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Multiple Time Scale Behaviors and Network Dynamics in Liquid Methanol

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Canonical ensemble molecular dynamics simulations of liquid methanol, modeled using a rigid-body, pair-additive potential, are used to compute static distributions and temporal correlations of tagged molecule potential energies as a means of characterizing the liquid state dynamics. The static distribution of tagged molecule potential energies shows a clear multimodal structure with three distinct peaks, similar to those observed previously in water and liquid silica. The multimodality is shown to originate from electrostatic effects but not from local, hydrogen bond interactions. An interesting outcome of this study is the remarkable similarity in the tagged potential energy power spectra of methanol, water, and silica, despite the differences in the underlying interactions and the dimensionality of the network. All three liquids show a distinct multiple time scale (MTS) regime with a $1/f^{\alpha}$ dependence with a clear positive correlation between the scaling exponent α and the diffusivity. The low frequency limit of the MTS regime is determined by the frequency of crossover to white noise behavior which occurs at approximately 0.1 cm^{-1} in the case of methanol under standard temperature and pressure conditions. The power spectral regime above 200 cm^{-1} in all three systems is dominated by resonances due to localized vibrations, such as librations. The correlation between α and the diffusivity in all three liquids appears to be related to the strength of the coupling between the localized motions and the larger length/time scale network reorganizations. Thus, the time scales associated with network reorganization dynamics appear to be qualitatively similar in these systems, despite the fact that water and silica both display diffusional anomalies but methanol does not.

1. Introduction

Considerable experimental as well as theoretical attention has been devoted to characterizing the structure and dynamics of hydrogen-bonded liquids.[1-10] The motivation for these studies is primarily due to the importance of water as a solvent for biological and chemical processes. A comparison of the behavior of water with other second-row hydrides, such as HF, NH_3, and CH_3OH, is essential for understanding the nature of hydrogen-bonded dynamics and the extent to which the behavior of water is unique. Methanol, in particular, is of interest because it is the simplest molecule which can exhibit both hydrogen bonding and nonpolar interactions.

While interactions in simple liquids are dominated by steep, short-range repulsions and long-range isotropic attractions, hydrogen-bonded liquids have strong, local anisotropic interactions. In the case of water, each molecule can form at most four hydrogen bonds, leading to a three-dimensional, open, locally tetrahedral network structure. The strength of hydrogen bonds is estimated to be between 5 and $10k_BT$ at melting[11] which is strong enough that a substantial fraction of hydrogen bonds will be intact at room temperature. Thermal fluctuations will, however, be large enough, in comparison to the bond strength to ensure that such bonds will have a finite lifetime of the order of picoseconds. As a result, the dynamics of the liquid will be dominated by the behavior of the three-dimensional, hydrogen-bonded network, parts of which are constantly broken and reformed. In the case of methanol, hydrogen bond strengths are similar to those in water,[12] but each methanol molecule can form at most three hydrogen bonds, of which only one can be as a proton donor. In liquid methanol, however, simulations as well as neutron scattering experiments show that the typical number of hydrogen bonds per molecule is two.[13-15] Consequently, linear chains with very rare branch points are seen, rather than the three-dimensional network characteristic of water.

Hydrogen-bonded liquids can be thought of as a subset of network forming liquids, other examples being ionic melts such as $ZnCl_2$, SiO_2, and BeF_2.[16] The strong local coupling of individual atomic or molecular units leads to the existence of multiple length and time scales corresponding to cooperative rearrangements of the network involving different numbers of molecules. To characterize the dynamical behavior of network-forming liquids, it is convenient to use the power spectral density of a mechanical quantity that is sensitive to motion on a number of different length scales. The power spectral density of an observable $A(t)$ as a function of time t over a time interval T is defined as[17]

$$S(f) = \lim_{T\to\infty} \frac{1}{T}\left|\int_{-T/2}^{T/2} A(t)\,e^{-2\pi i f t}\,dt\right|^2 \qquad (1)$$

where $S(f)$ is the spectral power associated with frequency f. In a recent set of studies, we have shown that the power spectrum associated with the tagged particle potential energy can be used to characterize the dynamics of tetrahedral, network-forming liquids, such as water[18-21] and SiO_2.[22] Simple liquids show a white noise power spectrum where $S(f)$ is independent of frequency. Network forming liquids, however, have a characteristic multiple time scale regime with $1/f^{\alpha}$ dependence on frequency f with α lying between 1 and 1.8.[23] The three liquids that we have studied all show a region of anomalous diffusivity

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