Theoretical Studies on Condensed Phase Dynamics

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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 and relaxation in solutions and functions of proteins. We have been investigating complex dynamics in supercooled liquids[1–3] and chemical reactions in biological systems[4] using molecular dynamics simulations and electronic structure calculations. In addition, we have been theoretically investigating liquid dynamics by using higher-order nonlinear IR spectroscopy.[5,6]

1. Multi-Time Density Correlation Functions in Glass-Forming Liquids: Probing Dynamical Heterogeneity and Its Lifetime[1]

A multi-time extension of a density correlation function is introduced to reveal temporal information about dynamical heterogeneity in glass-forming liquids. We utilize a multi-time correlation function that is analogous to the higher-order response function analyzed in multidimensional nonlinear spectroscopy. Here, we provide comprehensive numerical results of the four-point, three-time density correlation function from longtime trajectories generated by molecular dynamics simulations of glass-forming binary soft-sphere mixtures. We confirm that the two-dimensional representations in both time and frequency domains are sensitive to the dynamical heterogeneity and that these reveal the couplings of correlated motions, which exist over a wide range of time scales. The correlated motions detected by the three-time correlation function are divided into mobile and immobile contributions that are determined from the particle displacement during the first time interval. We show that the peak positions of the correlations are in accord with the information on the non-Gaussian parameters of the van Hove self-correlation function. Furthermore, it is demonstrated that the progressive changes in the second time interval in the three-time correlation function enable us to analyze how correlations in dynamics evolve in time. From this analysis, we evaluated the lifetime of the dynamical heterogeneity and its temperature dependence systematically. Our results show that the lifetime of the dynamical heterogeneity becomes much slower than the α-relaxation time that is determined from the two-point density correlation function when the system is highly supercooled.

2. Slow Dynamics in Random Media: Crossover from Glass to Localization Transition[2]

We study slow dynamics of particles moving in a matrix of immobile obstacles using molecular-dynamics simulations. The glass transition point decreases drastically as the obstacle density increases. At higher obstacle densities, the dynamics of mobile particles changes qualitatively from glass-like to a Lorentz-gas-like relaxation. This crossover is studied by density correlation functions, nonergodic parameters, mean square displacement, and nonlinear dynamic susceptibility. Our finding is qualitatively consistent with the results of recent numerical and theoretical studies on various spatially heterogeneous systems. Furthermore, we show that slow dynamics is surprisingly rich and sensitive to obstacle configurations. Especially, the reentrant transition is observed for a particular configuration, although its origin is not directly linked to the similar prediction based on the mode-coupling theory.

3. Relation between Conformational Heterogeneity and Reaction Cycle of Ras: Molecular Simulation of Ras[4]

Ras functions as a molecular switch by cycling between the active GTP-bound state and the inactive GDP-bound state.

It is known experimentally that there is another GTP-bound state called state 1. We investigate the conformational changes and fluctuations arising from the difference in the coordinations between the switch regions and ligands in the GTP- and GDP-bound states by using 830 ns molecular dynamics simulations in total. The present result suggests that the large fluctuations among multiple conformations of switch I in state 1 owing to the absence of the coordination between Thr-35 and Mg^{2+} inhibit the binding of Ras to effectors. Furthermore, we elucidate the conformational heterogeneity in Ras by using principal component analysis and propose a two-step reaction path from the GDP-bound state to the active GTP-bound state *via* state 1. The present study suggests that state 1 plays an important role in the signal transduction as an intermediate state of the nucleotide exchange process, though state 1 itself is an inactive state for signal transduction.

4. Molecular Dynamics Simulation of Nonlinear Spectroscopies of Intermolecular Motions in Liquid Water5)

Water is the most extensively studied of liquids because of both its ubiquity and its anomalous thermodynamic and dynamic properties. The properties of water are dominated by hydrogen bonds and hydrogen bond network rearrangements. Fundamental information on the dynamics of liquid water has been provided by linear infrared (IR), Raman, and neutron-scattering experiments; molecular dynamics simulations have also provided insights. Recently developed higher-order nonlinear spectroscopies open new windows into the study of the hydrogen bond dynamics of liquid water. For example, the vibrational lifetimes of stretches and a bend, intramolecular features of water dynamics, can be accurately measured and are found to be on the femtosecond time scale at room temperature. Higher-order nonlinear spectroscopy is expressed by a multi-time correlation function, whereas traditional linear spectroscopy is given by a one-time correlation function. Thus, nonlinear spectroscopy yields more detailed information on the dynamics of condensed media than linear spectroscopy. In this Account, we describe the theoretical background and methods for calculating higher-order nonlinear spectroscopy; equilibrium and non-equilibrium molecular dynamics simulations, and a combination of both, are used. We also present the intermolecular dynamics of liquid water revealed by fifth-order two-dimensional (2D) Raman spectroscopy and third order IR spectroscopy. 2D Raman spectroscopy is sensitive to couplings between modes; the calculated 2D Raman signal of liquid water shows large anharmonicity in the translational motion and strong coupling between the translational and librational motions. Third-order IR spectroscopy makes it possible to examine the time-dependent couplings. The 2D IR spectra and three-pulse photon echo peak shift show the fast frequency modulation of the librational motion. A significant effect of the translational motion on the fast frequency modulation of the librational motion is elucidated by introducing the “translation-free” molecular dynamics simulation. The isotropic pump–probe signal and the polarization anisotropy decay show fast transfer of the librational energy to the surrounding water molecules, followed by relaxation to the hot ground state.

5. Ultrafast Energy Relaxation and Anisotropy Decay of the Librational Motion in Liquid Water: A Molecular Dynamics Study6)

We theoretically investigate intermolecular motions in liquid water in terms of third-order IR spectroscopy. We calculate two-dimensional infrared (2D IR) spectra, pump–probe signals and three-pulse stimulated photon echo signals from the combination of equilibrium and nonequilibrium molecular dynamics simulations. The 2D IR spectra and the three-pulse photon echo peak shift exhibit that the frequency correlation of the librational motion decays with a time scale of 100 fs. The two-color 2D IR spectra and the pump–probe signals reveal that the energy transfer from the librational motion at 700 cm^{-1} to the low frequency motion below 300 cm^{-1} occurs with a time scale of 60 fs and the subsequent relaxation to the hot ground state takes place on a 500 fs time scale. The time scale of the anisotropy decay of the librational motion is found to be ~115 fs. The energy dissipation processes are investigated in detail by using the nonequilibrium molecular dynamics simulation in which an electric field pulse is applied. We show that the fast energy transfer from the librational motion to the low frequency motion is mainly due to the librational-librational energy transfer. We also show that the fast anisotropy decay mainly arises from the rapid intermolecular energy transfer.

References

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