Theoretical Studies on Heterogeneous Correlated Dynamics in Condensed Phases

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Liquids and biological systems show complicated dynamics because of their structural flexibility and dynamical hierarchy. Understanding these complicated dynamics is indispensable to elucidate chemical reactions, thermodynamical and dynamical properties in solutions, and functions of proteins. We have been investigating ultrafast fluctuations and relaxation dynamics in liquid water and solution by using linear and nonlinear spectroscopy.[1–4] In addition, we have been studying heterogeneous dynamics in supercooled liquids in terms of multi-time correlation function[5] and the molecular origin of anomalous thermodynamic properties of supercooled water.[6]

1. Fluctuations and Relaxation Dynamics of Liquid Water Revealed by Linear and Nonlinear Spectroscopy[1]

Many efforts have been devoted to elucidating the intra- and intermolecular dynamics of liquid water because of their important roles in many fields of science and engineering. Nonlinear spectroscopy is a powerful tool to investigate the dynamics. Because nonlinear response functions are described by more than one time variable, it is possible to analyze static and dynamic mode couplings. Here we review the intra- and intermolecular dynamics of liquid water revealed by recent linear and nonlinear spectroscopic experiments and computer simulations. In particular, we discuss the population relaxation, anisotropy decay, and spectral diffusion of the intra- and intermolecular motions of water and their temperature dependence, which play important roles in ultrafast dynamics and relaxations in water.

2. Molecular Origin of the Difference in the HOH Bend of the IR Spectra between Liquid Water and Ice[2]

The intensity of the HOH bend in the infrared (IR) spectrum of ice is significantly smaller than the corresponding one in liquid water. This difference in the IR intensities of the HOH bend in the two systems is investigated using Molecular Dynamics (MD) simulations with the flexible, polarizable, *ab intio* based TTM3-F model for water, a potential that correctly reproduces the experimentally observed increase of the HOH angle in liquid water and ice from the water monomer value. We have identified two factors that are responsible for the difference in the intensity of the HOH bend in liquid water and ice: (i) the decrease of the intensity of the HOH bend in ice caused by the strong anti-correlation between the permanent dipole moment of a molecule and the induced dipole moment of neighboring hydrogen bond acceptor molecules, and (ii) the weakening of this anti-correlation by the disordered hydrogen bond network in liquid water. The presence of the anti-correlation in ice is further confirmed by *ab intio* electronic structure calculations of water pentamer clusters extracted from the trajectories of the MD simulations with the TTM3-F potential for ice and liquid water.

3. Ultrafast Dynamics of Liquid Water: Frequency Fluctuations of the OH Stretch and the HOH Bend[3)]

Frequency fluctuations of the OH stretch and the HOH bend in liquid water are reported from the third-order response function evaluated using the TTM3-F potential for water. The simulated two dimensional infrared spectra of the OH stretch are similar to previously reported theoretical results. The present study suggests that the frequency fluctuation of the HOH bend is faster than that of the OH stretch. The ultrafast loss of the frequency correlation of the HOH bend is due to the strong couplings with the OH stretch as well as the inter-molecular hydrogen bond bend.

4. Multiple Length and Time Scales of Dynamic Heterogeneities in Model Glass-Forming Liquids: A Systematic Analysis of Multi-Point and Multi-Time Correlations[5)]

We report an extensive and systematic investigation of the multi-point and multi-time correlation functions to reveal the spatio-temporal structures of dynamic heterogeneities in glass-forming liquids. Molecular dynamics simulations are carried out for the supercooled states of various prototype models of glass-forming liquids such as binary Kob–Andersen, Wahnström, soft-sphere, and network-forming liquids. While the first three models act as fragile liquids exhibiting super-Arrhenius temperature dependence in their relaxation times, the last is a strong glass-former exhibiting Arrhenius behavior. First, we quantify the length scale of the dynamic heterogeneities utilizing the four-point correlation function. The growth of the dynamic length scale with decreasing temperature is characterized by various scaling relations that are analogous to the critical phenomena. We also examine how the growth of the length scale depends upon the model employed. Second, the four-point correlation function is extended to a three-time correlation function to characterize the temporal structures of the dynamic heterogeneities based on our previous studies [K. Kim and S. Saito, *Phys. Rev. E* **79**, 060501(R) (2009); *J. Chem. Phys.* **133**, 044511 (2010)]. We provide comprehensive numerical results obtained from the three-time correlation function for the above models. From these calculations, we examine the time scale of the dynamic heterogeneities and determine the associated lifetime in a consistent and systematic way. Our results indicate that the lifetime of the dynamical heterogeneities becomes much longer than the α-relaxation time determined from a two-point correlation function in fragile liquids. The decoupling between the two time scales is remarkable, particularly in supercooled states, and the time scales differ by more than an order of magnitude in a more fragile liquid. In contrast, the lifetime is shorter than the α-relaxation time in tetrahedral network-forming strong liquid, even at lower temperatures.

5. Frequency Dependence of Specific Heat in Supercooled Liquid Water and Emergence of Correlated Dynamics[6)]

Molecular origin of the well-known specific heat anomaly in supercooled liquid water is investigated here by using extensive computer simulations and theoretical analyses. A rather sharp increase in the values of isobaric specific heat with lowering temperature and the weak temperature dependence of isochoric specific heat in the same range are reproduced in simulations. We calculated the spatio-temporal correlation among temperature fluctuations and examined the frequency dependent specific heat. The latter shows a rapid growth in the low frequency regime as temperature is cooled below 270 K. In order to understand the microscopic basis of this increase, we have performed a shell wise decomposition of contributions of distant molecules to the temperature fluctuations in a central molecule. This decomposition reveals the emergence, at low temperatures, of temporally slow, spatially long ranged large temperature fluctuations. The temperature fluctuation time correlation function (TFCF) can be fitted to a William-Watts stretched exponential form with the stretching parameter close to 0.6 at low temperatures, indicating highly non-exponential relaxation. Temperature dependence of the relaxation time of the correlation function can be fitted to Vogel-Fulcher-Tamermann expression which provides a quantitative measure of the fragility of the liquid. Interestingly, we find that the rapid growth in the relaxation time of TFCF with lowering temperature undergoes a sharp crossover from a markedly fragile state to a weakly fragile state around 220 K.

References

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