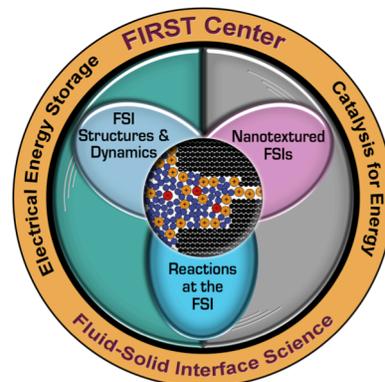


FIRST Center Research Perspective:

QENS studies of bulk and nanoconfined fluid diffusional dynamic properties

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Research Summary: We have proposed and experimentally verified that fluids in general exhibit two separate microscopic dynamic processes on pico- to nano-second time scales. The faster process can be described as a localized diffusion spatially constrained in the transient cage made by the neighbor particles. Despite often being referred to as “rotational” dynamics, we have repeatedly shown that these motions involve the displacements of the center-of-mass, and, as such, are not purely rotations. The slower process originates from the eventual breakup of the transient cage of the neighbor molecules and is associated with the structural rearrangements and long-range translational diffusion in fluids. Confinement of a fluid inside nano-pores or on solid particle surfaces does not affect the presence of these two separate dynamic processes.

Technical Details: Quasielastic neutron scattering (QENS) is the technique of choice for studying microscopic single-particle fluid dynamics on the time scale of pico- to nano-seconds, thanks to the spatial information that can be extracted from the signal dependence on the scattering momentum transfer, Q . This spatial information, lacking in complementary techniques (NMR, dielectric and optical spectroscopy, etc.), allows direct comparison with molecular dynamics (MD) simulations, yet introduces a substantial degree of complexity in the QENS data interpretation. We have demonstrated that fluids in general exhibit two separate dynamic processes on ps-ns time scale, both identifiable by QENS [1, 2]. The faster of the two processes can be described as a localized diffusion spatially constrained in the transient cage made by the neighbor particles. Despite often being referred to as “rotational” dynamics, these motions involve the displacements of the center-of-mass inside the cage. Thus, these motions are not strictly rotations. The slower of the two processes originates from the eventual breakup of the transient cage of the neighbor molecules. This process is associated with the structural rearrangements and long-range translational diffusion in fluids. While at high temperatures these two

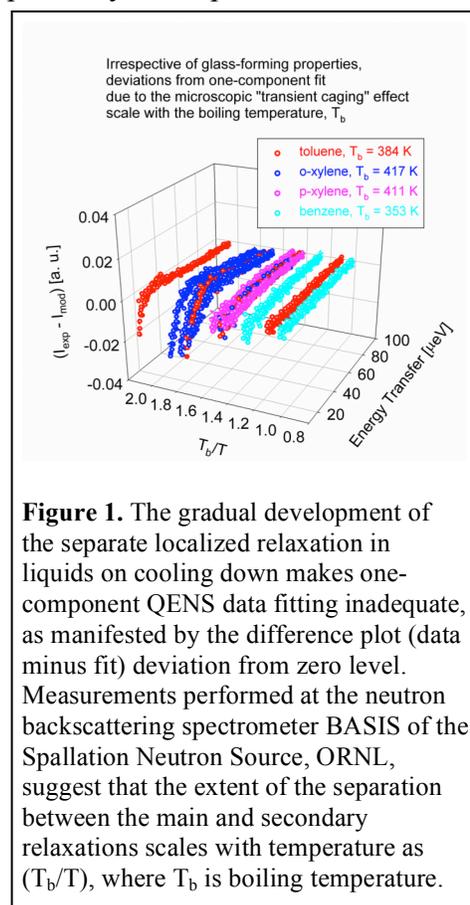


Figure 1. The gradual development of the separate localized relaxation in liquids on cooling down makes one-component QENS data fitting inadequate, as manifested by the difference plot (data minus fit) deviation from zero level. Measurements performed at the neutron backscattering spectrometer BASIS of the Spallation Neutron Source, ORNL, suggest that the extent of the separation between the main and secondary relaxations scales with temperature as (T_b/T) , where T_b is boiling temperature.

processes are merged, their separation becomes evident on cooling down. In a QENS experiment on a series of related aromatic molecular liquids [2], we have observed a gradual separation between the localized and long-range dynamic processes on cooling down as a function of (T_b/T) , where T_b is boiling temperature (**Figure 1**). This observation suggests universal microscopic dynamic behavior in fluids irrespective of their glass-forming properties. We have verified the presence of the two separate microscopic dynamic processes in a variety of liquid systems. These include water, glycerol, molten selenium, aromatic compounds, and various room-temperature ionic liquids (RTILs). Of particular interest to us is the influence of confinement on the microscopic dynamics of technologically important fluids, such as RTILs. We have found that confinement in nano-pores of carbon does not qualitatively change the character of microscopic dynamics of RTILs [3, 4], which is still characterized by the separate dynamic processes (see, e.g., **Figure 2**). Furthermore, even in the confined RTIL, each dynamic process involves center-of-mass motions, as evidenced by the Q -dependence of the scattering signal (**Figure 3**). Likewise, confinement on carbon nano-onion surface does not qualitatively alter the character of microscopic dynamics of phenanthrenequinone, provided

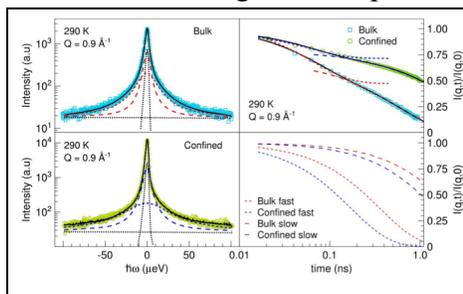


Figure 2. Neutron scattering spectra (left) and the derived scattering functions (right) for room-temperature ionic liquid 1-Butyl-3-Methyl-Imidazolium bis(trifluoromethanesulfonyl)imide in the bulk form (top) and confined in mesoporous (8.8 ± 1.1 nm diameter) carbon (bottom). The liquid invariably exhibits the localized and long-range microscopic dynamic processes. The measurements were performed at the neutron backscattering spectrometer BASIS of the Spallation Neutron Source, ORNL.

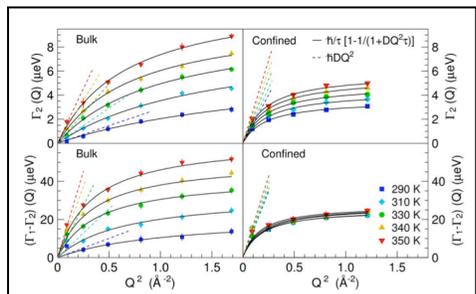


Figure 3. The Q -dependence of the QENS signal broadening measured from bulk and confined 1-Butyl-3-Methyl-Imidazolium bis(trifluoromethanesulfonyl)imide, as presented in Figure 2. The broadening that increases with Q is indicative of the center-of-mass motions associated with the fast (broader signal, bottom) and slow (narrower signal, top) dynamic components. The deviations from the fit at low Q indicate spatially localized character of the fast (but not the narrow) dynamic component. The localization is due to the transient cage formed by the neighbor particles in the liquid.

that the surface coverage is sufficiently high [5]. This observation is reminiscent of behavior of surface water in oxides, which also requires sufficient coverage to attain quasi-bulk dynamic state. Our research highlights the truly universal aspects of microscopic fluid dynamics and their dependence on the surface coverage or confinement dimensions, irrespective of the specifics of the fluid.

Significant Impacts on Science and Technology: Having elucidated the universal features of the microscopic single-particle fluid dynamics, we are now positioned to investigate systematically the influence of an interface on the molecular mobility of interfacial fluids. Our studies to date have demonstrated the applicability of the two dynamic processes description to ionic and molecular liquids in confinement and on surfaces, provided that the surface coverage is not too low. The dependence of the interfacial fluid microscopic dynamics on the surface coverage is to be investigated next. The following important questions will be addressed. At what exact coverage, in the units of particle per unit area, do the molecules on a surface transition from the state of adsorbate molecules to the state of interfacial fluid, with

the microscopic dynamic properties characteristic of bulk-like fluids, including the presence of the separate dynamic processes? Furthermore, it is well recognized that in the interfacial liquids, freezing is often suppressed in favor of glass formation, perhaps most famously in surface and tightly confined water. What microscopic dynamic features of the interfacial fluids are responsible for this behavior? While confinement usually suppresses the dynamics of fluids, can the very tight confinement in some cases facilitate the confined fluid mobility, due to the suppression of the “caging” effect by neighbor molecules, thus leading to improved characteristics of the devices that rely on nano-confined fluids? Such a possibility, in fact, can be suggested by our QENS measurements of microscopic dynamics of water confined in the subnanometer pores in carbide-derived carbon [6]. In these measurements, a single, albeit somewhat stretched, dynamic process could adequately describe the data. Addressing these and similar questions may lead to transformative breakthroughs in fundamental understanding and, eventually, technological applications of nano-confined fluids.

Publications and Manuscripts:

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