Theoretical Studies on Condensed Phase Dynamics

Department of Theoretical and Computational Molecular Science
Division of Computational Molecular Science

SAITO, Shinji   Professor
KIM, Kang   Assistant Professor
KOBAYASHI, Chigusa Post-Doctoral Fellow
YAGASAKI, Takuma   Post-Doctoral Fellow
UENO, Harumi   Secretary

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 and relaxation in solutions and functions of proteins. We have been investigating liquid dynamics and chemical reactions in biological systems using molecular dynamics simulation and electronic structure calculation. In addition, we have been analyzing complicated liquid dynamics using multi-dimensional spectroscopy.

1. Slow Dynamics in Random Media: Crossover from Glass to Localization Transition

The transport phenomena of fluids confined in random media is of great important in physics, chemistry, biology, and engineering, *e.g.* water in micelles or living cells. Spatial restrictions in random media can cause unusual slow dynamical properties. Recent experiments suggest that the glass transition temperature in spatially confined systems, *e.g.* a thin film or a porous media, is largely different from that in bulk, though little is understood about these phenomena.

Recently, the glass transition of hard-spheres confined in random media has intensively investigated based on the mode-coupling theory (MCT) and two notable results were predicted. First, the memory kernel in the MCT equation consists of the linear and nonlinear terms. Coupling coefficients in the memory kernel representing fluid-fluid and fluid-matrix interactions are controlled by varying fluid and matrix densities. Thus, the glass transition dynamics is characterized by two kinds of dynamics which are called the two-step type B dynamics at high fluid densities and the single-step type A dynamics at small fluid densities, respectively. Second prediction is the existence of the reentrant transition in low fluid density regime at a certain high matrix density, where delocalization of fluid particles occurs and the dynamics become faster in spite of the increase in the fluid density with a fixed matrix density.

In the present study, we carry out molecular dynamics simulations of soft sphere supercooled liquids and hard sphere liquids in random media to obtain quantitative information about dynamics over a broad range of fluid and matrix densities and the physical interpretation of the above theoretical predictions. Dynamical phase diagram of the liquid-glass transition at various fluid and matrix densities has been determined from simulations, which is well correlated with MCT's predictions. Two types of dynamics, type A and B, have been found in density correlation function, mean square displacement, non-ergodic parameter, and four-point correlation function. Furthermore, it is found that in the low fluid density at a certain high matrix density the reentrant transition exists as MCT predicts, where the delocalization of particles occur due to kick-out mechanics resulting from hopping motions of fluid particles surrounded by the random media.

2. Conformational Changes and Fluctuations of Ras

Ras superfamily is a signal transduction protein. Ras is cycled between two states of bound guanine nucleotide, the GTP- and GDP-bound states, by hydrolysis. Ras binds to effectors for regulation of cell proliferation in the GTP-bound state, whereas it is inactivated in the GDP-bound state. X-ray crystallography studies revealed conformational changes of two regions around a nucleotide binding site, switch I and switch II, in the two states. The conformational changes result from the difference of the coordinations of γ-phosphate, Gly60 and Thr35 in the two states. In addition to the conformational change between the GTP- and GDP-bound states, two states with different conformations are experimentally found in the GTP-bound state. The two states are called state 1 and state 2. The results of ^{31}P NMR show that the interconversion between states 1 and 2 is governed by the coordination between Thr35 and Mg^{2+} and that state 2 is a predominant form of H-Ras and

interacts with effectors. We investigated the conformational changes and fluctuations in the two states, states 1 and 2, in the GTP-bound state and the GDP-bound state by using molecular dynamics calculations.

We found the large difference of the secondary structure of switch I in states 1 and 2 and the GDP-bound state. The differences arise from the change in coordinations; Thr35 binds to Mg^{2+} in state 2, whereas the coordination is broken in state 1 and the GDP-bound state. The absence of the coordinations results in not only the distortions but also the large fluctuation of switch I in state 1. The present result suggests that the distortion caused by the breaking of the coordinations in switch I weakens affinities with effectors in state I.

In switch II, we found no significant difference between the secondary structure in states 1 and 2 because the coordinations in the region are conserved in these states. In contrast, structural change between the GTP- and GDP-bound states, arising from the breaking of the HB between γ-phosphate and Gly60, is found and Gly60 and its neighbor residues adopt an extended form in the GDP-bound state. Large fluctuations are experimentally found in switch II in GTP-bound state. As experimental results, large fluctuations in the α2 helix, the transitions among 3_{10}-helix, α-helix, and a partially unwound helix are found in states 1 and 2, on the other hand, any significant fluctuation in α2 helix is not seen in the GDP-bound state. We found that the fluctuations are correlated with the rearrangement of transient HBs involving the polar side-chains in switch II in the states 1 and 2. The present result implies that conformations in fluctuation are stabilized by transient HBs, so that interconversions among multiple states take place in GTP-bound state.
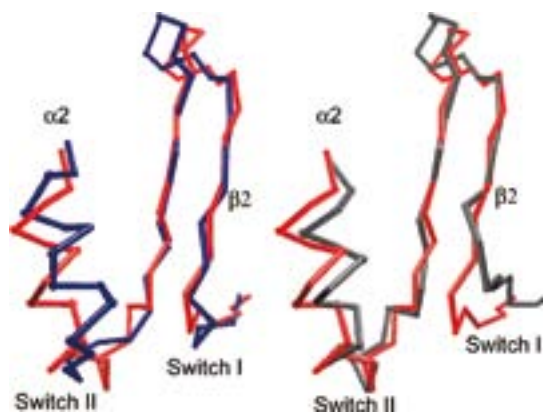

Figure 1. Superposition of the average Cα traces in switches I and II, and the neighbor region in state 1 (gray), state 2 (red), and GDP-bound state (blue), respectively.

3. Ultrafast Intermolecular Dynamics of Liquid Water: Theoretical Study of Two-Dimensional Infrared Spectroscopy

Physical and chemical properties of liquid water are domi-nated by hydrogen bond structure and dynamics. Recent studies of nonlinear vibrational spectroscopy of intramolecular motion provide new insight into ultrafast hydrogen bond dynamics. However, our understanding of intermolecular dynamics of water is still limited. In this study, we theoretically investigated intermolecular dynamics of liquid water in terms of two-dimensional infrared (2D IR) spectroscopy. We calculated the 2D IR spectrum by explicitly estimating the three-time correlation function of the total dipole moment, and thus obtained novel information about the time dependent mode couplings that cannot be available from the one-dimensional spectroscopy (Figure 2).

We found that the frequency correlation, *i.e.* the initial inhomogeneity, of the libration motion is lost with the time scale of ~110 fs. The energy of the libration motion relaxes to the low frequency motion with the time scale of ~80 fs. The energy relaxation to the low frequency motion is followed by the slow relaxation due to the hydrogen bond structural change induced by incident electric field pulses. We analyzed the effect of the hindered translation motion on these ultrafast dynamics. It was shown that both the frequency modulation of libration motion and the energy relaxation from the libration to the low frequency motion significantly slow down in the absence of the hindered translation motion. The present result revealed that the anharmonic coupling between the hindered translation and libration motions is essential for the ultrafast relaxation dynamics in liquid water.
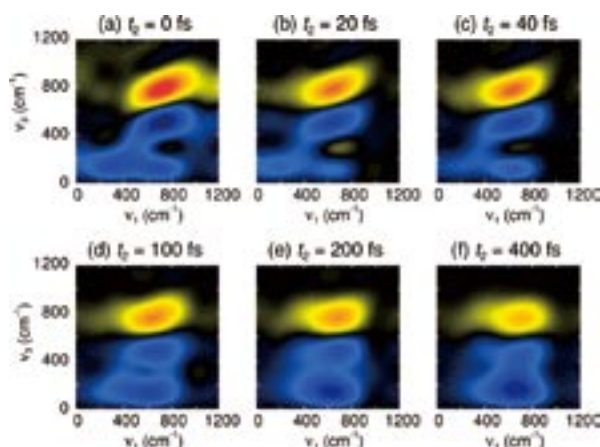

Figure 2. 2D IR correlation spectra of intermolecular motion of liquid water at several waiting times. The positive peak at (ν_1,ν_3) = (~700 cm^{-1},~800 cm^{-1}) is due to the stimulated emission and the bleaching of the libration motion and the negative peak at (~700 cm^{-1},~500 cm^{-1}) is due to the excited state absorption.

Reference

1) T. Yagasaki and S. Saito, J. *Chem. Phys.* **128**, 154521 (7 pages) (2008).