Theoretical Studies on Heterogeneous Condensed Phase Dynamics

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Education

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Nonlinear intermolecular interactions cause complicated motions in condensed phases, *e.g.* liquids and biological systems. These motions are spatially and temporally heterogeneous with a wide range of time and spatial scales and yield both static and dynamic properties of the systems. In particular, heterogeneity plays important role in strongly-interacting systems, *e.g.* supercooled and ionic liquids, and biological systems. The spatio-temporal non-uniform motions known as dynamic heterogeneity are considered to be a clue to understand supercooled liquids and glass transition. Furthermore, heterogeneous reaction rates have been found in biological systems. Therefore, understanding of spatio-temporal heterogeneous dynamics is essential to the elucidation of the structure, thermodynamics, dynamics, and functions of the systems.

We have been investigating inter- and intra-molecular dynamics of water by third-order nonlinear spectroscopy which provide the detailed dynamics that are not available from conventional IR spectroscopy. We examined two-dimensional IR spectra and the energy relaxation and revealed the molecular mechanism of the ultrafast energy relaxation, which is one of dynamical features of water, *i.e.* the fast energy relaxation is caused by the nonlinear strong coupling between the libration motion and other intra- and inter-molecular vibrational motions.

We have also investigated the dynamics of supercooled liquids. We quantified the lifetime of dynamic heterogeneity by introducing the three-time correlation function of density fluctuation, which is sensitive to the time evolution of dynamic heterogeneity. Our systematic analysis for various systems shows that the lifetime of dynamic heterogeneity is intimately related to configurational entropy and thus the temperature dependence of lifetime of dynamic heterogeneity is more sensitive to the fragility than that of α-relaxation time determined by one-time correlation function. In addition to the analysis of dynamic heterogeneity with multi-time correlation function, we have examined the molecular origin of anomalous temperature dependence of isobaric specific heat of water. The time scale involved in isothermal specific heat has been analyzed by analyzing complex specific heat. We examined the emergence of correlated motion in terms of the wavenumber (k) dependent complex specific heat and the shell-wise energy fluctuation.

Currently, we are investigating how slow motions, which are involved in functions, are induced in biological molecules.

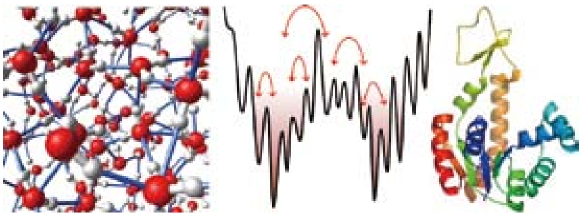

Figure 1. Schematic figure of rugged energy landscape (center) in supercooled water (left) and a biomolecule (right).

Selected Publications

- T. Yagasaki and S. Saito, *Acc. Chem. Res.* **42**, 1250–1258 (2009), *Annu. Rev. Phys. Chem.* **64**, 55–75 (2013).
- S. Imoto, S. Xantheas and S. Saito, *J. Chem. Phys.* **139**, 044503 (7 pages) (2013).
- K. Kim and S. Saito, *J. Chem. Phys. (Special T opic on Glass Transition)* **138**, 12A506 (12 pages) (2013).
- S. Saito, I. Ohmine and B. Bagchi, *J. Chem. Phys.* **138**, 094503 (7 pages) (2013).

1. Anomalous Dynamics of Supercooled Water in “No Man’s Land”

There exists no experimental study on dynamics of supercooled water between 155 K and 232 K, though several conjectures have been put forward. We carry out extensive molecular dynamics simulations from room temperatures down to as low as 130 K. Relaxation times are found to vary over twelve orders of magnitude in traversing this range, with occurrence of multiple anomalies. Structural, dynamical and thermodynamic properties all show a crossover, around 225 K, to a different, low density liquid state with different dynamical properties. On further cooling, this low density liquid again undergoes a dynamical transition around 197 K region where the density reaches its minimum, the dynamical heterogeneity starts to decrease after reaching maximum, and Stokes-Einstein relation, which is violated above 197 K, is recovered below 197 K. The temperature dependence of the relaxation times reveals three distinct branches, with discontinuities around 225 K and 197 K. From analysis of clusters of liquid-like and ice-like molecules, we attribute the latter anomalies to a pseudo-spinodal decomposition where the clusters of liquid-like molecules become fragmented (as if in a reverse percolation transition) and the small high density liquid droplets get surrounded by the dominant low density liquid. The third low temperature branch that appears below 197 K is studied here for the first time and is quite distinct from previous two branches. The relaxation time of this low temperature branch grows rapidly and the fitted relaxation time is projected to cross the 100 s mark around 135 K. We find that the number of defects in the liquid-like clusters serves as a good order parameter to describe this rapid growth. The approach to the amorphous ice is driven both by the rapid disappearance of the liquid-like droplets (below 180 K) and a simultaneous slow down of relaxation.

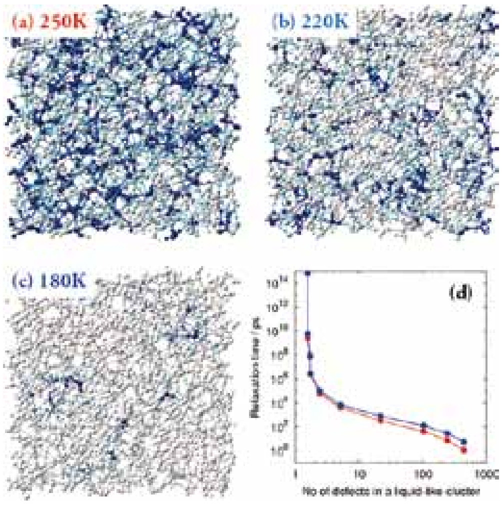

Figure 2. Snapshots of supercooled liquid water at (a) 250, (b) 220, and (c)180 K. (d) Relationship between the number of molecules in a liquid-like cluster and the relaxation times of translational (red curve) and rotational (blue curve) motions. A liquid-like cluster consists of HB defects and their first hydration molecules. Colored molecules in (a)–(c) are liquid-like clusters.

2. Theoretical Study on Excited States of Bacteriochlorophyll *a* in Solutions with Density Functional Assessment

We investigate the excited-state properties of bacteriochlorophyll *a* (BChl *a*) in triethylamine, 1-propanol, and methanol by using the quantum mechanical and molecular mechanical (QM/MM) reweighting free energy SCF method, which is an efficient geometry optimization method of a QM subsystem on a QM/MM free energy surface. We employ the time-dependent density functional theory for the excited-state electronic structure calculations with several density functionals. However, no prevalent functional can reproduce the experimental results, *i.e.* the absorption and reorganization energies of BChl *a* in solutions. We optimize the parameter μ in the range-separated hybrid functionals to reproduce the differences of the absorption energies in three solvents. The CAM-B3LYP functional with μ = 0.20 can also reproduce the reorganization energies in triethylamine almost quantitatively. We examine the origin of the difference of the absorption energies in the three solutions. It is considered that the density functional with an adjusted parameter is essential to the understanding of the excited-state properties of BChl *a* in proteins and also the mechanism of the photosynthetic systems.

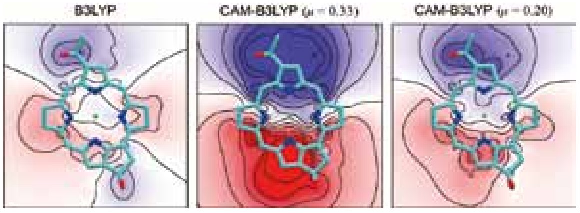

Figure 3. Functional dependence of the change in electrostatic potential of BChl *a* on the Q_y excitation in 1-propanol. The electrostatic potential distribution is calculated at the ground-state optimized geometry. Positive and negative values are shown by red and blue colors, respectively.

References

1) S. Saito, I. Ohmine and B. Bagchi, to be published.
2) M. Higashi, T. Kosugi, S. Hayashi and S. Saito, *J. Phys. Chem. B* (2014), in press.