Using Electrostatic Levitation and High-energy X-ray Diffraction to Probe the Nature of Deeply Supercooled Liquids

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Abstract

Over a half-century ago, David Turnbull observed that the temperature of liquid metals could be decreased below their equilibrium melting temperatures before crystallization occurred.[1] That liquids can be supercooled was not new; it was first reported for water in 1724.[2] What made Turnbull's report so interesting was that it was the first time that significant supercooling had been observed in a liquid metal. Since the densities and coordination numbers of metallic liquids and crystals are generally so similar, it was widely assumed that the short-range order in the two phases must be similar, giving a low nucleation barrier and allowing crystallization to proceed readily, as was commonly observed. To explain Turnbull's results, Charles Frank suggested that in spite of their similarities the structures of metallic liquids and crystals are actually quite different, with the liquid containing a significant degree of icosahedral short-range order (ISRO).[3] Surprisingly, Frank's hypothesis was only unambiguously confirmed by experiment very recently, by combining electrostatic levitation (ESL) and high-energy synchrotron radiation scattering techniques.[4] Although liquids are extremely common, our understanding of their properties and phase transitions is significantly inferior to that for gases and crystals. This is especially true for supercooled (nonequilibrium) liquids. Frank's hypothesis is only one illustration; the nature of the glass transition in supercooled liquids, one of the central unsolved problems in condensed matter physics and materials science, is another. The need for detailed structure and property measurements of solids at high temperatures provides further motivation. In addition to their fundamental interest, the lack of these data hinders the development of new materials for high temperature applications.

The primary impediment to quantitative experimental investigations of both solids and liquids at high temperature is contamination. Within the past twenty years, containerless methods have been developed that allow supercooling studies of samples with diameters ranging from millimeters to centimeter sizes. Such techniques eliminate the largest source of contamination, the container itself. Techniques have also been developed to measure physical properties of containerless liquids, such as the liquid density, surface tension, viscosity, specific heat, magnetization and, most recently, the liquid structure in equilibrium and nonequilibrium liquids. Contamination-free studies of structure, phase transitions and thermophysical and magnetic properties of solids at very high temperatures are also possible, providing critical information for demanding technological applications. While containerless studies *via* a variety of levitation methods have been possible for some time, the electrostatic levitation (ESL) technique[5-9] allows investigations that were not previously possible. With ESL a wide range of materials including insulators, semiconductors and conductors can be studied. Moreover, it is possible to control precisely the sample position, stability, heating and thermal gradients, allowing for unprecedented experimental control. At the same time, there have been exciting advances in x-ray scattering techniques and technology, including the realization of the current generation of x-ray sources, the development of efficient area detectors for fast data collection, and tremendous progress in the use of high-energy x-rays for structural measurements.

New ESL chambers have recently been constructed at Washington University and Iowa State University. The WU-BESL has been optimized for high-energy x-ray measurements at the APS that

provide insight into the local structural features of deeply undercooled liquids on timescales ranging from tens of milliseconds to minutes. The ISU-ESL has been optimized for measurements of thermophysical properties including, novel, contactless measurements of magnetic susceptibility and electrical conductivity using a novel tunnel diode method.[10] Even more recently, funding has been obtained for the construction of NESL, and ESL chamber optimized for neutron scattering measurements of structure and dynamics at the Spallation Neutron Source. Taken together, this suite of facilities will provide a great deal of new insight into the thermophysical properties, structure, and dynamics of deeply undercooled liquids.

Looking even further ahead, we envision improvements in x-ray flux and detector cycling speeds, or the incorporation of pump-probe methods that will enable us to move into the microsecond time domain, and beyond, to study the early stages of solid growth from supercooled liquids. The use of inelastic x-ray scattering for studies of liquid dynamics may be feasible, but the limited time available to study molten samples (with the attendant mass loss and compositional changes) will require even higher photon fluxes. Finally, high-energy small-angle scattering facilities for investigating issues such as phase separation in liquids are also possible.

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