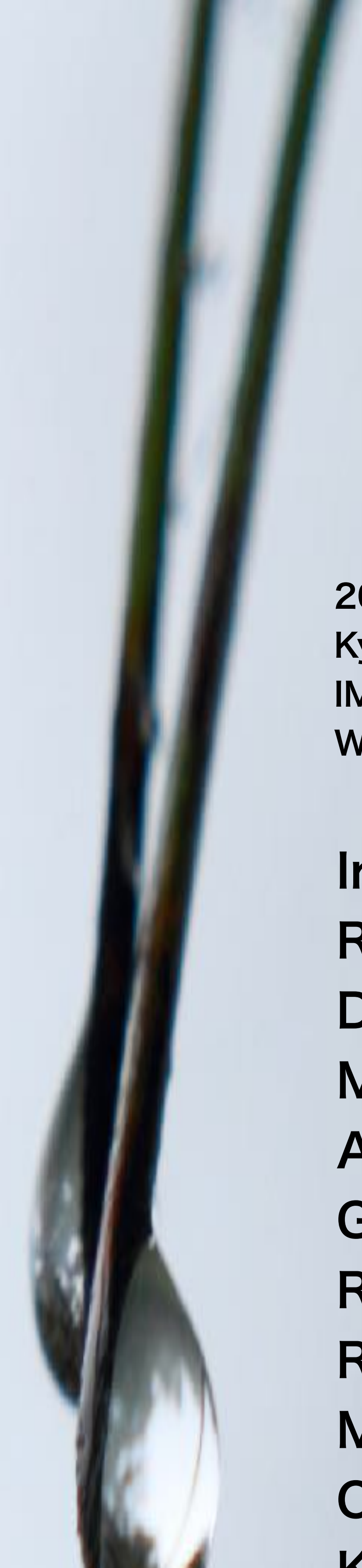

The 12th Mini-Symposium on Liquids

2018.6.30(Sat),7.1(Sun)
Kyushu University(Ito Campus)
IMI Auditorium (Room W1-D-413) 4th floor,
West Zone 1, Science Building

Invited Speakers:
R.Evans (Bristol, UK)
D.Ben-Amotz (Purdue, USA)
M.Hishida (Tsukuba, Japan)
A.Onuki (Kyoto, Japan)
G.Trefalt (Geneva,Switzerland)
R.Roth (Tübingen, Germany)
R.Yamamoto (Kyoto, Japan)
M.Terazima (Kyoto, Japan)
O.Mishima (NIMS, Japan)
K.Komatsu (Tokyo, Japan)

Organizers :
Ryo Akiyama (Kyushu)
Kenichiro Koga (Okayama)

http://phys.chem.okayama-u.ac.jp/msl2018/index.php

共催：岡山大学異分野基礎科学研究所

SCHEDULE

June 30, 2018

10:00-11:30 Registration & Poster Session & Lunch

12:55 Opening

13:00 Mafumi Hishida (Tsukuba)
Electrostatic double-layer force between anionic bilayers caused by heterogeneous distribution of added ions

13:30 Gregor Trefalt (Geneva)
Double-Layer and Structural Forces between Silica Particles in the Presence of Like-Charged Polyelectrolytes

14:00 Ryoichi Yamamoto (Kyoto)
Collective motions of crawling and proliferating cells on substrate: A particle-based model with contact inhibitions

14:30 Coffee Break

14:45 Masahide Terazima (Kyoto)
Time-resolve diffusion technique to probe conformation changes during protein reactions in aqueous solution

15:15 Rui Shi (Tokyo)
Impact of Salt Ions on the Structure and Dynamics of Water: Insight from a New Microscopic Structural Descriptor

15:25 Keiichi Yanase (Shinshu)
Critical fluctuations and dehydration behavior of a thermo-responsive polymer in aqueous media

15:35 Takashi Yoshidome (Tohoku)
A simulation study for solvation effect on a classification of cryo-electron microscopy data in terms of the structural polymorphism of a protein

15:45 Poster Preview and Poster Session

17:30 Akira Onuki (Kyoto)
Solute-induced phase separation in mixtures of water, alcohol, and solute

18:00 Robert Evans (Bristol)
Solvent mediated interactions between nano-particles: solvophobic versus solvophilic and the accompanying density fluctuations

18:30 Photo

19:00 Banquet at ITRI-ITO on campus

July 1, 2018

9:00 Poster Session

10:30 Kazuki Komatsu (Tokyo)
Phase transformation of salt-bearing amorphous ice under high pressure

11:00 Osamu Mishima (NIMS)
Polyamorphic Phase Relation of Water

11:30 Coffee Break

12:00 Haruka Kyakuno (Kanagawa)
Fast molecular dynamics and phase transition of water confined inside carbon nanotubes

12:15 Yuki Uematsu (Kyushu)
Charged surface-active impurities at nanomolar concentration induce Jones-Ray effect

12:30 Roland Roth (Tubingen)
Fluids with Competing Interactions in and out of Equilibrium

13:00 Dor Ben-Amotz (Purdue)
Hydration-shell structure and crossover transformations

14:20 Post-Symposium Discussion at Suginoya (Sake cellar)

Invited Talks

Electrostatic double-layer force between anionic bilayers caused by heterogeneous distribution of added ions

Mafumi Hishida[1]*, **Yoko Nomura**[1], **Ryo Akiyama**[2], **Yasuhisa Yamamura**[1], **Kazuya Saito**[1]

[1]*Department of Chemistry, University of Tsukuba, Japan.*
[2]*Department of Chemistry, Kyushu University, Japan.*

Dispersion and aggregation of colloids have been discussed by DLVO theory, in which the electrostatic double-layer force and van der Waals force balance. The electrostatic double-layer force has been formulated through Gouy-Chapmann or Debye-Huckel treatments, and the DLVO theory predicts that the force depends on the ionic-strength in the solution. On the other hand, we found that the lamellar repeat distances of an anionic lipid bilayer in saline solutions disagree with the prediction. The ion distribution in an aggregated colloidal system is roughly calculated by Gibbs-Donnan equilibrium. In the present case, the added ions are calculated to be expelled almost from the inter-bilayer water phase to bulk phase. This condition is much different from that considered in Gouy-Chapmann or Debye-Huckel treatments. Due to the heterogeneous distribution of ions, the electrostatic double-layer force becomes different form from the classical one used in DLVO theory, and the experimental results are well described with the new formula of the double-layer force [1]. The heterogeneous distribution of ions are also confirmed by good agreement between the experimentally observed surface potential of the lipid vesicles (zeta potential) and the calculated potential by Gibbs-Donnan equilibrium.

[1] M. Hishida, Y. Nomura, R. Akiyama, Y. Yamamura, K. Saito, *Phys. Rev. E*, **96**, 040601 (2017).

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Double-Layer and Structural Forces between Silica Particles in the Presence of Like-Charged Polyelectrolytes

Gregor Trefalt[1*], Mohsen Moazzami-Gudarzi[1,2], Plinio Maroni[1], Michal Borkovec[1]

[1]*Department of Inorganic and Analytical Chemistry, University of Geneva, Switzerland.*
[2]*National Graphene Institute, University of Manchester, Manchester M13 9PL, UK*

Damped oscillatory forces are observed between charged surfaces in the presence of like-charged polymeres. These interactions arise from the structuring of the polymers in the solution at high concentrations. This phenomenon has been described in the literature earlier and can be observed also for other types of depletants, e.g. nanoparticles. When the two surfaces come into close approach the double-layer forces become important. To get a better understanding of the double-layer forces and the interplay between the double-layer and structural forces, we measure the interaction between silica spheres in the presence wide range of concentrations of sodium poly(styrene sulfonate) (PSS) with colloidal probe technique based on atomic force microscope. A typical force profile measured in this system is shown in Fig.1. The oscillatory structural force can be observed at large distances, while the double-layer force is dominant at smaller distances below 15 nm. Interestingly, the double-layer forces are highly non-exponential in these systems. Furthermore, the total force can be well modeled by the superposition of the structural and double-layer forces. The two components of the interaction are connected through the phase shift. The thickness of the double-layer determines the phase shift of the structural force [2].

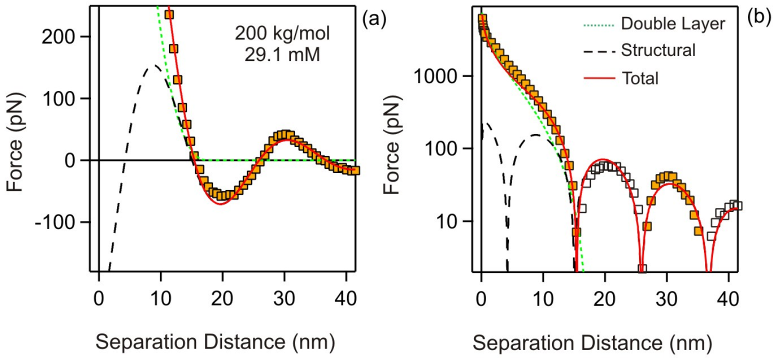

Fig 1. Interaction between two silica spheres in the presence of NaPSS solution. (a) Linear plot, and (b) semi-logarithmic plot.

[1] Y. Zeng et al., Soft Matter, 2011, 7, 10899-10909.

[2] M. Moazzami-Gudarzi et al., Phys. Rev. Lett., 2016, 117, 088001.

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Collective motions of crawling and proliferating cells on substrate: A particle-based model with contact inhibitions

Simon Schnyder[1], **John J. Molina**[2], and **Ryoichi Yamamoto***[2,3]

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[2]Department of Chemical Engineering, Kyoto University, Japan
[3]Institute of Industrial Science, The University of Tokyo, Japan

Contact inhibition plays a crucial role in collective motions of cells such as in wound healing processes and tumor formation. By mimicking the mechanical motion of cells crawling on a substrate, we constructed a minimal model of migrating cells that naturally gives rise to contact inhibition of locomotion (CIL) and the contact inhibition of cell proliferation (CIP). The model cell consists of two disks, a front disk (a pseudopod) and a back disk (cell body), which are connected by a finite extensible spring. Despite the simplicity of the model, the collective behavior of the cells is highly non-trivial and depends on both the shape of the cells and whether CIL/CIP is enabled or disabled. The present model has been applied to simulate the collective motions of crawling cells [1] and also to growing colony composed of proliferating cells (Fig.1). As it will be shown in the presentation, some basic properties seen in real crawling cells have been successfully reproduced. The true mechanisms behind such complex biological systems will be discussed in physical context in the presentation.

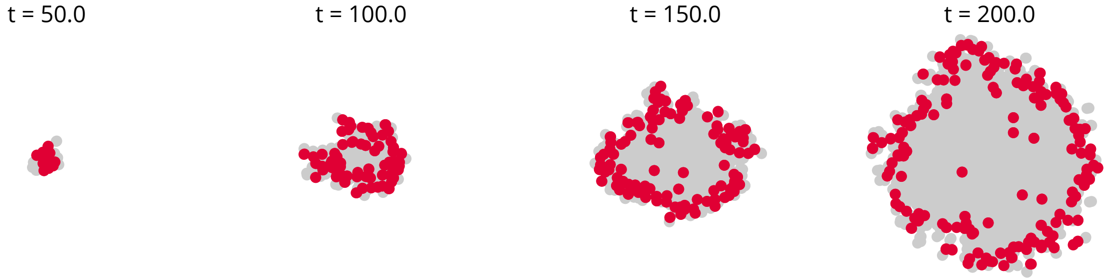

Fig.1 A typical time-development of growing cell colony composed of simple m odel cells with CIL and CIP. The gray domains show shapes of colonies at diffe rent times, and the red dots represent the dividing cells. It is clearly shown that the cell divisions can only occur along the rim due to CIP.

[1] S. Schnyder, Y. Tanaka, John J. Molina, R. Yamamoto, *Sci. Rep.* **7**, 5163 (2017).

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Time-resolve diffusion technique to probe conformation changes during protein reactions in aqueous solution

Masahide Terazima

Department of Chemistry, Kyoto University, Kyoto, 606-8502, Japan.

The translational diffusion coefficient (D) is an important physical property that reflects not only a molecular size but also conformation and intermolecular interactions of a macromolecule. Many techniques, e.g., dynamic light scattering, Taylor dispersion, capillary method, NMR spectroscopy, have been developed to monitor the molecular diffusion so far. However, this property has never been considered to be time dependent, because it usually takes a long time (e.g., several minutes or hours) to measure D. This difficulty, the slow time resolution of the traditional diffusion measurement, was overcome by using the pulsed-laser induced transient grating (TG) technique. Now, one can use D as a powerful probe to investigate chemical reaction dynamics.

By using this dynamical diffusion detection method, we have studied a variety of reactions of proteins, such as a blue light sensor protein phototropin, which controls the phototropism of a plant. We will present reaction schemes of a variety of LOV2 (Light-Oxygen-Voltage 2) domains of phototropins monitored by this technique. In particular, we succeeded in detecting the unfolding reactions of the helices of the LOV2 domain of phototropin by the diffusion detection method. A mutant that renders the A'α helix unfolded in the dark state showed unfolding of the Jα helix upon photoexcitation with a time constant of 1 ms, which is very similar to the time constant reported for the wild-type LOV2-linker sample. Furthermore, we observed a signal transduction process from the photosensing LOV domain to the kinase domain in a time-resolved manner. On the basis of these experimental results, we will discuss the light signal sensing mechanism of phototropins.

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Solute-induced phase separation in mixtures of water, alcohol, and solute

Ryuichi Okamoto[a] and Akira Onuki[b]

[a] Research Institute for Interdisciplinary Science, Okayama University

[b] Department of Physics, Kyoto University

Long-standing research has been made on the role of hydrotropes in aqueous mixtures. Short-chain alcohols are typical examples of hydrotropes, which have an amphiphilic character but form no ordered structures in water due to their small sizes. A hydrotrope interacts with both water and hydrophobic solutes attractively, increasing the solute solubility as a cosolvent. Then liquid-liquid phase separation occurs in ternary mixtures of water, alcohol, and a hydrophobic solute even if water and alcohol are miscible in any proportion.

We present a theory of a hydrophobic solute in a mixture solvent composed of water-like and alcohol-like species. We examine how the solute density n_3 is coupled to the solvent densities n_1 and n_2. For small compressibility, the concentration fluctuations of the solvent yields a large solute-solute attractive interaction. Next, we investigate solute-induced gas-liquid and liquid-liquid phase transitions, where the solvent is close to its gas-liquid coexistence and the solute interacts repulsively with the water-like species but attractively with the alcohol-like one. We calculate the binodal and spinodal curves in the phase diagrams and examine nucleation for these two phase transitions. Below, we show phase behaviors at $T = 300$ K and $p = 1$ atom in a ternary mixture with a liquid-liquid critical point ($\circ$). In the metastable region in (a), emulsification occurs due to cosolvent amphiphilicity.

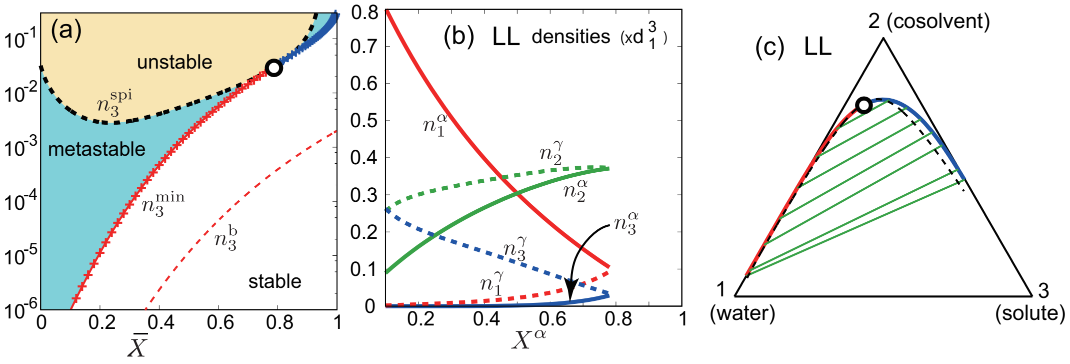

FIG. 1: (a) In plane of alcohol fraction X and solute density n_3. n_3^{spi} is the spinodal, n_3^{min} the liquid-liquid binodal, and n_3^{b} the gas-liquid binodal. (b) Densities in iquid-liquid coexistence. X^α is fraction in solute-poor phase. (c) Triangular diagram with tie lines.

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Solvent mediated interactions between nano-particles: solvophobic versus solvophilic and the accompanying density fluctuations.

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Using classical density functional theory (DFT), we calculate the density profile and local compressibility of a simple liquid solvent in which a pair of blocks with (microscopic) rectangular cross section are immersed [1]. We consider blocks that are solvophobic or solvophilic and also blocks that have both solvophobic and solvophilic patches. Large values of the local compressibility correspond to regions in space where the liquid density is fluctuating most strongly. We seek to elucidate how enhanced density fluctuations correlate with the solvent mediated force between the blocks. For sufficiently solvophobic blocks, at small block separations and small deviations from bulk gas-liquid coexistence, we observe a strongly attractive (near constant) force, stemming from (local) capillary evaporation of the liquid, i.e. gas-like intrusions between the blocks. The accompanying local compressibility reflects the incipient gas-liquid interfaces that develop. Our model system provides a means to understand the basic physics of solvent mediated interactions between nanostructures, and between objects such as proteins in water that possess hydrophobic and hydrophilic patches.

[1] B. Chacko, A. J. Archer and R. Evans J.Chem. Phys. **146**, 124703 (2017)

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Phase transformation of salt-bearing amorphous ice under high pressure

Kazuki Komatsu[1,*]

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Water is the most generally used solvent, which makes various solutions with dissociation of salts. The ordinary water ice – ice Ih, however, does not make solid solution with salts. This fact may be empirically well known from rather earlier times. On the other hand, the reaction between salts and other ice polymorphs, particularly in terms of stable phases under pressure, is less investigated until quite recently, despite the phase relation in the salt-ice system is indispensable knowledge to understand the interior of icy planets or moons. In 2009, S. Klotz and co-workers discovers that substantial amount of LiCl can be incorporated into ice VII, which is a high pressure form of ice, by annealing a salt-bearing amorphous ice from low-temperature[1]. The point of this method is to glassify salt solution at low temperature and ambient pressure and to crystallize it via solid-solid phase transformation under high pressure from the glass without the phase separation of ice and salts.

In this presentation, more recent studies for the phase transformation of salt-bearing amorphous ice by using a novel techniques of in-situ high-pressure and low-temperature x-ray and neutron diffraction, are going to be shown [2,3].

[1] S. Klotz et al., Nature Materials, 8, 405-409 (2009)
[2] S. Klotz, K. Komatsu et al., Scientific Reports, 6, 32040 (2016)
[3] M. Watanabe, K. Komatsu et al., Japanese Journal of Applied Physics,

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Polyamorphic Phase Relation of Water

Osamu Mishima

National Institute for Materials Science (NIMS)

The discovery of the high-density amorphous ice (HDA) in 1984 and the discovery of the apparently discontinuous change in volume of amorphous ice in 1985 indicated experimentally clearly the existence of two kinds of disordered structure (polyamorphism) in a one-component condensed-matter system. This fact has changed our viewpoint concerning water and provided a basis for a new explanation; when cooled under pressure, water would separate into two liquids.

So far, there is no definitive experimental proof of this liquid-liquid critical point (LLCP) hypothesis of supercooled water. This is because water crystallizes easily at low temperatures. However, from accumulative indirect experiments, simulations and theoretical plausibility, there seems to be a growing number of researchers who think there is an adequate circumstantial evidence for the LLCP.

I will talk the following thermodynamic relations which seem to be consistent with the LLCP hypothesis.
Pressure-temperature-volume relation of liquid and amorphous ices.
Melting lines of crystalline ices and the LLCP.
Pressure-temperature-Gibbs energy relation of water.

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Fluids with Competing Interactions in and out of Equilibrium

Roland Roth

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Competing interactions are potentials that in addition to a hard repulsive core possess an attraction at short and a weak repulsion at longer distances between particles. Fluids with these interactions can show a variety of interesting phenomena. In thermal equilibrium one can observe equilibrium cluster formation and micro phase separated states in which the particle clusters form periodic structures. In this talk we study fluids with competing interactions in thermal equilibrium using classical density functional theory. Beside lamellar structures we find 2D hexagonal, cluster BCC and gyroid structures in the bulk, which are periodic in one, two and three directions, respectively. We also study the influence of walls on the inhomogeneous bulk structures. When the structures are subjected to shear a non-equilibrium phase transition between inhomogeneous structures can be observed. We study those using dynamical density functional theory.

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Hydration-shell structure and crossover transformations

Dor Ben-Amotz

Purdue University,USA

Raman multivariate curve resolution (Raman-MCR) spectra are exquisitely sensitive to solute-induced changes in hydration-shell structure. Temperature and pressure dependent hydration-shell spectra of both hydrophobic and hydrophilic solutes reveal hydrophobic crossovers, the formation of weak hydrogen-bonds, and cooperative water restructuring.

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Short Invited Talks

Impact of Salt Ions on the Structure and Dynamics of Water: Insight from a New Microscopic Structural Descriptor

Rui Shi[1], Anthony J. Cooper[1,2], Hajime Tanaka[1]

[1]Institute of Industrial Science, University of Tokyo
[2]Physics Department, Rutgers University-Camden, Camden, NJ

Water is one of the most fundamentally important materials in characterizing a diverse range of biological and chemical processes. Despite its simple appearance, water possesses a large variety of dynamic and structural anomalies that have been rigorously studied yet still elude complete understanding. Since water is often found in ion solutions, studying the effects of ions on the structure and dynamics of water is of great interest. With computer simulations of NaCl solution, we found that salt ions have dual effects on water's structure and dynamics. At room temperature, salt ions retard water's dynamics, whereas at lower temperatures, ions facilitate water's movement. The former effect supports the traditional classification of NaCl as a structure maker and the latter shows its "unusual" structure-breaker nature at low temperature. Here by accessing microscopic structural information by a new structural descriptor, we reveal that salt ions can perturb water's structure up to the third shell. The competition between the spontaneous local structural ordering of water molecules and the ion-water interactions determines the dual effects of salt ions and thus the properties of salt solutions. Our results challenge the old concept of structure maker and breaker that was traditionally defined at room temperature, and advance our understanding of aqueous solutions at various thermodynamic conditions.

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Critical fluctuations and dehydration behavior of a thermo-responsive polymer in aqueous media

Keiichi Yanase, Richard Buchner[1], and Takaaki Sato*

Department of Chemistry and Materials, Shinshu University, Japan.
[1]*Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Germany*

Poly(*N*-isopropylacrylamide) (pNIPAm), whose aqueous solution exhibits a lower critical solution temperature, has been studied as an ideal model for water-soluble thermo-responsive polymers undergoing a coil-to-globule transition. Despite a long study, there are still unsettled issues on the counter intuitive phase behavior of aqueous pNIPAm. For example, recent Raman multivariate curve resolution study revealed that unexpectedly, the spectrum in the OH-band frequency range significantly changes above the cloud-point temperature, where the pNIPAm chains collapse [1].

We studied the interplay of critical fluctuations and hydration/dehydration behavior in semi-dilute solutions of pNIPAm (M_W: 29 kDa) by means of simultaneous small- and wide-angle X-ray scattering and dielectric relaxation spectroscopy. We present experimental evidence for close-coupling of dehydration of the polymer chains and the power-law divergence of the correlation length. Furthermore, real-space decoding of an observed interference peak in an intermediate scattering vector region demonstrate partial globule formation even below a spinodal temperature T_S, suggesting that the polymer-rich phase above T_S can be viewed as a high-density assembly of these micro-globules (Figure). Besides the ordinary density order parameter, we are able to identify the local number density of the micro-globules as a microscopic order parameter governing the coil-to-globule transition of pNIPAm [2].

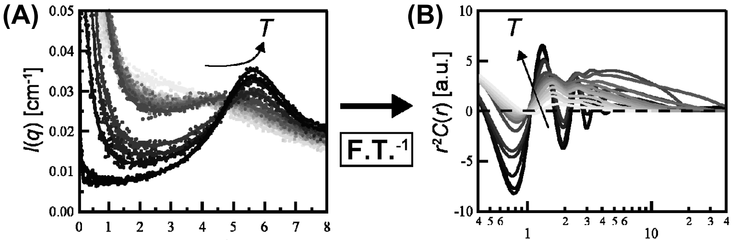

Figure. Identification of the micro-globule as revealed by the scattering experiment. (A) Scattering intensities, $I(q)$, of 13wt% pNIPAm in aqueous media and (B) corresponding density autocorrelation functions, $r^2C(r)$, calculated from the $I(q)$ data shown in Fig. (A).

[1] K. Mochizuki and D. Ben-Amotz, ***J. Phys. Chem. Lett.***, **8**, 1360 (2017).

[2] K. Yanase, R. Buchner, and T. Sato, submitted (2018). * takaakis@shinshu-u.ac.jp

A simulation study for solvation effect on a classification of cryo-electron microscopy data in terms of the structural polymorphism of a protein

Naoto Takano and Takashi Yoshidome*

Department of Applied Physics, Tohoku University, Japan.

Recent progress of techniques of cryo-electron microscopy (cryo-EM) enables us to obtain high-resolution protein structures without crystallization. Cryo-EM opened structural analyses of biological particles such as membrane proteins, which are difficult or impossible to crystallize.

It has been suggested that near future protein structures with different states will be obtained through a single Cryo-EM experiment. The reason is as follows. In performing cryo-EM experiment, a sample composed of large amount of protein particles solvated into water is first prepared. Since each particle takes different state in water, structures of protein with different states can be obtained if experimental data, two-dimensional projection images, are classified from the viewpoint of the structural polymorphism of the protein.

Here, we propose through a simulation for cryo-EM experiment of a protein that the classification of the projection images in terms of its structural polymorphism is possible using a manifold-learning technique [1]. We first obtained projection images from molecular dynamics (MD) simulation data of a protein in explicit water (Figure 1). Since the protein was hardly seen in the projection images due to the solvation effect, we applied low-pass filter to them to clarify the protein image (Figure 1). Then the images were classified using a manifold-learning technique. The classification was successful for the projection images after applying the filter, while it was failed for the projection images before applying the filter. Thus, the solvation effect strongly affects the classification.

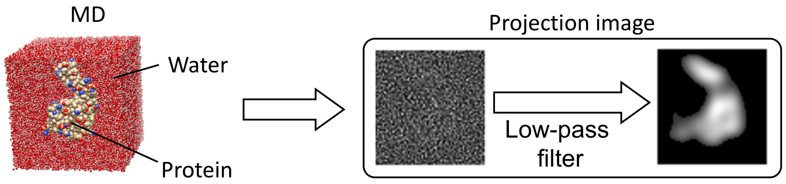

Fig. 1 A projection image was obtained using a MD data.

[1] T. Yoshidome, T. Oroguchi, M. Nakasako, and M. Ikeguchi, Phys. Rev. E, **92**, 032710 (2015).

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Fast molecular dynamics and phase transition of water confined inside carbon nanotubes

<u>H. Kyakuno</u>[1,2,*], K. Matsuda[2], R. Ichimura[1], T. Saito[3], K. Hata[4], Y. Maniwa[1]

[1] *Department of Physics, Graduate School of Science and Engineering, Tokyo Metropolitan University, Hachioji, Japan*
[2] *Institute of Physics, Faculty of Engineering, Kanagawa University, Yokohama, Japan*
[3] *Nanomaterials Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan*
[4] *CNT-application Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan*

Single-walled carbon nanotubes (SWCNTs) provide atomically smooth nanocavities that encapsulate various guest molecules. These confined materials exhibit unusual properties that do not appear in the bulk. Water was reported to have extremely high mobility inside SWCNTs, and thus SWCNTs are an attractive model system to reveal the function of hydrophobic biological channels and to design high performance filtering/separation devices. Meanwhile, nanoconfinement suppresses water crystallization below ca. 235 K. It is therefore expected that SWCNTs enable the exploration of liquid states that cannot be achieved in bulk super-cooled water.

In this study, water dynamics inside SWCNT samples with mean diameters larger than ca. 1.4 nm were investigated systematically using ^{2}H nuclear magnetic resonance spectroscopy. The results are discussed with those of differential scanning calorimetry and X-ray diffraction measurements, and molecular dynamics calculations [1]. Fast water rotational dynamics is found to continue down to ca. 220 K in SWCNTs. On further cooling, water undergoes a phase transition between fast and slow dynamics states, where the transition temperature is dependent on the SWCNT diameter and is extrapolated to a singularity temperature of ca. 230 K for bulk water. This observation may provide some insight into the unsolved mysterious properties of bulk water [2].

[1] H. Kyakuno, *et al.* J. Chem. Phys. 145, 064514 (2016).
[2] H. Kyakuno, *et al.* Sci. Rep. 7, 14834 (2017).

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Charged surface-active impurities at nanomolar concentration induce Jones-Ray effect

Yuki Uematsu[1,2]*, **Douwe Jan Bonthuis**[2], **and Roland R. Netz**[2]

[1] *Department of Chemistry, Kyushu University, Japan.*
[2] *Department of Physics, Free University of Berlin, Germany.*

Generally, electrolytes increase the surface tension of aqueous solutions except for acidic and very large electrolytes. However, the electrolyte surface tension exhibits a characteristic minimum around a salt concentration of 1mM for all ion types, known as the Jones-Ray effect [1]. This minimum has been debated for a long time and various mechanisms have been proposed so far [2]. Yet the complete quantitative theory is still lacking. In the figure, we show experimental data [3] and our calculation of the surface tension difference of NaCl solution which has a minimum as a function of the salt concentration [4]. For the theoretical calculation, we assume charged impurities in the water at 1.4nM with a surface affinity typical for surfactants. This impurity concentration is well below the typical experimental detection limit. Our modeling reveals salt-screening enhanced impurity adsorption as the mechanism behind the Jones-Ray effect: for very low salt concentration added salt screens the electrostatic repulsion between impurities at the surface, which dramatically increases impurity adsorption and thereby reduces the surface tension.

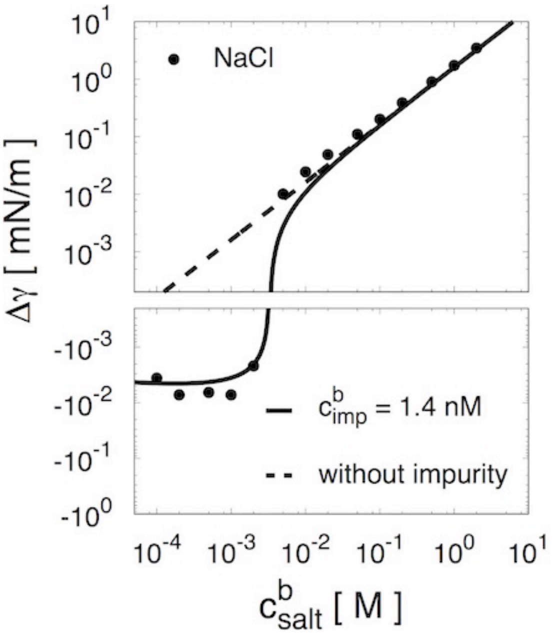

Figure. Surface tension of NaCl solution.

[1] G. Jones and W. A. Ray, J. Am. Chem. Soc. 57, 957-958 (1935).
[2] M. Dole, J. Am. Chem. Soc. 60, 904-911 (1938).
[3] G. Jones and W. A. Ray, J. Am. Chem. Soc. 63, 3262−3263 (1941).
[4] Y. Uematsu, D. J. Bonthuis, and R. R. Netz, J. Phys. Chem. Lett. 9, 189-193 (2018).

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Poster Session

A new plastic phase of water from computer simulation

Yuji　Adachi

Okayama University

High-pressure ice VII has a body centered cubic (BCC) structure composed of interpenetrating low pressure cubic ice lattices. In previous work, the existence of Plastic phase in ice VII has been suggested by calculation and the existence of crystal structure which different from conventional ice VII under ultrahigh pressure of over 26 GPa is suggested by experiments. As described above, the existence of various crystal structures is suggested in ice VII, but whole picture is unknown. In this study, the behavior of ice VII was analyzed using molecular simulation. As a result of the calculation using a reactive force field that can describe bond generation and cleavage, it is suggested that ice VII has three phases of "ice VII", "Low Density Plastic phase" and "High Density Plastic phase".

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Radial distribution functions for hard sphere fluid calculated by MC and by an integral equation theory with a bridge function

Y. Nakamura, S. Arai[1], A. Yoshimori[1], M. Kinoshita[2], and R. Akiyama[3]*

University of Electro-Communications, Japan.
[1]*Niigata University, Japan.*
[2]*Kyoto University, Japan.*
[3]*Kyushu University, Japan.*

Solute-solvent radial distribution functions are calculated by using an integral equation theory with a bridge function. Various hard sphere fluid systems are examined. The distribution functions are compared with those calculated by Monte Carlo simulations. The agreement is much better than the agreements between the functions calculated by Monte Carlo simulations and those calculated by conventional integral equation theories, such as OZ-PY theory, although the systems have only hard spheres. The agreement is remarkably good, even when the size ratio of solute particle to solvent particle is 20.

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Molecular absorption in the porous polymer crystals of P4MP1 and sPS

Ayano Chiba

Keio University

We study slective absorption from solvent mixture in the syndiotactic polystyrene (sPS) crystal as well as isotactic poly(4-methyl-1-pentene) (P4MP1) cryatal by IR spectroscopy and x-ray diffraction. We confirmed that decane molecules are more absorbed into these crystals when the polymer films are immersed in solvent mixtures such as decane-hexane-chloroform mixtures.

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Diffusion coefficients of sphere and plate-like micro-particles near the bottom

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Understanding the behaviors of microparticles in solutions near walls is important for the improvement of filtration operation in solid-liquid separation of water treatment and the risk assessment of transportation of microparticles in soil. We measured the diffusion coefficients of spherical and non-spherical microparticles in the bulk and near the bottom. The experimental results were compared with the theoretical values. The diffusion coefficient of each particle in the bulk is close to with the theoretical value within 10% of the error, and the diffusion coefficient near the bottom is reduced to about 60% of the bulk value. In addition, the addition of ions decreased the diffusion coefficient near the bottom.

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Accuracy of OZ Theory: Solvation Free Energy of LJ Diatomic Solute in LJ Solvent

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The accuracy of the solvation free energy (SFE) evaluated from Ornstein-Zernike (OZ) theory is studied for the Lennard-Jones (LJ) homonuclear diatomic solute in an LJ monatomic solvent. HNC and KH closures overestimate the SFE. An empirical sigma enlarging bridge (SEB) function is applied to the OZ theory. The parameter required in the SEB correction is assumed to be identical to the one for the monatomic solute. The SEB correction significantly improves the SFE. Transferability of the SEB parameter is also discussed.

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Basic Cell Size Dependence of Diffusion Coefficient for Macromolecule in a two-dimensional Lennard-Jones Fluid.

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We examined basic cell size dependence of diffusion coefficient for macromolecule in a two-dimensional Lennard-Jones fluid by using molecular dynamics simulation. Diffusion coefficients for various macromolecule has been calculated. Those are not so easy because motion of macromolecule causes a flow of solvent molecules. The hydrodynamic effect is important in the calculation because this flow affects long range and the convergence of system size dependence is slow. Actually, the diffusion coefficient calculated using basic cell, of which size is finite, is less than the value obtained in the infinite system. In the present study, basic cell size dependence was analyzed for a two-dimensional simple model and we found appropriate scaling.

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Diffusion coefficient of a large particle calculated by radial distribution functions in hard-sphere systems

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We have studied the effects of the solvation structure on the diffusion of a large hard sphere immersed in small hard spheres. Using our recently developed perturbation theory [1][2], we calculate the diffusion coefficient from the radial distribution function g(r). We compare the diffusion coefficients calculated from g(r) obtained by Monte Carlo simulations, the Ornstein-Zernike integral equation with the hypernetted-chain (HNC) closure and with the Percus-Yevick (PY) closure, and the integral equation theory with a bridge function proposed by Kinoshita [3]. The calculated results show that the diffusion coefficients obtained by the integral equation theory with a bridge function are well agreement with those obtained by the Monte Carlo simulation. In contrast, the diffusion coefficients are overestimated (underestimated) by the HNC (PY) closer. The diffusion coefficient depends on the details of g(r), in particular the values of the first peak and first minimum.

We have also calculated the diffusion coefficient in a binary hard-sphere solvent mixture using g(r) obtained by the integral equation theory with a bridge function. The diffusion coefficient deviates from the Stokes-Einstein relation with the slip boundary condition due to the high density of the solvent spheres around the solute.

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Transient hole-burning spectra in organic solvents: simulation and analysis by molecular dynamics

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Abstract: We developed equilibrium molecular dynamics simulation to estimate transient hole-burning spectra in solution. Transient spectra of model organic solutes in various organic solvents, such as tetrahydrofuran, acetonitrile, and methanol were obtained. The present results show that the spectral bandwidth relaxes slower than that of the center of spectra, which corresponds to experimental results reported by one of the present authors. In addition to MD simulation, we have also performed theoretical calculations on the basis of diffusion model, where anharmonicity of the free-energy profile can explain the different dynamics of the spectral behavior. A detailed molecular view of the free-energy profile in solution may be related to an elaborated design of functional nanomaterials, where self-assembly templates serve as a key synthetic technique.

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Charge regulation at a solid-liquid interface in an applied electric field

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We investigate ionization at a solid-water interface in an applied electric field. We attach an electrode to a dielectric film bearing silanol or carboxyl groups with areal density Γ_0 , where the degree of dissociation α is determined by the proton density in water close to the film. We show how α depends on the density of NaOH in water and the surface charge density σ_m on the electrode. For positive σ_m, the protons are expelled away from the film, leading to an increase in α. In particular, when $0<\sigma_m<e\Gamma$, self-regulation occurs to realize $\alpha e \Gamma \simeq \sigma_m$ for sufficiently small density of NaOH.

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Role of Mg2+ Ions in DNA Hydrolysis by EcoRV, Studied by 3D-RISM and MD

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The role of Mg2+ ions in DNA hydrolysis by the homodimeric restriction enzyme EcoRV was elucidated based on the 3D-RISM theory and the MD simulation. From an analysis of the spatial distribution of Mg2+ in an active site using 3D-RISM, we identified a new position for Mg2+ in the X-ray EcoRV–DNA complex structure (1rvb), which turns out to play a crucial role in the reaction. We refer to the position as site IV†. Site IV† is almost the same position as that of a Ca2+ ion in the superimposed X-ray crystallographic active-site structure of the PvuII–DNA complex (1f0o). 3D-RISM was also used to locate the position of water molecules including the water nucleophile at the active site. MD simulations were carried out with the initial structure having two Mg2+ ions at site IV† and at site I, experimentally identified by Horton et al., to find a stable complex structure in which rearrangement of the DNA fragment occurred to orient the scissile bond direction toward the water nucleophile. The equilibrium active-site structure of the EcoRV–DNA complex obtained from the MD simulation was similar to the superimposed X-ray crystallographic structure of the BamHI–DNA complex (2bam). In the active-site structure, two metal ions have almost the same position (≤ 1.0 Å) as that of 2bam, and the scissile phosphate is twisted to orient the scissile bond toward the water nucleophile as is the case in 2bam. We propose the equilibrium active-site structure obtained in this study as a precursor of the hydrolysis reaction of EcoRV.

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Semiconducting nanoparticles: morphology, alloy and composites

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The II-VI and IV-VI semiconductor nanoparticles were fabricated with solution-based method. The nanowire morphology of ZnSe, CdSe, CdTe, PbS, PbSe were shown along with their characterization including TEM, SEM, XRD and UV-vis. TEM reveals high aspect ratio of nanowires morphology for all materials. XRD indicates phase admixture of zinc blende and wurtzite structure of II-VI semiconductor nanowires while rock salt structure appears on IV-VI semiconductor nanowires. Their alloy and composites were also conducted with solution-based method. Tunable nanowire compositions and heterostructure of nanowires/nanoparticles were successfully fabricated.

I would like to thank Prof. Katsura Nishiyama for discussion, collaboration and hospitality during my stay at Meijo University.

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Anionic charge dependence of effective interaction between macroanions in electrolyte solution

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Effective interaction between macroanions immersed in an electrolyte solution has been studied by using various methods. In this subject, the calculation of electric double layer around charged macromolecules is important because macroanions are surrounded by electric double layer, and they interact through it. The thickness of the double layer depends on the electrolyte concentration and on ion valences. The Debye-Hückel(DH) theory has been often used to study the behavior of the electric double layer, because the theory has the analytical expressions. However, the DH theory is not valid when the electrolyte concentration is high or/and the charge of ions are large. [G.Trefalt, I.Szilagyi, M.Borkovec, J. Colloid Interface Sci. 406 (2015) 111, M. Hishida, Y. Nomura, R. Akiyama, Y. Yamamura, K. Saito, Phys. Rev. E 96 (2017) 040601.].

In the present study, anionic charge dependence of effective interaction between macroanions was calculated by using an integral equation(IE) theory. HNC-OZ theory is adopted because the system has charged particles. Figure (a) shows the dependence of the interaction on the anionic charges under constant ionic strength ($1.0\text{x}10^{-2}$ mol dm^{-3}) calculated by the IE theory. As the anionic charge increases, the effective repulsion becomes stronger. The effective interaction obtained by the IE theory depends on the anionic charge although that obtained by the DH theory does not depend on the anionic charge . On the other hand, the behaviors of the interaction are reversed, when the concentration of cation is constant ($1.0\text{x}10^{-2}$ mol dm^{-3}). The interaction obtained by the IE theory has little dependence on the anionic charge when the IE theory is adopted (See Fig.(b)), whereas ionic strength is depends on the anionic charge. We will discuss these results.

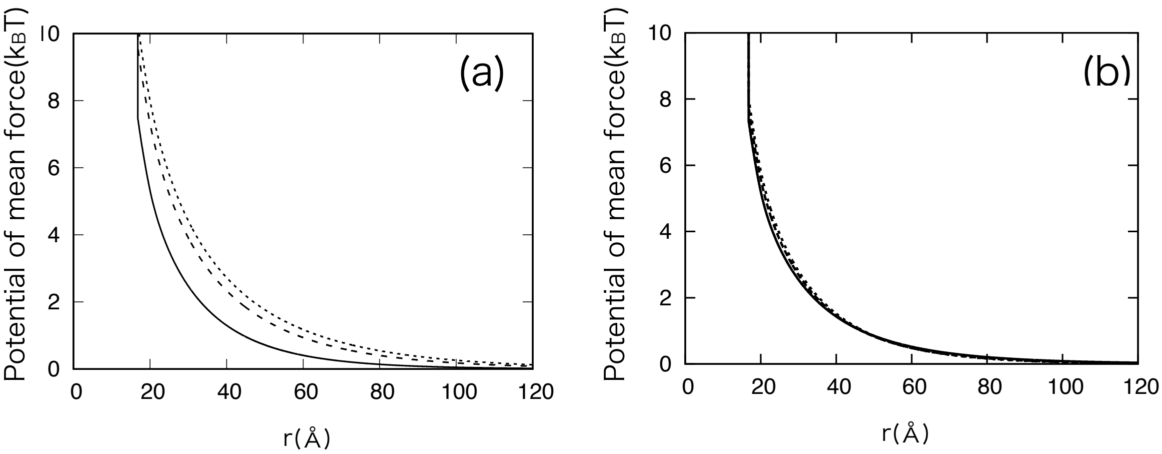

Fig : Potential of mean forces calculated by using the integral equation theory. (a)constant ionic strength (1.0×10^{-2}mol dm^{-3}) and (b)constant cation concentration (1.0×10^{-2}mol dm^{-3}). The anionic charges are -e(solid curves), -2e(dashed curves) and -2.5e(dotted curves).

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Charge reversal of sulfate latex particles: Effects of trivalent counter-ions and its hydrolyzed forms

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We have measured electrophoretic mobilities of sulfate latex particles with three different pH-independent surface charge densities as a function of $LaCl_3$ concentration and pH. These experimental results were compared with a simple model including an ion-ion correlation model [1] with specific adsorption energy [2] for hydrolyzed forms of La^{3+} ions. The experimental results of the mobility at low pH indicated the charge reversal around 10 mM $LaCl_3$ concentrations for highly charged latex. The concentration at the charge reversal increased with decreasing the surface charge density of sulfate latex, and the charge reversal was no longer observed at the lowest charge. This trend can be qualitatively explained with the ion-ion correlation model. The effect of pH on the charge reversal was more pronounced despite their pH-independent surface charge. Above 0.167 mM $LaCl_3$ concentrations, the charge reversal occurred above pH 8. This charge reversal in higher pH was attributed to the adsorption of hydrolyzed La species and it could be captured by introducing presumable values of its intrinsic energy of adsorption. These results suggest that the ion-ion correlation can rationalize the charge reversal at low pH, while the excess adsorption of hydrolyzed La ions is essential to describe the reversal in higher pH.

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Theoretical analysis on free energy profile for protein folding

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Understanding the dominant factor in folding stability of protein remains an open challenge. Kauzmann's hydrophobic interaction hypothesis, which considers hydrophobic interactions between nonpolar groups as the dominant factor, has been widely accepted for about sixty years. The hypothesis, however, has not been verified or disproved as it is difficult, both theoretically and experimentally, to quantify the hydrophobic interaction effects on the free energy change in protein folding. Here, we developed a computational method for extracting the dominant factor behind folding stability of a small designed protein, chignolin. The resulting free energy profile is consistent with experiments. Decomposition of the free energy profile indicates that intramolecular interactions predominantly stabilize folded conformations whereas solvent-induced interactions, including hydrophobic interactions, rather destabilize them. The unfolded state becomes stable with increasing temperature because an increase in conformational entropy of the unfolded protein overwhelms the solvent-induced interactions that promote compact conformations at high temperatures. The unfolded state becomes stable with increasing pressure as well, but now due to changes in the solvent-induced interactions. The dominant factor in folding stability is attributed to the intramolecular interactions rather than the hydrophobic interactions and a balance between the two opposing factors, the intramolecular and solvent-induced interactions, determines the native structure. Especially, the latter, i.e., the solvent-induced interactions, are the physical origin of softness of bio/soft materials in water.

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Displacement of Solvation Motor in Infinite System

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We have proposed a solvation motor (Fig. 1) as a simple model for an analysis of the motion of macromolecule induced by a chemical reaction [1]. In this study, the hydrodynamic effect on a solvation motor was studied by using molecular dynamics simulations of Lennard-Jones solvents [2]. We examined the dependence of the displacement of solvation motor induced by the chemical reaction on the basic cell size. The displacement obtained by the simulation sat on a straight line as a function of the cell size (Fig. 2), and the displacement in an infinite system was estimated from the plot.

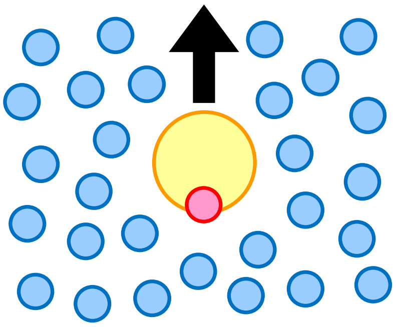

Fig. 1. A solvation motor.

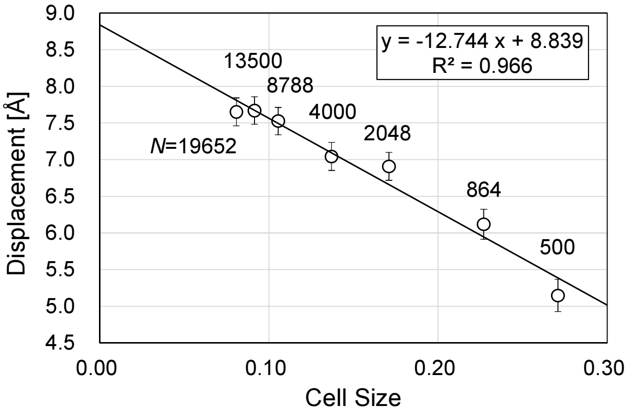

Fig. 2. Basic cell size dependence of displacement of a solvation motor.

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Molecular dynamics simulation study on shear thinning of liquid hexane

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Cox-Merz rule is an empirical relation between the frequency-dependent linear complex viscosity, $\eta^*(\omega)$, and nonlinear shear viscosity under strong shear, $\eta(\gamma)$. We have examined the Cox-Merz rule on some low molecular-weight lubrication oils, and found that the Cox-Merz rule holds fairly well when the oil is composed of rod-like molecule [1]. In this work, both equilibrium and non-equilibrium molecular dynamics (MD) simulations are performed on liquid hexane under ambient conditions in order to clarify the origin of the Cox-Merz rule of liquids composed of rod-like molecules.

The united-atom TraPPE model is employed to describe liquid hexane. The NVT ensemble simulations are performed, where the density is fixed to the experimental one at the ambient condition. The temperature of the system is controlled to be 298 K using Nosé-Hoover thermostat. The complex shear viscosity is evaluated from the time correlation function of the shear stress in equilibrium MD simulation, whereas the nonlinear viscosity is calculated from the average value of the shear stress in non-equilibrium MD simulation under simple shear.

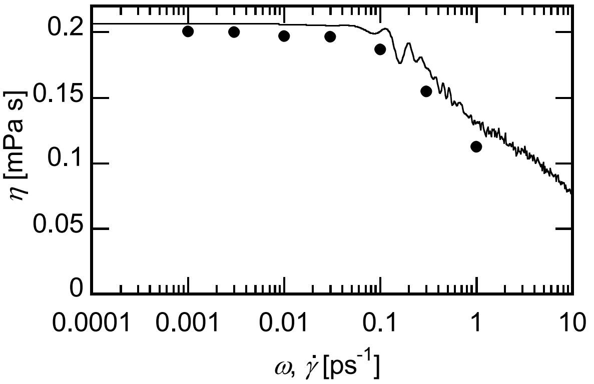

Figure 1. The amplitude of complex linear shear viscosity, $|\eta^*(\omega)|$ (solid curve), and nonlinear viscosity, $\eta(\gamma)$ (filled circles).

Figure 1 shows $\eta^*(\omega)$ and $\eta(\gamma)$, demonstrating that the Cox-Merz rule holds well on liquid hexane. From the analysis of the orientational order, the viscoelastic relaxation around 0.3 ps^{-1} is assigned to the translation-orientation coupling. The origin of the Cox-Merz rule will be discussed based on the shear-induced orientation.

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Cation and water distributions at the active site of the BamHI–DNA complex calculated by 3D-RISM

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Restriction enzymes recognize a specific DNA sequence and selectively cut double-stranded DNA. This hydrolysis reaction requires divalent cations. One of the type II restriction enzymes, BamHI, is a homo dimer and requires Mg2+ for its function. In the present study, cation distributions in the BamHI–DNA complex were calculated using the three-dimensional reference interaction site model (3D-RISM) theory. The X-ray structure of the BamHI–DNA complex (PDB ID: 2bam) at the step prior to the hydrolysis of a DNA fragment was adopted as a solute structure. The X-ray crystal with which the 2bam structure was determined was formed with Ca2+ to prevent hydrolysis of DNA. The structure 2bam harbors two divalent metal ions, Ca2+ ions, per active-site. The position of the two Ca2+ ions in the X-ray structure, 2bam, was reproduced by 3D-RISM with the prepared solute structure without the two Ca2+ ions. The distribution of Mg2+ extended to the interface region in the active site between the DNA fragment and the polypeptide side chains, both of which had negative charges. The distributions of solvents including not only cation but also water oxygen and hydrogen around the active site were investigated by comparing with our preceding calculations of EcoRV–DNA complex. This work is the first step toward elucidating the reactions of restriction enzymes whose function requires divalent cations.

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