The 9th Mini-Symposium on Liquids

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Abstracts of invited talks

Hiroshi Imamura

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"Self-interaction of proteins in aqueous solution probed by small angle X-ray scattering"

Self-interaction of a protein governing its aggregation or precipitation increasingly attracts attention as one of the critical issues in the biopharmaceutical field, where commercial use of proteins such as an antibody has been widely spread. A mechanism, preventing proteins from aggregation, is likely to exist in naturally occurring soluble proteins, while that is yet to be elucidated. We used a small angle X-ray scattering derived from a spatial arrangement of protein molecules in solution to probe the self-interaction. We found that the interaction potential of myoglobin becomes more attractive by removal of the heme, which is consistent with the fact that myoglobin without heme is aggregation-prone. Recently, we developed an integral equation method, which divides both the direct correlation function and the interaction potential into two terms, i.e. hard sphere term and an excess term. Accordingly, the excess term is determined from the scattering data without assuming model potential functions. The analysis of SAXS profile of concentrated lysozyme solution by the model-potential-free method reveals that lysozyme molecules contacted are the most stable while those slightly separated are highly unstable. It is supposed that, in addition to screened coulomb repulsion, protein dehydration accompanying protein's association contributes to an increase in the activation barrier.

Yoshiharu Suzuki

National Institute for Materials Science

"Polyamorphism of glassy dilute glycerol-water solution ~interrelationship between the glycerol and the two kinds of water ~"

In order to study the water polyamorphism in aqueous solution systems, we observed the pressure-induced amorphous-amorphous transition in the glassy dilute glycerol-water solution at low temperatures. We examined the effect of the glycerol concentration on the polyamorphic transition and estimated the location of the liquid-liquid critical point. In addition, the high-density glassy sample was heated at 1 atm and the change in some molecular vibrations of glycerol during the high-density to low-density transition was examined using Raman spectroscopy. It was found that the polyamorphic transition of the solvent water induced the change in the molecular vibrations of glycerol. This study suggests a possibility that the water polyamorphism plays important roles in the dynamics of the macromolecule in the aqueous solutions.

Tatsuhiko Miyata

Department of Physics
Ehime University

"Thermodynamic significance to correct the location of first rising region in radial distribution function estimated from Ornstein-Zemike theory for Lennard-Jones fluids"

The accuracy of hypernetted chain (HNC), Kovalenko-Hirata (KH), Percus-Yevick (PY) and Verlet modified (VM) approximations in an Ornstein-Zernike (OZ) integral equation theory has been studied in terms of internal energy, pressure, and solvation free energy by comparing with molecular dynamics simulation for Lennard-Jones (LJ) fluids. HNC and KH approximations significantly overestimate these thermodynamic quantities, whereas PY and VM approximations give relatively accurate results. It is found that the error in these quantities for HNC and KH approximations mainly comes from the inaccurate location of the first rising (FR) region in the radial distribution function. Thus, we propose one of the necessary conditions for improving thermodynamic quantities for LJ fluids in the OZ theory: i.e., the precise location of the FR region in g(r).

Ryuichi Okamoto

Department of Chemistry
Tokyo Metropolitan University

"Nanobubble formation in water induced by a solute"

Phase separation can occur in water outside its coexistence curve with addition of a small amount of a solute. A Hydrophobic solute can be expelled from the liquid to form gaseous domains while the surrounding liquid pressure is higher than the saturated vapor pressure. We set up a bubble free energy G for bulk and surface bubbles. It becomes a function of the bubble radius R under the Laplace pressure balance. Then, for sufficiently large solute densities above a threshold, G exhibits a local maximum at a critical radius and a minimum at an equilibrium radius. We also examine solute-induced nucleation taking place outside CX, where bubbles larger than the critical radius grow until attainment of equilibrium. We furthermore investigate an attractive force between hydrophobic surfaces mediated by a surface bubble.

Kenji Mochizuki

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Okayama University

"Solid-liquid critical behavior of water in carbon nanotubes"

The non-existence of solid-liquid points is commonly accepted, largely because of the symmetry argument and the lack of experimental observations. However, recent computer simulations have demonstrated that freezing may occur continuously as well as discontinuously in quasi-one- and quasi-two-dimentional systems. In this study, we perform extensive molecular dynamics simulations of water confined in carbon nanotubes and provide unambiguous evidences for solid-liquid critical points: macroscopic solid-liquid phase separation below a critical temperature, diverging response functions at around the critical point and finite-size scaling analysis of the density distribution. We also give a molecular-level explanation for continuous freezing.

Undulation Amplitude of a Fluid Membrane Immersed in a Near-Critical Binary Fluid Mixture

Faculty of Science & Technology, Keio University   Youhei Fujitani

We calculate the equilibrium average of the shape fluctuation amplitude of an almost planar fluid membrane immersed in a near-critical binary fluid mixture in the homogeneous phase, within the linear approximation with respect to the amplitude. The ambient fluid is not a simple bath; the fluctuation of its chemical potential is correlated with the shape fluctuation. It is thus convenient to consider

Figure 1: A one-component membrane is surrounded by binary fluid mixtures sharing the same properties on both sides.

the dynamics in the limit of no dissipation. We use the Gaussian free-energy functional for the mixture and assume weak preferential attraction between the membrane and one component of the mixture. The coefficient of the square gradient term, the surface field, and the bending rigidity are respectively denoted by M, h, and c.
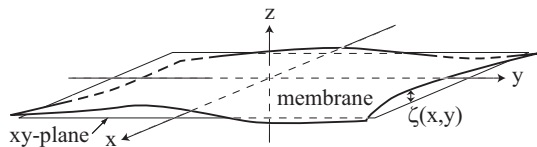
As shown in Fig. 1, the membrane fluctuates around the xy-plane, having the height $\zeta(x, y)$. Imposing the periodic boundary condition with the period l in each of the directions of x and y, we introduce the Fourier transform $\hat{\zeta}(\boldsymbol{k})$, where $\boldsymbol{k}$ denotes (k_x, k_y). We write K for $|\boldsymbol{k}|\xi_{\mathrm{c}}$, where ξ_{c} denotes the bulk correlation length. Calculating the stress exerted on the membrane up to the order of h^3, we find the equilibrium average of $\hat{\zeta}(\boldsymbol{k})\hat{\zeta}(-\boldsymbol{k})$ to be given by

$$\frac{k_{\mathrm{B}}T}{l^2}\left\{\frac{c|\boldsymbol{k}|^4}{2} + \frac{2h^2}{M\xi_{\mathrm{c}}}d(K)\right\}^{-1} \tag{1}$$

when the membrane has no lateral tension [1]. Here, the function $d(K)$ is defined as $K^2/(1+K)$ and $k_B T$ is the product of the Boltzmann constant and the temperature. The result above cease to be valid when $K \gtrsim 1$. The ambient near-criticality thus tends to suppress the undulation amplitude. In Eq. (1) for $K \ll 1$, $d(K)$ is approximately K^2, which can overwhelm the $|\boldsymbol{k}|^4$-term due to the bending rigidity. Our recent results beyond the regime of the weak preferential attraction and the Gaussian model may be also mentioned in the presentation.

References

[1] Y. Fujitani, Phys. Rev. E **91**, 042402 (2015).