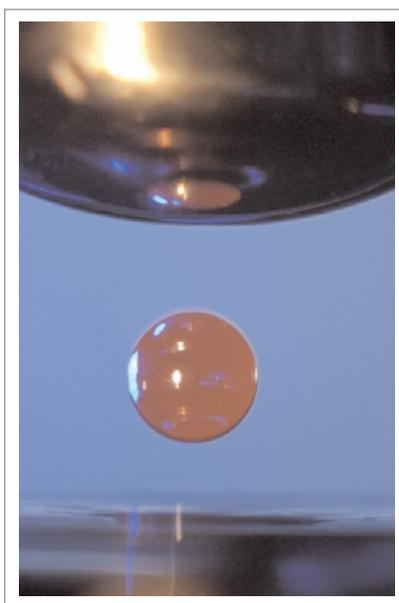


Fig. 1. Electrostatically levitated 2.5-mm-diameter droplet of molten  $\text{Ti}_{39.5}\text{Zr}_{39.5}\text{Ni}_{21}$ , held near the liquidus temperature (1083K).

Space Flight Center, and MU-CAT studied the undercooling behavior of  $\text{Ti}_{39.5}\text{Zr}_{39.5}\text{Ni}_{21}$ . Electrostatic levitation in vacuum ( $\sim 10^{-7}$  Torr) was used to create a containerless environment, which was needed to avoid the masking effects of heterogeneous nucleation. The levitated droplets were  $\approx 2.5 \text{ mm}$  in diameter and were positively charged by induction. The charge was maintained through the photoelectric effect by using intense ultraviolet light. Samples were melted with a fiber-coupled diode laser and then allowed to drop in temperature through free radiation cooling. Optical pyrometers measured sample temperature, and high-energy x-rays (125 keV,  $0.099 \text{ \AA}$ ) provided a scattering range of  $0 \leq q \leq 9 \text{ \AA}^{-1}$ .

The researchers measured an increasing ISRO in the Ti-Zr-Ni liquid with undercooling, finding that this increasing ISRO in the liquid phase is responsible for the nucleation of a metastable Ti-Zr-Ni icosahedral quasicrystal phase (*i* phase) instead of the stable polytetrahedral C14 Laves phase, which also tends to nucleate easily over a wide composition range. Two recalescence events were observed (see Fig. 2): in the first, the temperature rose from 953K to 1058K, followed within a few seconds by a second rise in temperature to 1083K. *In situ* x-ray diffraction analysis showed that the metastable *i* phase nucleates and grows during the primary recalescence from 953K, releasing evolved heat of fusion, which causes sample temperature to rise. This *i* phase subsequently transforms within a few seconds to the stable C14 Laves phase during the second recalescence event from 1058 to 1083K, which is the equilibrium solidus temperature.

In summary, the researchers demonstrated an enhanced icosahedral short-range order with undercooling in Ti-Zr-Ni liquids that decreases the barrier for the nucleation of a metastable *i* phase to below that for the formation of stable polytetrahedral crystal phases. In this way, the data demonstrate the connection between the local order of the liquid and the nucleation barrier. This verifies Frank's hypothesis that the origin of the barrier to nucleation of crystallographic phases is the formation of local icosahedral order in the liquid.

The data demonstrate that local order in the liquid phase strongly influences the nucleation of specific phases even in metallic liquids, in which atomic interactions are weak and relatively isotropic. This indicates that the influence of preexisting local order in the liquid is an important ingredient in the liquid/solid phase transition that should be considered in theoretical treatments of nucleation. ○

### References

- [1] F.C. Frank, Proc. R. Soc. London A **215**, 43 (1952).  
 [2] K.F. Kelton<sup>1</sup>, G.W. Lee<sup>1</sup>, A.K. Gangopadhyay<sup>1</sup>, R.W. Hyers<sup>2</sup>, T.J. Rathz<sup>3</sup>, J.R. Rogers<sup>3</sup>, M.B. Robinson<sup>3</sup>, and D.S. Robinson<sup>4</sup>, Phys. Rev. Lett. **90**(19), 195504-1 to 195504-4 (16 May 2003).

**See:** Reference [2] is the source for this article.

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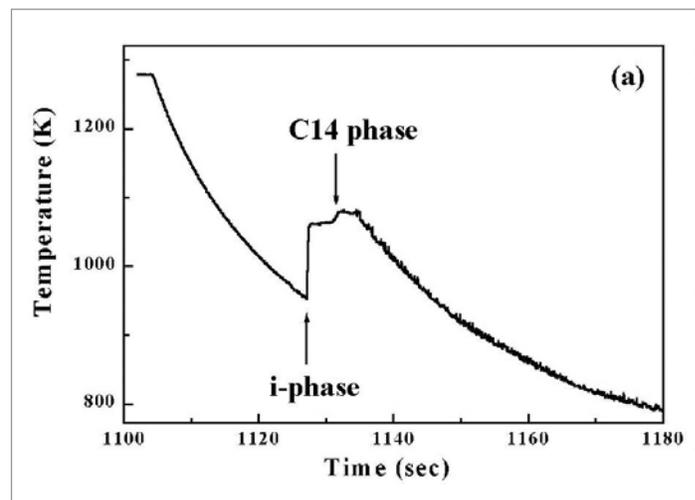


Fig. 2. Cooling curves for electrostatically levitated 2.5-mm droplet of  $\text{Ti}_{39.5}\text{Zr}_{39.5}\text{Ni}_{21}$  as a function of temperature, showing two recalescence events (indicated by arrows). The first event corresponds to the nucleation and rapid growth of a metastable icosahedral quasicrystal; the second event indicates the transformation to the stable C14 crystal phase.

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## EXPLORING PUZZLING PROPERTIES OF POLYSTYRENE FILMS

Studies of thin polymer films provide a glimpse into their intrinsic properties and also help determine surface characteristics that could be useful in designing new technologies, from biocompatible medical implants to next-generation computer disk drives, adhesives, and optical coatings.

In simple bulk liquids, such as water and helium, thermally excited capillary waves are a primary determinant of the roughness at the surface/vapor interface. In thin, viscous polymer films on a substrate, however, other forces—including molecular interactions between the film and the substrate, the molecular structure of the polymer, surface tension, and viscosity—can alter surface roughness. These effects make it more difficult to predict surface roughness and tension by using capillary wave theory.

Previous studies of surface roughness in highly viscous liquids, an oil-water-surfactant interface, and very thin polymer films found that the surface roughness was lower than expected from capillary wave theory. The discrepancies are poorly understood.

In this study, researchers from Northern Illinois University; Argonne National Laboratory; the University of California, San Diego; the Massachusetts Institute of Technology; and Yale

University used high-brilliance synchrotron x-rays to characterize polystyrene films of varying thickness on silicon substrates. When comparing the results of the measured x-ray scattering with capillary wave theory, the research team found that the variation of the measured intensity with wave-vector agreed with theory over a wide range of wave-vectors. In addition, the surface tension was found to be only slightly higher than expected from theory, which was in contrast with previous studies which had claimed very large values for the surface tension (Fig. 1).

The research team prepared the films by spin-casting onto silicon substrates. The solvent was removed by annealing the samples at 150° for 12 h, and the thickness of the films was manipulated by varying the concentration of polystyrene in the toluene to achieve a range of thickness from 84 to 359 nanometers.

The 8-ID beamline at IMMY/XOR, APS sector 8, was used to measure the samples. The x-ray beam was generated by an APS undulator A. A germanium channel-cut double-bounce monochromator was used to select a narrow slice of energy from the harmonic. The beam was aligned vertically and horizontally, and stray scattering was intercepted by a beamstop

placed in front of a Princeton Instruments charge coupled device camera. By adjusting the angle of incidence, the team was able to deliver a glancing beam that penetrated the films by only 9 nm.

The study found that the surface tension of the supported polymer films was slightly greater, 20%, than that measured in bulk material. At capillary wavelength scales of 2 nm, the team also found slightly greater roughness than predicted by capillary wave theory. In addition, surface roughness was found to increase at higher temperatures and in thinner films.

Surface x-ray scattering can measure total surface roughness and can also determine the extent to which surface roughness depends on capillary wavelength. This study found that surface tension properties were in better agreement with values predicted for bulk materials than was found in previous studies. These observations provide a more accurate description of surface roughness and tension of supported polymer films, which correspond better with capillary wave theory. ○

**See:** L. Lurio<sup>1</sup>, H. Kim<sup>2</sup>, A. Rühm<sup>3</sup>, J. Basu<sup>1</sup>, J. Lal<sup>4</sup>, S. Sinha<sup>2</sup>, and S.G.J. Mochrie<sup>5</sup>, "Surface Tension and Surface Roughness of Supported Polystyrene Films," *Macromolecules* **36**, 5704-5709 (2003).

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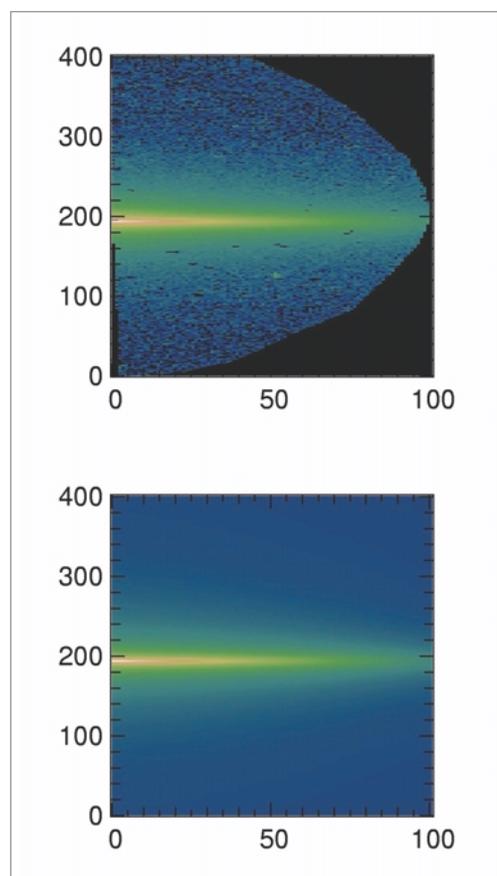


Fig.1. The top figure depicts static diffuse scattering measured from a 359 nanometer polystyrene film. The bottom figure shows a theoretical calculation of the diffuse scattering based on thermally driven capillary waves.

## COLLECTIVE STRUCTURE OF NANOPARTICLE FLUIDS AND GELS

From biotechnology to microelectronics fabrication, the behavior of dense colloidal and nanoparticle suspensions is of immense technological importance. Depending on the effective interactions between particles, a suspension may undergo a dramatic transition from a fluid to a gel state, which strongly influences how these materials are used. Control of the microstructural and mechanical properties of gels, therefore, is of great current interest but is poorly understood. Recently, researchers from the University of Illinois at Urbana-Champaign carried out a systematic study [1] at the UNI-CAT 33-ID beamline at the APS to determine the structural changes that take place during the approach to the gel transition and in the soft gel state, and they compared the results with theoretical calculations.

A widely used experimental system for studying particle gelation is a suspension to which small nanometer-size (radius of gyration,  $R_g$ ) nonadsorbing polymers are added. The polymers induce exquisitely controllable, short-range "depletion attractions" between the particles that increase in strength with

polymer concentration. Their initial effect is to induce equilibrium nanoparticle clustering over many length scales, and they ultimately trigger an abrupt nonequilibrium transition to a gel state where long-range diffusive motion is absent.

The researchers synthesized silica nanoparticles with radii of  $59 \pm 3$  nm that behave as model hard spheres when dispersed in the solvent decalin. Polystyrene with  $R_g$  of  $\sim 3$ -4 nm was added to induce attraction between the nanoparticles. The collective colloid structure at a high particle volume fraction of  $\phi \sim 40\%$  was experimentally measured as a function of polymer concentration from zero up to, and well beyond, values that induce gelation.

Structural determinations were carried out using ultra-small-angle x-ray scattering. The measurements were made with the facility's Bonse-Hart camera operated at 10-keV photon energy and a  $q$  range of  $2 \times 10^{-4}$  to  $2 \times 10^{-1} \text{ \AA}^{-1}$  (resolution  $\Delta q = 2 \times 10^{-4} \text{ \AA}^{-1}$ ). The scattered x-rays were analyzed with a rotating Si crystal and solid-state detector. The colloidal structure factor  $S(q)$  was determined from the measured scattering

intensity of the colloid-polymer mixture  $I(q)$  and the polymer-free, dilute colloid scattering intensity  $P(q)$ .  $S(q)$  yields information about the mean spacing of nanoparticles, the coherence of the local (cage) order, and suspension compressibility.

As the polymer concentration was increased in the fluid phase, particle concentration fluctuations increased in the low-angle scattering region, the length scale of the local cage structure decreased, and the intensity of the wide-angle peak that quantifies local cage coherence varied nonmonotonically, first decreasing at a low polymer concentration (weak attractions) and then increasing up to the gel transition (see Fig. 1). These equilibrium structural reorganizations on multiple length scales were shown to be in excellent agreement with no-adjustable-parameter theoretical calculations based on a novel version of the Polymer Reference Interaction Site Model (PRISM) theory for polymer-particle suspensions of Fuchs and Schweizer [2]. In the gel, multiple nonequilibrium structural reorganizations occurred, including local particle densification, enhancement of cage order, and suppression of intermediate scale compressibility. In addition, large amplitude scattering intensity emerged at relatively small wave vectors. Detailed analysis implies the formation of narrow interfaces and a characteristic cluster size or quenched heterogeneity length scale of roughly 4-5 nanoparticle diameters. By combining all the experimental and theoretical results, a consistent picture of the colloid microstructure has been constructed (see Fig. 1).

Ultras-small-angle x-ray scattering (USAXS) has been shown in this work to be a powerful tool for identifying the onset of colloidal gelation and for quantitatively testing predictive theories of the structure and thermodynamics of nanoparticle-polymer suspensions. Such studies are possible because of the high brightness of the third-generation synchrotron at the APS. Ongoing and future work is focused on systematically characterizing the gel microstructure as a function of colloid volume fraction and polymer concentration and size [3]. The structural studies have provided a foundation for experimentally and theoretically understanding and controlling the elasticity and bulk mechanical properties of nanoparticle gels [3,4]. ○

## References

[1] S.A. Shah, Y.L. Chen, S. Ramakrishnan, K.S. Schweizer, and C.F. Zukoski, "Microstructure of Dense Colloid-Polymer Suspensions and Gels," *J.Phys. Condens. Matter* **15**, 4751-4778, (2003).

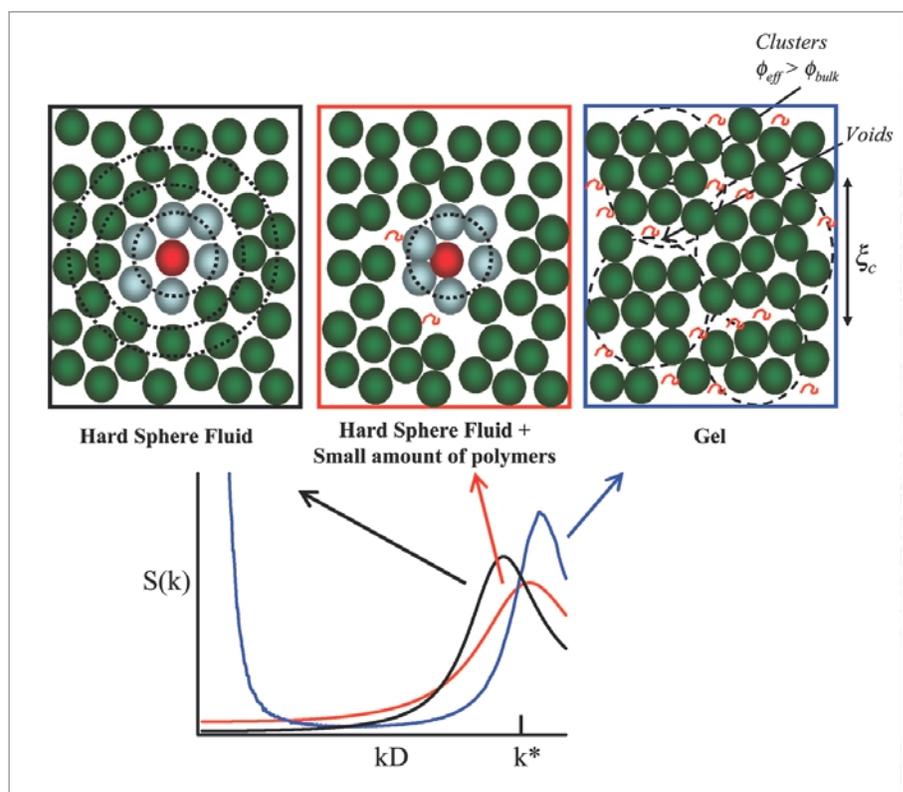


Fig. 1. Illustration (left to right) of particle organization in a hard sphere fluid, weakly clustered nanoparticle fluid, and a gel composed of dense percolated clusters with a locally increased effective volume fraction and an average size  $\xi_c$ . Also shown is a schematic illustrating changes in the structural correlations as equilibrium fluids transform to dense gels.

[2] M. Fuchs and K.S. Schweizer, "Structure of Polymer-Colloid Suspensions," *J. Phys. Condens. Matter* **14**, R239-R269 (2002).

[3] S. Ramakrishnan, Y.L. Chen, K.S. Schweizer, and C.F. Zukoski, "Elasticity and Collective Structure in Concentrated Depletion Gels," *Phys. Rev. Lett.* (submitted February 2004).

[4] S.A. Shah, Y.L. Chen, K.S. Schweizer, and C.F. Zukoski, "Viscoelasticity and Rheology of Depletion Flocculated Gels and Fluids," *J. Chem. Phys.* **119**, 8747-8760 (2003).

**See:** Reference [1] above is the source for this article.

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## DETAILED CHARACTERIZATION OF TWO DISTINCT PHASE TRANSITIONS AT THE SURFACE OF POLY(*n*-ALKYL ACRYLATES)

X-ray reflectometry (XR), grazing incidence x-ray diffraction (GIXD), and infrared-visible sum-frequency generation spectroscopy (SFG) were all used to unambiguously delineate the two distinct surface phase transitions that poly(*n*-alkyl acrylate) comb polymers with alkyl side chains undergo when heated above the bulk melting temperature  $T_m$ . Researchers from the University of Akron, Kent State University, and Iowa State University used synchrotron x-rays produced at the MU-CAT 6-ID beamline at the APS for the XR and GIXD measurements.

Previous research performed at the University of Akron by this group had already demonstrated a two-step transition from order to disorder for short alkyl chains chemically linked to a flexible polymer backbone. That particular research was limited to surface-sensitive SFG spectroscopy alone. In this technique, the SFG intensity is proportional to the direction of the alkyl side chains; therefore, the measured SFG intensities were used to determine the side-chain orientations.

Depending on the size of the alkyl side chain, the first transition was found to occur at 1–2°C above  $T_m$ . The second surface transition was found to take place at 10–20°C above  $T_m$ . (Again, the variation in phase transition temperature depended on the length of the particular alkyl side chain present.)

While SFG spectroscopy established the existence and temperature ranges of the phase transitions for the material studied, it was, by itself, inadequate for describing the structure in different phase regimes. The XR, GIXD, and SFG techniques together provided the data necessary to determine the changes in the polymer's surface structure associated with its two-phase transitions.

For this study, poly(*n*-alkyl acrylate) comb polymers with varying alkyl side-chain lengths were synthesized and probed. However, this paper mainly discusses results for the comb polymer having 21 methylene and 1 methyl unit side chains ( $n = 22$ ). Differential scanning calorimetry (DSC)—with heating and cooling rates of 0.3°C/min—was used to determine this material's bulk melting temperature of 64.9°C, while its temperature of crystallization ( $T_f$ ) was found to be 60.8°C.

At 60°C (4.9°C below  $T_m$ ), and at an incident angle of 0.5 times the critical angle (the angle of total external reflection), the GIXD measurements showed the presence of a crystalline

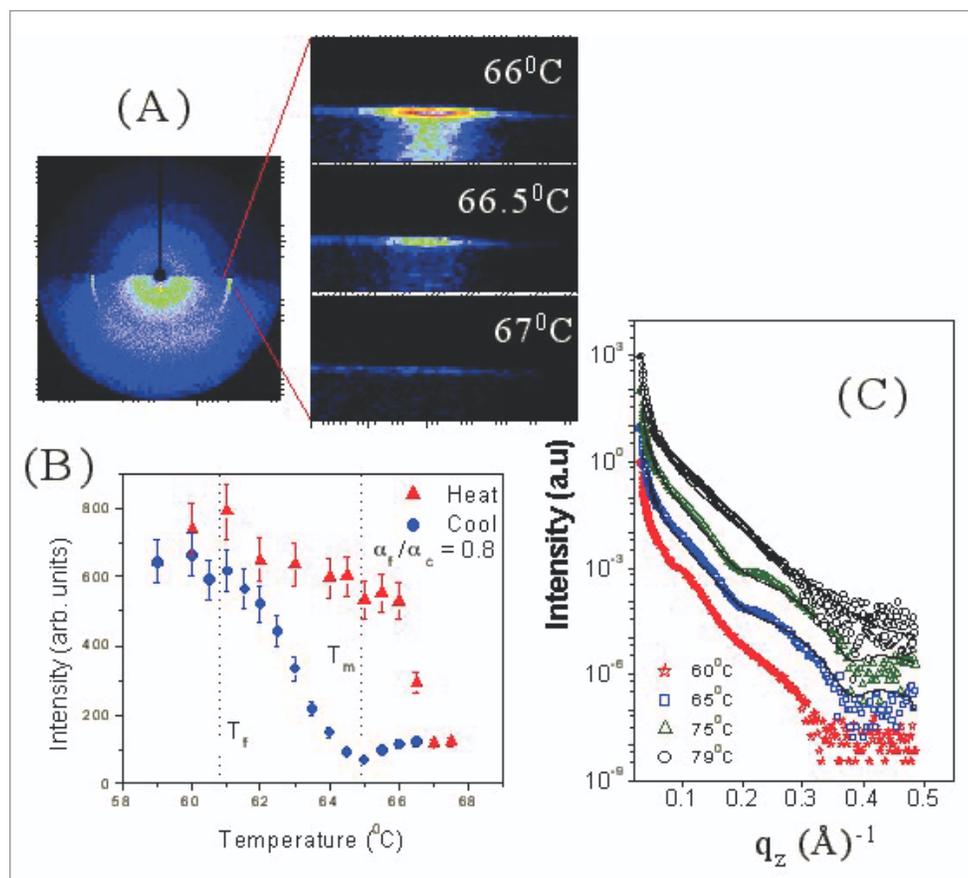


Fig. 1. (A) Image of the diffraction patterns on the plate detector at 60°C, and expanded views of the diffraction patterns obtained above the bulk-melting temperature  $T_m$  (64.9°C). (B) X-ray intensity as a function of temperature at a fixed value of  $\alpha_f$ (diffraction angle)/ $\alpha_c = 0.8$  in the heating (triangles) and cooling (circles) cycles. The dashed lines are bulk transition temperatures measured by using DSC at a heating and a cooling rate of 0.3°C/min. (C) X-ray intensity plotted as a function of  $q_z$  (Å<sup>-1</sup>) for four different temperatures. These measurements were done in the cooling cycle. The Kiessig fringes, above the first transition, correspond to a 33-Å high-density ordered monolayer on the surface.

surface layer with a lattice spacing of 4.2 Å (Fig. 1). That lattice spacing translates to a side-chain-to-chain spacing of 4.85 Å and an area per side chain of 20.4 Å<sup>2</sup> per chain. All these quantities reveal that the crystallized alkyl chains are oriented normal to the surface.

An abrupt change in measured GIXD intensity at 66.5°C (1.6°C above  $T_m$ ) indicated the melting of surface alkyl side chains. This temperature marked the first phase transition. Beyond 67°C (2.1°C above  $T_m$ ), GIXD measurements indicated the loss of the long-range crystalline order. But XR analysis showed the presence of a higher density surface layer above 67°C, indicating that the material—even though it was no

longer in a crystalline form—still possessed at least some sort of molecular ordering. At 74.9°C (10°C above  $T_m$ ), the second phase transition occurred, and the surface layer became completely disordered.

The SFG data verified and complemented the results from the GIXD and XR measurements. The SFG data for the first phase transition, associated with melting of the surface chains, was consistent with the GIXD results. Further heating above the first transition temperature indicated the presence of ordered alkyl side chains at the surface, which was consistent with the XR results above  $T_m$ . At 10° above  $T_m$ , however, a pronounced drop in SFG intensity showed the transition (i.e., the second phase transition) from a noncrystalline, smectic-like state to a disordered surface layer. When the process was reversed (that is, when the material was cooled), the transitions from the disordered to “semi-ordered,” to crystalline state occurred in the expected sequence, but a hysteresis effect was encountered. In other words, the temperatures marking the transition from one

phase to another were slightly lower when the material was being cooled than when it was being heated.

A detailed understanding of the surface structure and transition temperatures of the type of material examined in this study has important potential applications in the design of heat-responsive surface adhesives, as well as ramifications in other areas of research. ○

**See:** K.S. Gautam<sup>1</sup>, S. Kumar<sup>2</sup>, D. Wermeille<sup>3</sup>, D. Robinson<sup>3</sup>, and A. Dhinojwala<sup>1</sup>, “Observation of Novel Liquid-Crystalline Phase above the Bulk-Melting Temperature,” *Phys. Rev. Lett.* **90**, 215501-1 to 215501-4 (30 May 2003).

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## UNUSUAL STRUCTURE IN THIN ALKANE FILMS

A microscopic theory of lubrication requires a detailed understanding of the physical configuration of the thin films that make up the lubricating coat—how their molecules are configured in each layer of a film. Alkane molecules are particularly attractive for such studies, not only because they are the principal constituents of commercial lubricants but also because they are a simpler molecule that serves as a prototype of the more complex polymers that are used in coatings, adhesives, and electronic devices.

There have been intriguing hints about the peculiarities of how alkanes configure themselves at boundaries and interfaces. An alkane fluid-air interface was discovered in which a solid alkane phase immediately adjacent to the air not only persists a few degrees above the bulk melting point, but in which the rod-like alkane molecules align themselves perpendicular to the interface, standing on end.

Subsequent studies of an alkane film adsorbed onto silicon dioxide (SiO<sub>2</sub>)-coated substrates found an unusual growth mode. Next to the substrate, the long alkane molecules (chemical formula C<sub>32</sub>H<sub>66</sub>, denoted “C32” and known as dotriacontane) lay down parallel to the surface, in a film one or two molecular layers thick. Just above this parallel layer, though, is an alkane layer in which the molecules are aligned perpendicular to the substrate, standing up on end, one molecular layer thick. Above this perpendicular phase, alkane molecules are observed to nucleate in bulk particles.

This novel growth mode of alkane on silicon dioxide was inferred using the optical method of high-resolution ellipsometry—experiments that use the change in the polarization state of visible laser light to measure optical thickness—but it had not received direct microscopic confirmation. Using x-ray specular scattering measurements conducted at the MU-CAT 6-ID-B beamline at the APS, a team from the University of Missouri-Columbia, Pontificia Universidad Católica de Chile, Brookhaven National Laboratory, Technical University of

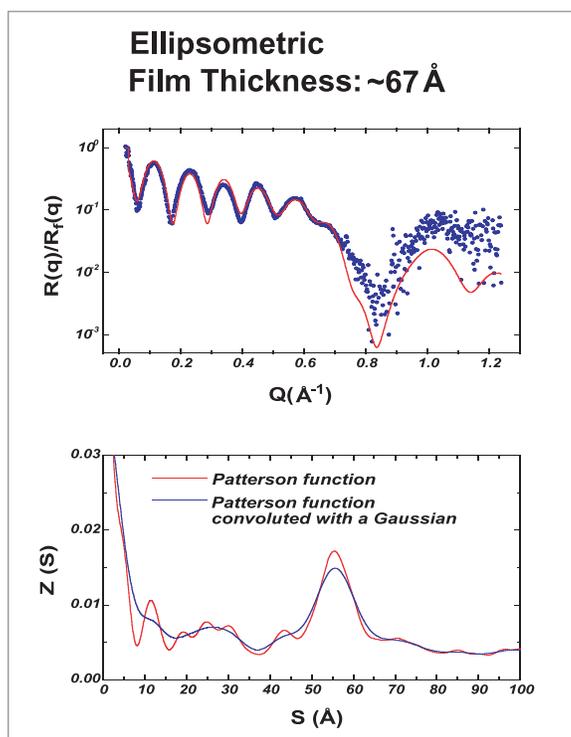


Fig. 1. Top: Representation of a normalized x-ray reflectivity, as a function of photon momentum transfer, for C<sub>32</sub>/SiO<sub>2</sub> sample with a C<sub>32</sub> thickness of 67 Å. Bottom graph represents a transformation of the reflectivity curve showing the thickness of the dominant layers in the C<sub>32</sub> film.

Denmark, and the University of Wisconsin-Milwaukee determined the thickness of the parallel and perpendicular alkane film phases. In addition, they showed that the coexisting bulk phase consists of two different structures, both of which are preferentially oriented with respect to the film.

The x-ray beam was scattered off the C32 film, and its reflectivity was scanned and plotted as a function of the incident angle. Peaks and valleys in the reflectivity spectrum are used to infer the thicknesses of the parallel and perpendicular films. A thickness of 11.7 Å was inferred for the parallel-phase film, about twice the width of the C32 molecule, corresponding to a molecular bilayer. (Other samples yielded a parallel film only one molecular layer thick.) The perpendicular-phase film was determined to be 43.2 Å thick, which is about the length of the C32 molecule. In no case was the perpendicular-phase film found to be in direct contact with the silicon dioxide substrate. The coexisting bulk phase was found to exist atop the perpendicular phase in two different structures: an orthorhombic phase and a monoclinic phase.

The present results show that thin films can grow on substrates in novel, unexpected ways, while raising questions about whether a minimum molecular length is required to sta-

bilize the perpendicular monolayer phase and whether the type of substrate, and the nature of the alkane deposition, matters. ○

**See:** H. Mo<sup>1</sup>, H. Taub<sup>1</sup>, U.G. Volkman<sup>2</sup>, M. Pino<sup>2</sup>, S.N. Ehrlich<sup>3</sup>, F.Y. Hansen<sup>4</sup>, E. Lu<sup>5</sup>, P. Miceli<sup>1</sup>, "A novel growth mode of alkane films on an SiO<sub>2</sub> surface," Chem. Phys. Lett. **377**, 99-105 (2003).

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## SHEAR EFFECTS ON INTERFACIAL STRUCTURE IN LIQUIDS

The effect of shear flow on interfacial structures is a relatively unexplored phenomenon, particularly at nanoscale dimensions. While x-ray scattering is a useful technique in the study of liquid structure near interfaces, it is difficult to study shear effects with this means because of the necessity of enclosing the liquid under study within solid substrates and the resultant attenuation and scattering of the x-ray beam caused by the substrates. Under such limitations, only strong signals from bulk liquid structure are normally detectable, rather than weaker signals from interfacial boundaries. A team from Northwestern University managed to overcome these difficulties in order to study shear flow effects on the interfacial structures of two nonpolar liquids, tetrakis (2-ethylhexoxy)silane (TEHOS) and poly(dimethylsiloxane) (PDMS), using the MR-CAT 10-ID beamline at the APS and the MATRIX beamline X18-A at the National Synchrotron Light Source.

The Northwestern team created a sample chamber consisting of a stainless steel liquid sample holder encased in a circular housing with a Kapton window allowing access by the x-ray beam (Fig. 1). A silicon substrate protruded slightly above the top of the sample holder, permitting x-rays to encounter the sample at small incidence angles. To apply shear, the outer housing of the sample chamber was rotated, with the sample liquid confined between the Kapton window and a magnetic seal.

X-ray scattering data from unsheared TEHOS shows a scattering maximum at 0.63 Å<sup>-1</sup>, which indicates layering of the interfacial TEHOS with an approximately 10 angstrom spacing

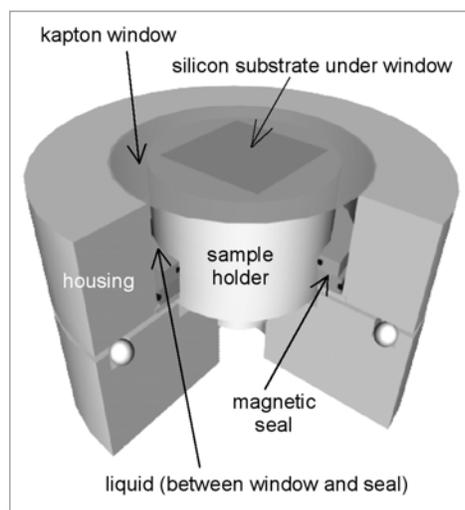


Fig. 1. Schematic diagram of experimental setup. The outer housing and attached kapton window are rotated to apply shear.

between individual layers. After shear stress is applied at a rate of 0.17 turns per second for 1 minute, and reflectivity is measured at various distances from the center in regions with different shear rates, the diffraction peak diminishes, while maintaining the same shape and position as observed without shear. This suggests that the number of ordered layers is not reduced but an increasing part of the substrate surface is covered by disordered rather than layered TEHOS. The peak takes several hours to recover following the removal of shear stress.

These effects are quite distinct from those observed by the Northwestern researches in PDMS, a polymeric liquid of long and flexible molecules. Without the application of shear stress, PDMS displays no dif-

fraction peak attributable to layering. Only at very high shear rates, approximately 104 s<sup>-1</sup>, does a change occur, demonstrating molecular layering at a thickness of approximately 30 angstroms in the ordered region of the interface. Because the layered PDMS region returned to a disordered state in approximately 3 hours, the experimenters suggest that the layering observed under shear stress is due to the disentanglement of the polymeric chains.

The Northwestern/MR-CAT sector 10 results provide a clear demonstration of the usefulness of shear effects in the observation and study of interfacial molecular structure. Shear effects can be applied in order to manipulate molecules at interfacial regions to provide direct evidence of microscopic structure under x-ray reflectivity observation. ○

**See:** C. Yu, G. Evmenenko, J. Kmetko, and P. Dutta, "Effects of Shear Flow on Interfacial Ordering in Liquids: X-ray Scattering Studies," *Langmuir* **19**, 9558-9561 (2003).

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## PHASE TRANSITIONS IN SUSPENSIONS OF COLLOIDAL *fd* VIRUS

Whether of biological or technological origin, liquid crystals are composed of elongated rod-like molecules that undergo phase transitions in which the molecules spontaneously rearrange themselves, not unlike the phase transition when liquid water transforms into crystalline ice. In the simplest of these phase transitions, the rods change from an "isotropic" phase, where each rod points in a random direction, to a "nematic phase" where all rods point more or less in the same direction.

What drives this phase transition? Molecules in a liquid both attract and repel one another. Repulsive interactions tend to dominate in fluids, as molecules bounce off that hard-core potential that exists. Long rod-like viruses are particularly interesting for the study of such phase transitions, because they're so large that the underlying repulsive interactions dominate over quantum mechanical interactions and van der Waals (attractive) forces. Consequently, the free energy is dominated by entropy, which counterintuitively implies that the low-symmetry liquid crystalline nematic phase is actually more disordered than the high-symmetry isotropic phase. In the 1940s, Onsager developed a theory of such phase transitions, modeling the isotropic to nematic phase transition via a tour de force of statistical mechanics.

Testing Onsager's theory is possible by using the *fd* virus in solution. One must measure a central quantity in his theory: the probability that a molecule points at a certain angle, called the angular distribution function. *fd* viruses, discovered in the sewers of New York City in the 1970s, have a high aspect ratio, with a length-to-diameter ratio of 130:1, and importantly, they are monodispersed—all of the same length. Until this experiment, these two qualities had never before been realized in a physical system, making this the most complete test of Onsager's theory. (Polymer chemists are yet unable to produce polymers all of the same length, something nature has been doing for three billion years.) Unlike some science today, where physicists are turning to biological questions, here biology has come to the aid of physics.

In order to measure the angular distribution function, x-ray diffraction was done at the small-angle x-ray scattering (SAXS) station on the IMMY/XOR 8-ID beamline at the APS by experimenters from Brandeis University, Massachusetts Institute of Technology, Northern Illinois University, and Yale University.

Insofar as the assumptions of Onsager hold—that electrostatic repulsions are minimized, a condition obtained by adding the *fd* virus to a high salt solution—his theory was found to be quite accurate. (The salt serves to screen the long-range attractions.) However, as electrostatic interactions become stronger (that is, as salt concentrations become weaker, or virus concentrations become high), Onsager's theory begins to fail, indicating a need for further theory in terms of charged macromolecules. Thus, in order to understand biopolymers, such as actin or neurofilaments or even DNA, which in their biological milieu are highly concentrated and aligned in liquid crystalline states, additional theory is needed. ○

**See:** K.R. Purdy<sup>1</sup>, Z. Dogic<sup>1</sup>, S. Fraden<sup>1</sup>, A. Ruhm<sup>2</sup>, L. Lurio<sup>3</sup>, S.G.J. Mochrie<sup>4</sup>, *Phys. Rev. E* **67**, 031708-1 to 031708-12 (2003).

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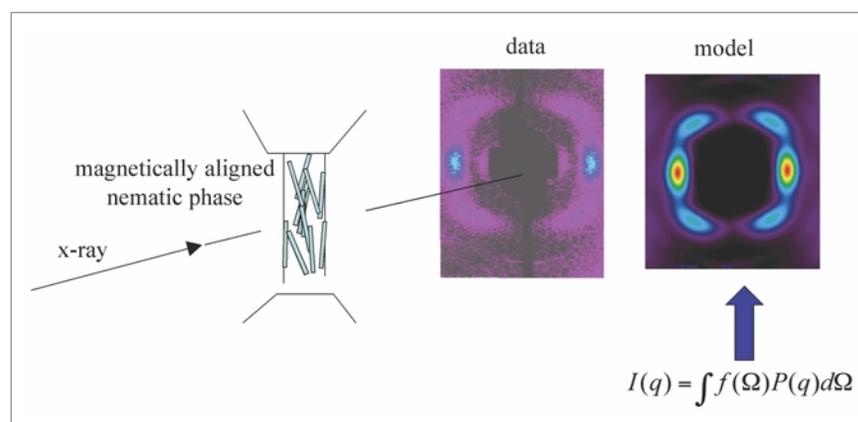


Fig. 1. The *fd* virus consists of about 2700 copies of a single protein helically arranged to form a hollow cylinder into which is stuffed the viral DNA. The periodic arrangement of the proteins causes x-rays to be scattered as distinct spots arranged in layers perpendicular to the virus axis. The x-ray scattering pattern from a perfectly aligned virus shows peaks that are very sharp and are confined to horizontal planes. Shown is an example of scattered x-rays from a nematic sample compared with the calculated data. Different angular distribution functions are used to model the data, and the one that best fits the data is used to calculate the phase transition order parameter.

## SURFACE DYNAMICS OF POLYMER FILMS

Thin polymer films are attracting considerable attention because they have a wide variety of technological applications, ranging from the creation of bio-compatible surfaces for medical implants to expanding the limits of computer disk drive technology.

Recent theoretical work has raised questions about whether thermal effects could cause polymer thin films to stratify such that their viscosity varies with depth. Clearly, such an effect would present a challenge—or an opportunity—for applications that depend on surface properties of such films. However, it is not clear how well the theory holds for films with a thickness on the same order as the length of the polymer chains.

The first experiments testing the theoretical premise behind this predicted effect have been conducted at IMMY/XOR beamline 8-ID. The emerging technique of x-ray photon correlation spectroscopy (XPCS) was used to measure random thermal fluctuations in the surface height of a thin polystyrene film as a function of lateral length scale. The results support the theory in question: namely, that the surface dynamics of a polymer film take the form of overdamped thermal capillary waves. Such waves are something like the ripples spreading from a pebble dropped in water.

The method used, XPCS, extends a well-established laser technique to the smaller length scales accessible with x-rays. It exploits the coherence of synchrotron x-rays to generate a speckle pattern that reflects spatial inhomogeneity. The method is particularly well suited to studying spatial dynamics on relatively slow time scales (seconds to minutes).

The goal of the initial experiment was to determine how fast the surface disturbances relax, or smooth out, and also whether this relaxation time varies depending on the wavelength (or wave vector) of the disturbance. The XPCS method allows simultaneous measurement of features at several length scales. In this case, the relaxation times were measured for wave vectors ranging from  $10^{-3}$  to  $10^{-2}$  nm $^{-1}$ .

The samples studied were polystyrene films ( $M_w = 123,000$  g/mol) with thicknesses ranging from 84 to 333 nm, prepared by spin-casting on silicon substrates. Measurements were taken at temperatures ranging from 150 to 170°C (above the polystyrene glass transition temperature). Effects of interaction between the film and substrate were excluded by choosing an incident beam angle that limited the depth of penetration to  $\sim 9$  nm. The off-specular diffuse scattering from the polymer surface was recorded with a direct-illumination CCD camera.

Figure 1 shows a CCD image and a fit to the capillary wave model for an 84-nm film. The good agreement between the data and

the model confirms that the surface morphology of the film is governed by capillary waves. The results also showed that the surface tension and viscosity are consistent with that of bulk polystyrene and that the overall film viscosity is independent of both film thickness and the length scale of the disturbance. The data also confirm the expected relationship between the wave vector and the relaxation time and film thickness: long-wavelength ripples damp out more slowly than small ones, and all relaxation times are faster in the thicker films.

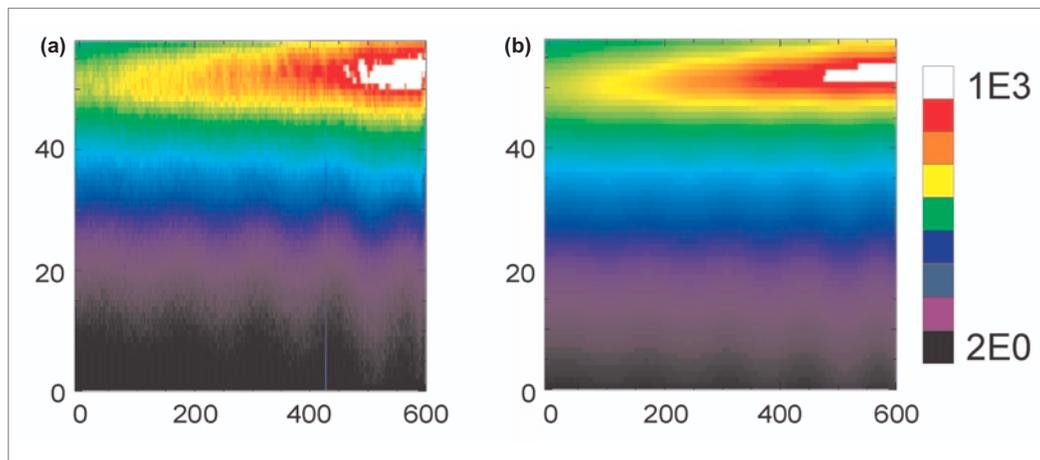


Fig. 1. (a) Time-averaged thermal diffuse scattering from the surface of an 84-nm-thick polystyrene film at 160°C. (b) Results of capillary wave model for same film thickness and temperature. The close agreement with (a) shows that this model holds for polymer films.

These initial results were used in a preliminary analysis of the potential for viscosity to vary with depth in the film. The calculations show that if a high-mobility surface layer were present, it would not be more than 10 nm thick. This layer might cause the viscosity of the thin film to differ from that of the bulk, but only in films thinner than  $\sim 20$  nm. Further experiments are in progress to explore such effects. ○

**See:** H. Kim<sup>1,2,3</sup>, A. Rühm<sup>4,5</sup>, L.B. Lurio<sup>4,6</sup>, J.K. Basu<sup>1,7</sup>, J. Lal<sup>1</sup>, D. Lumma<sup>4</sup>, S.G.J. Mochrie<sup>8</sup>, and S.K. Sinha<sup>1,2</sup>, "Surface Dynamics of Polymer Films," *Phys. Rev. Lett.* **90**(6), 068302-1 to 068302-4 (14 February 2003).

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