(Present Research at Toyota Physical & Chemical Research Institute)

Studies on Static and Dynamic Fluctuations of Disordered Materials and Functions Caused by Fluctuations

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Purpose of the Research

"Fluctuation" is a concept to express the deviation from the average. Spatial molecular distributions (static fluctuations) and temporal fluctuations (dynamic fluctuations) determine the structure and physical properties of the system and cause its subsequent development over time. I take up the mixed state of solutions (static fluctuations) and the dynamics in phase change (dynamic fluctuations) as systems in which fluctuations are manifested in materials science. From various experiments, I observe fluctuations from various angles and systematically, express them quantitatively, elucidate the characteristics of each fluctuation and the mechanisms causing them, and relate them to the function of the fluctuation field.

Methods

[Static Fluctuations]

When two types of samples are mixed, various mixing states occur, reflecting the properties and interactions of the components. Kirkwood & Buff and Bhatia & Thornton theoretically showed that quantitative knowledge of the mixing state can be obtained. Based on the former theory (KB theory), it is quantitatively expressed as Kirkwood-Buff Integral (KBI), and experimentally, the three thermodynamic quantities must be obtained and combined. In the latter theory (BT theory), it is expressed as density fluctuation and concentration fluctuation, and one of the above thermodynamic quantities (second-order derivative of Gibbs energy by concentration) can be replaced by the scattering intensity obtained from small-angle scattering experiments, which has a strong structure-science color. Although many researchers in the world have used KB theory to study solution structures, my group is at the forefront of using BT theory to experimentally determine the mixing state of solutions. Several experiments have shown that BT theory's methods are superior in terms of data accuracy and applicability. It is also shown that KBI can be linked to various fluctuations mathematically.

In addition to simple aqueous solutions of molecular liquids (e.g., aqueous alcoholic solutions), I take up systems related to life science; for example, I elucidate how solvent fluctuations affect the dissolved state of proteins. In addition, my group is considering the development of supercritical solution systems. In this system, it is not possible to obtain the experimental results using KB theory, so we conduct experiments using the method of BT theory. In addition, we have recently experienced the inconvenience of applying BT theory to such a system. We will seek experimental methods to overcome these shortcomings.

[Dynamic Fluctuations]

Not only in physical and chemical changes in materials, but also in life phenomena, heat is always absorbed of released when they are changing. If we can track the phenomenon with enough sensitivity to detect the heat in and out and with a scanning speed matching the change occurring, we can also obtain information on the dynamics.

In the past, it was difficult to capture the dynamic fluctuations that occur during the phase transition as the heat input and output. However, we have succeeded in capturing them using the instrument developed in my laboratory and a suitable sample selection.

The instrument is an ultra-sensitive differential thermal analysis system. In the commercially available devices, the sensitivity and stability of 3 to 5 μW and the scanning speed for raising and lowering the temperature are usually 1 to 10 K/min (60 to 6 seconds for 1 K temperature change). The instrument we developed so far has a sensitivity of 3 nW (about 1000 times better than the commercial device) and the slowest scanning speed is 0.01 mK/s (28 hours for 1 K temperature change). Also, the appropriate samples are ionic liquids. My group has found that many of the ionic liquids exhibit very slow and specific phase change behaviors and are best suited to track the dynamics during phase change. In other words, they are systems that can directly observe the dynamic behaviors of fluctuations and turbulence in the phase transition as if in slow motion mode. Using several representative ionic liquids as samples, the phase behaviors in terms of dynamic fluctuations are elucidated by the ultra-sensitive differential thermal analysis apparatus.

The time scales on which these dynamic fluctuations are occurring are the time domains in which NMR excels, and we follow the dynamics from an NMR perspective by making full use of longitudinal and lateral relaxation time measurements. When applied to ionic liquids, the kinetics of each part of the constituent ions are different, which leads to complex phase behavior due to fluctuations in the kinetics of the ions. NMR measurements are applied to representative ionic liquids in order to relate the dynamics of phase change to the dynamics of constituent ions and atoms.

Expected Results

Many of the fluctuation phenomena in material science occur in mesoscale space. A spatial domain of this size is described as a "lost domain", and mesoscale science is the most lagging field. Academically, “fluctuation” will represent the disordered structure in terms of mesoscale and will propose a new methodology for mesoscale structural chemistry and property science. In application, the quantification of the heterogeneity of solution mixing by concentration fluctuations leads to the design of reaction and separation fields from a new perspective that is sensitive to fluctuations. In other words, the mixing state can be freely designed according to the combined substances, concentration, and temperature.

In addition, the dynamic fluctuations elucidated in ionic liquids can be considered as a slow-motion version of the phase change behavior, and it is possible to discuss the phase change based on the fluctuations that can be applied to general materials. In terms of applications, the phase behaviors of complex ionic liquids can be used as devices for thermal energy treatment such as heat storage and heat exchange systems.