Theoretical Studies of Reactions, Functions, and Fluctuations in Many-Body Molecular Systems

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Many-body molecular systems, such as liquids and bio-molecular systems, take disordered conformations, and show heterogeneous dynamics, due to complicated molecular interactions. Furthermore, various reactions and biological functions occurs in these kinds of systems. Therefore, understanding of the complicated structures and dynamics is essential for the elucidation of the reactions and functions in the systems.

Multidimensional nonlinear spectroscopy can provide detailed information on dynamics that can not be obtained from conventional IR or Raman spectroscopy. We have developed computational methods of multidimensional nonlinear spectroscopy. As a result, we have revealed the molecular origin of the ultrafast energy relaxations and heterogeneous fluctuations in water based on theoretical two-dimensional (2D) IR spectra.

We have also explored the spatiotemporal heterogeneous dynamics in supercooled liquids referred to as the dynamic heterogeneity. Especially, we have examined the lifetime of dynamic heterogeneity by using the three-time correlation function of density fluctuation, and elucidated the relationship between the lifetime and fragility.

In addition, we have been examining the molecular origin of anomalous properties of water. By performing extensive molecular dynamics simulations, we find that structural and dynamical instabilities of water are hidden in the experimentally inaccessible region between 235 K and 150 K. We also find a crucial role of specific three-coordinated defects in the structural relaxation and glass transition temperature. Now, we investigate how slow but persistent structural relaxations proceed at a very low temperatures to understand the freezing of motions toward the glass transition.

The heterogenous conformational fluctuations/dynamics are also found in biomolecular systems. It is considered that such conformational dynamics are essential for biological functions. We examine the molecular mechanisms of biological functions, i.e., the efficient excitation energy transfer in photosynthetic proteins and the robust circadian rhythm in clock protein KaiC. In addition, we investigate dynamic effects of enzymatic reactions, and explore conformational change dynamics of proteins at the molecular level by using stochastic theory.
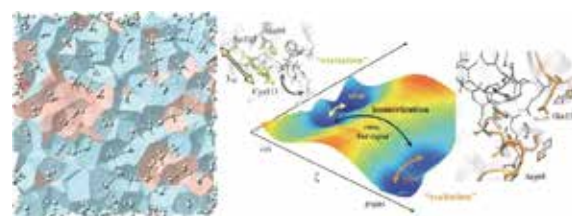

Figure 1. Snapshot of two-state model in supercooled water consisting of high- and low-density liquids (left) and schematic of 2D free energy surface for enzymatic reaction (right).

Selected Publications

• T. Yagasaki and S. Saito, *Annu. Rev. Phys. Chem.* **64**, 55–75 (2013). T. L. C. Jansen, S. Saito, J. Jeon and M. Cho, *J. Chem. Phys.* **150**, 100901 (17 pages) (2019). (Perspective)
• K. Kim and S. Saito, *J. Chem. Phys. (Special Topic on Glass Transition)* **138**, 12A506 (12 pages) (2013).
• S. Saito, B. Bagchi and I. Ohmine, *J. Chem. Phys.* **149**, 124504 (8 pages) (2018).
• J. Ono, S. Takada and S. Saito, *J. Chem. Phys. (Special Topic on Multidimensional Spectroscopy)* **142**, 212404 (13 pages) (2015).
• T. Mori and S. Saito, *J. Phys. Chem. Lett.* **10**, 474–480 (2019).

1. Thermodynamic Picture of Vitrification of Water through Complex Specific Heat and Entropy: A Journey through 'No Man's Land'[1]

We investigate thermodynamic properties of supercooled water across the "no man's land" onto the formation of amorphous ice. The calculations are aided by very long computer simulations, often more than 50 μs long, with the TIP4P/2005 model potential. Density fluctuations that arise from the proximity to a putative liquid-liquid (LL) transition at 228 K, cast a long shadow on the properties of water, both above and below the LL transition. We carry out the calculations of the quantum mechanical static and frequency-dependent specific heats by combining seminal studies of Lebowitz, Percus, and Verlet and Grest and Nagel with the harmonic approximation for the density of states. The obtained values are in quantitative agreement with all available experimental and numerical results of specific heats for both supercooled water and ice. We calculate the entropy at all the state points by integrating the specific heat. We find that the quantum corrected-contributions of intermolecular vibrational entropy dominate the excess entropy of amorphous phases over the crystal over a wide range of temperatures. Interestingly, the vibrational entropy lowers the Kauzmann temperature, T_K, to 130 K, just below the experimental glass-to-liquid water transition temperature, T_g, of 136 K and the calculated T_g of 135 K in our previous study. A straightforward extrapolation of high temperature entropy from 250 K to below however would give a much higher value of $T_K \sim 190$ K.
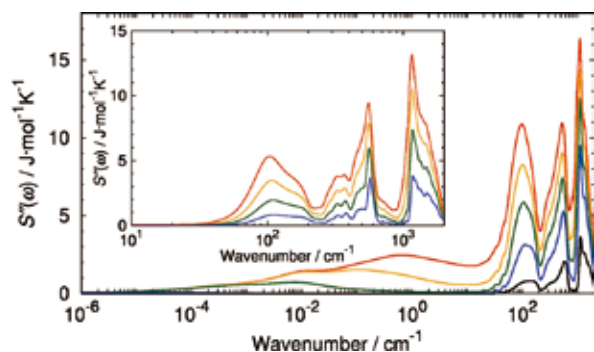

Figure 2. Imaginary part of complex entropy of (liquid, supercooled, and amorphous) water at 300 (red), 250 (orange), 220 (green), 180 (blue), and 100 (black) K. The inset shows those at 250 (red), 200 (orange), 150 (green), and 100 (blue) K of ice Ih.

2. Theory of Coherent Two-Dimensional Vibrational Spectroscopy[2]

Two-dimensional (2D) vibrational spectroscopy has emerged as one of the most important experimental techniques useful to study the molecular structure and dynamics in con-

densed phases. Theory and computation have also played essential and integral roles in its development through the nonlinear optical response theory and computational methods such as molecular dynamics (MD) simulations and electronic structure calculations. In this article, we present the fundamental theory of coherent 2D vibrational spectroscopy and describe computational approaches to simulate the 2D vibrational spectra. The classical approximation to the quantum mechanical nonlinear response function is invoked from the outset. It is shown that the third-order response function can be evaluated in that classical limit by using equilibrium or non-equilibrium MD simulation trajectories. Another simulation method is based on the assumptions that the molecular vibrations can still be described quantum mechanically and that the relevant molecular response functions are evaluated by the numerical integration of the Schrödinger equation. A few application examples are presented to help the researchers in this and related areas to understand the fundamental principles and to use these methods for their studies with 2D vibrational spectroscopic techniques. In summary, this exposition provides an overview of current theoretical efforts to understand the 2D vibrational spectra and an outlook for future developments.

3. Site-Dependent Fluctuations Optimize Electronic Energy Transfer in the Fenna-Matthews-Olson Protein[3]

Light absorbed by light-harvesting antennae is transferred to the reaction center (RC). The excitation energy transfer (EET) to the RC is known to proceed with nearly perfect quantum yield. However, understanding of EET is still limited at molecular level. Here, we examine the dynamics in the Fenna–Matthews–Olson (FMO) protein by developing an efficient molecular dynamics simulation that can properly describe the electronic properties of the bacteriochlorophylls. We find that the FMO protein consists of sites with heterogeneous fluctuations extending from fast to slow modulation. We also find that efficient EETs are facilitated by site-dependent fluctuations that enhance the resonance condition between neighboring sites with large site-energy differences and circumvent exciton trapping on the pathway to the RC. Knowledge of site-dependent fluctuations is an important component of understanding optimization of EET in photosynthetic systems.

References

1) S. Saito and B. Bagchi, *J. Chem. Phys.* **150**, 054502 (14 pages) (2019). (Featured Article)

2) T. L. C. Jansen, S. Saito, J. Jeon and M. Cho, *J. Chem. Phys.* **150**, 100901 (17 pages) (2019). (Perspective)

3) S. Saito, M. Higashi and G. R. Fleming, *J. Phys. Chem. B*, in press.