

## Poster Presentations

P1. *Yuichi Kawabata* (Kyushu University)

### **Theoretical Approach to Partial Molar Volume of Single Ions in Water : Molecular Simulation Study**

We examined a method to calculate partial molar volume of single ions in water on the basis of molecular simulations and Kirkwood-Buff(KB) like theory. In KB theory, partial molar volume of a solute at infinite dilution can be obtained from Kirkwood-Buff integral (KBI)  $G$  that is defined by integration of radial distribution function. According to literature[1], the value of KBI is independent on the definition of “position of molecule”. If the net charge of solute molecule is zero, this is true. However, it is not always adequate in simulation condition when single ions are considered as solute molecule. We will discuss our results and this problem at the poster presentation.

References

[1] Lockwood, D. M., Rossky, P. J., *J. Phys. Chem. B* 103, 1982(1999).

P2. *Yasuhiro Watanabe* (Shimane University)

### **Development of rare-earths laser materials dispersed in organogels: elucidation of molecular interactions between the complexes and gel interfaces**

We have dispersed rare-earth complexes in phenol + AOT organogels, and employed these materials as potential lasing devices. An advantage of using gel as a hosting media is that we can disperse complexes about 8 times as much as concentration in the gel environment compared with that in conventional liquids. In this contribution, we discuss lasing possibilities of the rare-earth complexes dispersed in organogels and liquids, in terms of molecular interactions between the complexes and the organogel interfaces. We have proven that the complexes dispersed in the organogel have shown remarkable possibility as laser materials, supported by the measurements of time-dependent emission intensity,  $I(t)$ .

In this study, we aim to produce laser materials emitting in the green – orange region without using wavelength conversions. Rare-earth complexes using Eu, Tb, ... therefore serve as possible candidates for this purpose.

The  $I(t)$  curves were measured by a third harmonics of a YAG laser (355 nm) as an excitation source. In these measurements,  $\text{Eu}(\text{hfa})_3(\text{phen})$  dispersed in the organogel was contained in a

quartz cuvette keeping a gel format, or fabricated in a thin film with spin coating. The  $I(t)$  curves as observed can be basically fit by two exponential components both for these sample formats. At this present point of our investigation, we ascribe this phenomenon to amplified spontaneous emission (ASE), which indicates possible applications towards lasing materials.

P3. *Yuchi He* (Peking University)

**Phase of quasi-one dimensional water**

This presentation will mainly focus on some interesting behaviours of Q1D water as well as depict and explain how fluctuations are suppressed in a quasi-one-dimensional system by weak transverse interactions to restore long-range order such that there exists quasi first order phase transition in comparatively large caliber nanotube.

P4. *Katsura Nishiyama* (Shimane University)

**Synthesis of color-tunable rare-earths nanoparticles emitting in the visible region by means of a homogeneous precipitation method**

We have synthesized nanoparticles composed of rare-earth materials, where Eu, Tb, ..., are doped in the Y nanoparticle. Upon UV excitation, these particles emit in the visible region. An emitting wavelength of the intermediate among the dopants has been achieved by co-doping, or, an excitation-wavelength control. Along with emitting properties of these nanoparticles, we discuss chemical structures of the micelles formed in the course of the homogeneous precipitation method, in connection with surfactant / rare-earth interactions.

P5. *Tomonari Sumi* (Okayama University)

**An integral equation study of protein interactions using small-angle X-ray scattering data**

We present an integral equation analysis of protein interactions using small angle X-ray scattering (SAXS) data in dense protein solutions. In this method, an integral equation is introduced to extrapolate experimental structure factor onto a wide-angle region. We applied this approach to dense Lysozyme solutions to clarify the validity of the approach. The structure factors that are obtained from the integral equation theory agree well with the experimental SAXS data that is used as the input of the integral equation. Effective protein interaction

potentials that are determined from the integral equation are qualitatively different from the potential form of the DLVO model that is generally employed for analysis of protein interactions. On the basis of the theoretical results obtained from the integral equation approach, we introduced a solvent-induced interaction as a correction term on the DLVO model potential. The DLVO potential with the solvent-induced interaction reproduced the experimental SAXS data as well as the theoretical effective protein interaction very well.

P6. *Toshihiro Kaneko* (Tokyo University of Science)

**The role of beta sheets formation in the early stage self-assembly of peptide amphiphile worm-like micelles: A replica-exchange molecular dynamics study**

We study secondary structures of one or two molecules of peptide amphiphiles in implicit solvents by replica-exchange molecular dynamics simulations. Though one or two molecules in water without any constraint prefer alpha helix, a beta-bridge formation is observed when the distance between the hydrophobic group of one molecule and that of the other is fixed. According to the experiment by Shimada et al [J. Phys. Chem. B, 2012], a beta-sheet formation is predicted in an early stage of wormlike micelle formation. Our simulation result supports this experiment.

P7. *Yukako Kasai* (Kyushu University)

**Theoretical Analysis of Co-Solvent Effects on Intramolecular Proton Transfer Reaction of Glycine in Water-Acetonitrile Mixture**

Co-solvent effects on the intramolecular proton transfer reaction of glycine in water-acetonitrile mixture were considered. The free energy profiles were computed for various concentrations. We used the reference interaction site model self consistent field (RISM-SCF) method to take account of the interaction between the solute and solvent, such as hydrogen bonding. The RISM-SCF method is a hybrid method of ab initio electronic structure theory and statistical mechanics for molecular liquid. The set of profiles clearly showed that the zwitterionic form became unstable with increase of acetonitrile concentrations. From the energy decomposition analysis of the free energy of solvation, we found that the contribution of the excess chemical potential occupied in the total free energy change was larger than that of the electronic reorganization energy. We also found the major factor that stabilizes the zwitterionic form with

decrease of acetonitrile fraction from the solvent distribution analysis, which was the hydrogen bond between a hydrogen atom in solvent water and the oxygen atom in solute glycine.

P8. *Ayumi Suematsu* (Kyushu University)

#### **Phase stability of a double-minimum potential system**

We study the relation between two-body interaction and phase transition, using interaction potential with two minima, named the Lennard-Jones-Gauss (LJG) potential. We calculate the stability of gas, liquid, fcc and bcc crystals by the thermodynamic perturbation theory. The calculation shows that the stability of an fcc crystal depends largely on position of the second minimum in the potential. When an fcc crystal is stabilized, the second minimum is located at the position of the first or third nearest neighbor particles of the crystal. Then the freezing pressure closes to zero. Also we find that a bcc crystal is more stable than an fcc crystal when the second minimum is located at the position of the second nearest neighbor particles of bcc crystals. Our results show that the solid phase stability of the system can be controlled by the position of the second minimum.

P9. *Takuya Fukudome* (Kyushu Institute of Technology)

#### **An analytical expression of the Ornstein-Zernike integral equation of hard-sphere liquid derived from the extended scaled particle theory**

The integral equation methods based on the Ornstein-Zernike equation have been widely used to obtain radial distribution functions,  $g(r)$ , of molecular liquids. The closer which connects a direct correlation function,  $c(r)$ , with a total correlation function,  $h(r)$ , is necessary for solving the integral equation. However, in most cases physical meaning of the closer is ambiguous, even if the distribution functions are reproduced quantitatively. Until now, we succeeded in reproduce a radial distribution function of hard-sphere liquid in the range up to first solvation shell. In this work, we have obtained an analytical expression of the radial distribution function of hard-sphere liquid at all radial distances through a cavity function derived from the extended version of scaled particle theory which we have developed for non-spherical particles.

The closer in this work is derived in the same manner as the Kovalenko-Hirata closer[1] but cavity functions in the closer have the analytical expression given in XSPT. In the case of hard-sphere liquid, our new integral equation gives quantitative values of the radial distribution

function. Especially, the contact value, which is a value of the first peak of the function, agrees with the Monte Carlo simulation results better than that of the PY equation. Our integral equation method in this work is expected to extend to the particles with non-spherical shapes in the next step in order to apply the method to hydration of a protein.

A. Kovalenko and F. Hirata, Chem. Phys. Lett. 349, 496 (2001)

P10. *Ken-ichi Amano* (Tohoku Pharmaceutical University)

**Relationship between a force curve measured on a solvated surface and the solvation structure: Simple relational expressions for a binary solvent and a molecular liquid**

Recent frequency modulated atomic force microscopy (FM-AFM) can measure force curves between a probe and a sample surface in several solvents. For example, the force curves can be measured in a simple liquid, a binary solvent, and a molecular liquid, etc. The force curve is supposed to be the solvation structure formed on the sample surface in some cases, because its shape is generally oscillative and pitch of the oscillation is about the same as diameter of the solvent particle. However, the force is not solvation structure. Therefore, we have recently derived the relational expression between them in a case of a simple liquid. To obtain those expressions for the binary solvent and molecular liquid, we derive them in the base of statistical mechanics of liquid in the present paper. This study deepens understanding of the force curve measured by the liquid AFM from theoretical side.

P11. *Kenji Nishizawa* (Kyushu University)

**Glass-like behavior in cells**

Mechanics intricately influences the vast range of cell behavior. The physical understanding of the actual intracellular condition is, however, still mostly elusive. While reconstituted networks of relatively stiff protein filaments, i.e. cytoskeletons, have been studied intensively as likely determinant of intracellular mechanics, it has been recognized recently that the molecular crowding (0.3-0.4mg/ml solid contents) can also affect the cell viscoelasticity significantly.

Here we investigate crowding effects on cell mechanics. We carry out high-bandwidth microrheology on two different in vitro model systems which lack cytoskeletal networks and compare those with results directly probed in the cultured cells. For the model systems,

viscoelasticity of BSA (family of globular proteins taken from bovine serum) and extracts taken from *Escherichia coli* (*E.coli*) were measured by systematically changing their concentrations. Samples were intensively washed ( $\sim 10000$  times) in HEPES buffer using membrane filter until the aging of the viscoelasticity becomes negligible. Passive microrheology was performed for these model systems because they were in equilibrium satisfying fluctuation-dissipation theorem.

High-bandwidth technology revealed the purely viscous response for both BSA and cell extracts in wide frequency and concentration range. The concentration dependence of viscosity shown in Fig.1 fits well to empirical Vogel-Fulcher-Tammann function  $\eta = \eta_0 \exp\{A\phi/(\phi_0 - \phi)\}$  which is known to describe the characteristic behavior for the slow dynamics near glass transition. The concentration  $\phi_0$  at which the viscosity diverges, however, seems largely different between BSA solutions ( $> 0.6\text{g/ml}$ ) and extracts from cells ( $\sim 0.3\text{g/ml}$ ). The yellow-colored band in the figure indicates the physiological solid concentration in living *E.coli* which is higher than  $\phi_0$  for cell extracts.

Mechanics of intracellular situations, which is far from equilibrium, was measured by optical-trap based active microrheology. Feedback mechanism was implemented to the conventional setup in order to stably track a probe particle which is subjected to the large athermal fluctuations in cells. We found that the viscosity in cells is much lower than that in cell extracts prepared with similar concentrations regardless of the additional contribution from the cytoskeletal structure in cells. The uncaging in model systems are driven purely thermally while the spontaneous athermal forces can facilitate flows in cells or active systems. In this contribution, we speculate more detailed mechanism to describe the out-of-equilibrium mechanics in dense and crowded materials.

P12. *Masao Inoue* (Kyushu University)

### **Effects of particle correlation on microrheology**

We consider that a probe particle is embedded into a colloidal dispersion system and pulled at a constant velocity through it. In this situation, a probe particle is subjected to resistance force from surrounding colloidal particles. In the present work, we study effects of interactions between colloidal particles on the resistance force by numerical calculations. For the purpose, we employ time dependent density functional theory (TDDFT) which is successful in describing liquid states. Also, we approximate the TDDFT to a simple form, assuming small density of

colloidal particles. This approximation ensures the accuracy of the calculation to the second order of the density. In addition, we ignore hydrodynamic interactions in the system. We calculated the resistance force in the following two cases: one is that interactions between colloidal particles are ignored, and the other is that the interactions are given by hard spheres. The values of the resistance force in the case of hard-sphere interactions are smaller than those in the case that the interactions are ignored. Also, the difference between the values in two cases increases with the density of colloidal particles.

P13. *Hiraku Oshima* (Kyoto University)

**A theoretical analysis for sugar-induced thermal stability of a protein**

It is experimentally known that the heat-denaturation temperature of a protein is raised by sugar addition. In earlier works, we proposed a physical picture of thermal denaturation of proteins in which the measure of the thermal stability is defined as the solvent-entropy gain upon protein folding at 298 K normalized by the number of residues. A larger value of the measure implies higher thermal stability. The water-sugar solution is modeled as a binary mixture of hard spheres. The thermal stability is determined by a complex interplay of the diameter of sugar molecules and the total packing fraction of the solution. We find that the protein is more stabilized as the sucrose or glucose concentration becomes higher and the stabilization effect is stronger for sucrose than for glucose. These results are in accord with the experimental observations. We analyze the contributions from the protein-solvent pair and many-body correlations to enhancement of the thermal stability. The contribution from the many-body correlation becomes stronger as the degree of thermal-stability enhancement increases, suggesting that the solvent crowding is made more serious by sugar addition, leading to an increase in the solvent-entropy gain upon folding.

P14. *Takashi Yoshidome* (Yokohama City University/Graduate School of Medical Life Science)

**A novel computation method of hydration free energy: A hybrid of the method of energy representation and the morphometric approach**

We propose an efficient method to compute the hydration free energy (HFE) by combining the method of energy representation (ER) with the morphometric approach (MA). Our method is based on the following computational result: The HFE is approximately described by

$\langle u \rangle / 2 + \text{constant}$ , where  $\langle u \rangle$  is the ensemble average of the protein-water pair interaction energy  $u$ . The constant, referred to as indirect component hereafter, is considered to represent the free energy arising from the indirect interactions such as the excluded volume effects. In accordance with the result, we propose the following protocol for calculating the HFE. We perform a MD simulation of a solution system with the structure of a solute fixed, and obtain  $\langle u \rangle$ . Using the solute structure in the solution, the indirect component is calculated by a hybrid of the MA and the method of ER. The HFE is a sum of  $\langle u \rangle / 2$  and the indirect component. Our method achieves a high computational efficiency compared to other computational methods of the HFE because only a MD simulation of a solution system is required once the coefficients in the MA are determined in advance. In the presentation, we will discuss validities and usefulness of our method.

P15. *Yuka Nakamura* (Kyushu Univ.)

#### **Perturbation theory of large particle diffusion in a binary solvent**

We have developed a new theory of diffusion in a binary solvent to study effects of solvation structure around a large diffusing particle. When a solvent consists of two components, the solvation structure greatly depends on the size ratio and packing fraction of solvent particles. To develop the theory, we expand microscopic equations for dynamics of binary-solvent particles by assuming that a solvent particle is much smaller than a diffusing particle. By the expansion, we obtain an analytical expression of the diffusion coefficient. It is calculated by the radial distribution functions of a binary solvent. The developed theory is applied to a large hard-sphere immersed in a binary hard-sphere mixture. Due to the solvation effect, the diffusion coefficient deviates from the value predicted by the Stokes-Einstein (SE) relation. We show the dependence of the deviation from the SE relation on the packing fraction of solvent particles.

P16. *Kyohei Takae* (Kyoto University)

#### **Applying electric field to charged and polar particles between metallic plates: Extension of the Ewald method**

We develop an efficient Ewald method of molecular dynamics simulation for calculating the electrostatic interactions among charged and polar particles between parallel metallic plates, where we may apply an electric field with an arbitrary size. We use the fact that the potential



from the surface charges is equivalent to the sum of those from image charges and dipoles located outside the cell. We present simulation results on boundary effects of charged and polar fluids, formation of ionic crystals, and formation of dipole chains, where the applied field and the image interaction are crucial. For polar fluids, we find a large deviation of the classical Lorentz-field relation between the local field and the applied field due to pair correlations along the applied field. As general aspects, we clarify the difference between the potential-fixed and the charge-fixed boundary conditions and examine the relationship between the discrete particle description and the continuum electrostatics.

P17. *Kouhei Matsubara, Takuya Fukudome and Masayuki Irida* (Kyushu Institute of Technology)

**Three-body distribution functions in hard sphere fluids calculated by using extended scaled particle theory**

Three-body distribution functions of associated three particles in hard sphere fluids, which correspond to the probabilities of three hard-sphere particles making contacts each other, are calculated. The three-body distribution functions in hard sphere fluids are calculated through the solvation free energies of the three-body solute making contacts. Extended scaled particle theory (XSPT), which we have developed, is used in the solvation free energy calculations. Our calculated results are compared with the Monte Carlo simulation results done by Kubota, M. and Akiyama, R. The three-body distribution functions have been qualitatively reproduced by our results with XSPT.

P18. *Keiichi Yanase* (Shinshu Univ.)

**Multifaceted static structure analysis for globular proteins in solution using small angle X-ray scattering**

Small angle scattering (SAS) probes both intraparticle and interparticle structures of complex systems in solution. SAXS experiments were carried out on a series of globular protein solutions. The experimental form factor,  $P(q)_{\text{exp}}$ , is obtained at dilute protein concentration, where intermolecular interactions can be neglected.  $P(q)$  is the reciprocal space function associated with the pair distance distribution function, which contains information about size, shape, and internal structure of the protein molecule. We reconstructed a 3-D structure of

proteins from  $P(q)_{\text{exp}}$  using an ab initio technique (GASBOR).

With increasing concentration, we observed effects of intermolecular interactions represented by static structure factor,  $S(q)$ . Generalized indirect Fourier transformation technique tries to separate  $P(q)$  and  $S(q)$  assuming interaction potential models, while letting  $P(q)$  virtually model-free. However, because of structural features of proteins, such as irregular shape, distributed patches, and inhomogeneous charge distribution, intermolecular interactions may not be regarded as those of simple colloidal particles. Then, we employed an interaction potential model-free analysis of the experimental structure factor,  $S(q)_{\text{eff}}$ . We further extracted concentration dependence of the mean nearest-neighbor distance and coordination number from the effective pair correlation function,  $g(r)_{\text{eff}}$ . The multifaceted static structure analysis allows us to describe protein-protein interactions even when  $S(q)_{\text{eff}}$  shows eccentric shape.

P19. *Yasuhiro Yamashita* (Kyushu University)

#### **Hydrodynamic friction of phase-separated agarose gel**

It has been reported that the phase separation of the gel, due to the spinodal decomposition, occurs when the aqueous solution of agarose is quenched below the gelation temperature. The spatial density fluctuations are, then, frozen into the polymer network of the gel. Entire structure of the polymer network, thus, becomes porous, which influences the mechanical properties of the gel. Among others, the frictional property of the polymer network is one of the most important mechanical properties of the gel. We, therefore, determine the friction coefficient between solvent and the polymer network of the gel. It is found that the friction coefficients of the phase separated agarose gels are smaller more than two orders of magnitudes than the homogeneous poly(acrylamide) gels. The correlation length of the spatial density fluctuations is determined by the small-angle laser light scattering from the gel independently. We, then, discuss the frictional properties of the gel in terms of the phase separation structures of the gel.

P20. *Takeshi Akahane* (Shinshu Univ.)

#### **Structural and kinetic properties of hydrated polyethylene glycol chains in diverse soft materials**

Polyethylene glycol (PEG) has been used in a wide range of medical applications, such as PEG-conjugated proteins and surface modifications of liposomal products. We hypothesize that

excluded volume effects of hydrated PEG chains, instead of bare PEG chains, are essential for such functionalities.

For the better understanding of the nature of hydrated PEG chain at the molecular level, we performed small angle X-ray scattering (SAXS) and dielectric relaxation spectroscopy (DRS) on water/octaethylene glycol monododecyl ether (C12E8) in  $0 \leq w \leq 0.9$ , where  $w$  is the weight fraction of C12E8. The results indicate that bulk-like water still presents even in liquid crystal (LC) phases. The relaxation amplitude and relaxation time of bulk-like water change continuously in the entire concentration range. In contrast the relaxation time of hydrated PEG chains shows critical-like behavior at micelle (L1) - hexagonal LC (H1) phase boundary, increasing steeply in the LC phase. The relaxation amplitude grows continuously across the L1 - H1 phase boundary, but decreases at  $w > 0.5$ , because the number of the water molecules is no longer sufficient to exhibit such large polarization fluctuation at higher surfactant concentration. We also present the results of tetra-PEG solution, PEG-lipid micelles, and artificial red cells.

P21. *Naoya Yamaguchi* (Graduate School of Fukuoka Institute of Technology )

#### **Liquid Crystal Phase of Aqueous Colloidal Solutions of DNA-Nanosheet Mixture**

We recently reported that the colloidal solution of clay mineral nanosheets fluorohectorite shows liquid crystallinity. On the other hand, an aqueous solution of double-stranded DNA, a rigid polymer with the persistence length about 60 nm, is known to form liquid crystal phases at high concentrations. In this study, we investigated the liquid crystal phases of aqueous solutions of fluorohectorite nanosheets/DNA mixture by polarized optical microscopy and small-angle X-ray scattering (SAXS). The mixture system showed an isotropic-to-liquid crystal phase transition at lower concentration than the solutions of fluorohectorite or DNA alone. Furthermore, SAXS measurement revealed that the liquid crystal phase of the mixture have higher structural order than the single-component systems.

P22. *Shingo Fujihara* (Kyushu University)

#### **Attractive interaction between macroanions mediated by multivalent cations in a biological fluid**

Although G-actin is negatively charged protein, the monomers associate each other and form fibrils in biological condition. In the previous study strong effective attraction between

macroanions was shown on the basis of an integral equation theory with a simple model. The attraction was mediated by monovalent cations. In the present study, the effective interaction is studied in electrolyte solution consisted of monovalent cations, divalent cations, monovalent anions, and solvent molecules, because the association behaviors depend on the concentration of multivalent cations in case of biological systems. The correlation functions are calculated by Hyper-Netted Chain-Orstein Zernike(HNC-OZ) theory with a charged hard sphere model. This shows that the strong attraction is observed even if the composition of solution mimics Ringer solution(150 mM monovalent cations, 5.0 mM divalent cations). In case of the stable dimer association is mediated by divalent cations. This result qualitatively agrees with related experimental results for actin. Macroanions dimer is stabilized by the exchange of monovalent cations for divalent cations at the location where the attraction is mediated.

P23. *Shunya Sunaba* (Kyushu Institute of Technology)

#### **Cation distribution in EcoRV-DNA complex calculated by using 3D-RISM**

In this study, cation distributions in the EcoRV-DNA complex were calculated by using 3D-RISM, where NaCl or MgCl<sub>2</sub> aqueous solution was used as a solvent. The X-ray structure of EcoRV-DNA complex (PDBID: 1rvb), which corresponds to the step prior to the hydrolysis reaction of a DNA fragment, was adopted as a solute structure. The calculated local densities of divalent cation, Mg<sup>2+</sup>, at the active site in EcoRV with a MgCl<sub>2</sub> aqueous solution are about twice as high as those of monovalent cation, Na<sup>+</sup>, with a NaCl aqueous solution. Both the distributions of Na<sup>+</sup> and Mg<sup>2+</sup> cations around the active site are similar, but slightly different from each other. The distribution of Na<sup>+</sup> ions has a sharp peak at the same position in the active site, where a Mg<sup>2+</sup> ion is found in the X-ray structure. The distribution extends to the polypeptide side chains which are directly bonded to the Mg<sup>2+</sup> ion in the X-ray structure. On the other hand, the distribution of Mg<sup>2+</sup> ions also has a sharp peak at almost the same position as the previous Na<sup>+</sup> case, but extends to the interface region between the DNA fragment and the polypeptide side chains, both of which have negative charges.

P24. *Takumi Yamashita, Ryo Akiyama* (Kyushu Univ.)

**Difficulty of detection of solvation effects on effective interaction between colloidal particles**

Attractive interaction driven by translational motion of solvent molecules is important not only to discuss effective interaction between colloidal particles but also to calculate stability of protein's conformation and other behaviors in biological system. However, researchers had not given enough attention to the effect. The importance has been studied in the first decade of this century. In this study, we calculated the distribution function between two colloidal particles in a solution  $g(r)$  by using the HNC-OZ theory. Although the solvation effect is clear in the distribution function  $g(r)$ , the effect almost disappear in the scattering factor  $S(k)$ . Therefore, it seems that the detection of the effect is difficult by using small-angle X-ray scattering, although other effects are reasonably shown in the scattering factor. This study presumably explains that the solvation effect has not been recognized enough.

P25. *Hisasi Tani* (Tokyo University of Science)

**Weakly nonlinear analysis for the radial fingering phenomena with the effect of viscous normal stress**

Hele-Shaw problem, which is about a time evolution of an interface between two fluids in a Hele-Shaw cell, has been intensively studied since it can be related with a wide variety of phenomena such as the growth of a snow crystal and the enhanced oil recovery. Under the assumptions that (i) both fluids are incompressible, and (ii) the flows obey the Darcy's law, the problem to be solved is a Laplace equation with appropriate boundary conditions; the kinematic boundary condition and the Young – Laplace equation. However, the validity of the Young – Laplace equation has been discussed. In fact, recently, the more generalized boundary condition including the effect of the viscous normal stress (VNS) was studied (H. Kim et al., 2009). On the other hand, their results are limited in the linear analysis, while the nonlinearity may plays an essential role on the instability of the interface.

Under such backgrounds, we derive extended mode coupling equation with the VNS effects, by following the weakly nonlinear analysis due to Miranda (J. Miranda and M. Widom, (1998)). Then we numerically analyze the derived equation and discuss the effects of VNS on the instability and the behavior of the radially growing interface.

P26. *Yoji Kubota* (Kyushu University)

#### **Dielectric Relaxation of Water around a Pair of Ions**

Suzuki and co-worker observed dielectric spectra for aqueous solutions of alkali halide and of various proteins, such as actin filaments in the frequency range 0.2 - 26 GHz. The spectra involved a component higher than the peak related to the orientational relaxation of bulk water. The observation suggested that the dielectric relaxation of water in the hydration shell was faster than that of bulk water and named hyper-mobile water. On the other hand, it was difficult to show the fast relaxation by molecular dynamics simulations.

We developed a method of calculation for local dielectric relaxation of water around ions on molecular dynamics simulations. We calculated the local dielectric relaxation around Na and Cl ions. The local dielectric relaxation in the hydration shells around Na cation is faster than that of the bulk water, whereas the fast component is not found around Cl anion and intermediate region between Na and Cl ions.

P27. *Yuutarou Yamashita* (Kyushu University)

#### **Phase behavior of binary polymer solution: Gelatin-PEG-water system**

Gelatin and poly(ethylene glycol)(PEG) are both water soluble polymers. It is known that gelatin-PEG-water system show phase separation with a decrease in temperature. We examined the effects of molecular weight of PEG ( $M_{peg}$ ) and the PEG concentration ( $C_p$ ) on the phase separation temperature. As a result, we found that phase separation temperature is increased with increases in  $M_{peg}$  and  $C_p$ .

P28. *George Mogami, Takashi Miyazaki, Tetsuichi Wazawa, Nobuyuki Matubayasi, and Makoto Suzuki* (Tohoku University)

#### **Anion-Dependence of Fast Relaxation Component in Na-, K-Halide Solutions at Low Concentrations Measured by High-Resolution Microwave Dielectric Spectroscopy**

High-resolution microwave dielectric spectra of NaX, KX (X: F, Cl, Br, I) aqueous solutions of  $c = 0.05$  M and 0.1 M measured in the frequency range 0.2–26 GHz at 10 °C were analyzed. The dielectric relaxation (DR) spectrum of each solution, which deviates slightly from the bulk-water spectrum, was mathematically divided into the bulk-water spectrum and the spectrum of solute particles covered with a water layer using a mixture theory by assuming the

existence of continuous bulk-water phase. The solute spectra above 3 GHz were fitted with a linear series of pure water component (gamma dispersion with DR frequency  $\omega$ ), fast Debye component-1 with DR frequency  $\omega_1$  ( $> \omega$ ) and slow Debye component-2 with DR frequency  $\omega_2$  ( $< \omega$ ). Component-2 was only found for the fluorides. The results indicated that component-1 and -2 were from water modified by ions, thus, denoted as “hypermobile water” and “constrained water”, respectively. Thus, except for the fluorides, it was reported that the modified water by salt ions exhibited only Debye component-1 other than gamma dispersion, indicating the existence of a water-ions collective hypermobile mode in each solution.

P29. *Kiharu Abe* (Okayama University)

#### **Solubility of hydrophobic molecules at the liquid-vapor interface of water and simple liquids**

The solubility of hydrophobic molecules at the liquid-vapor interface is calculated using NVT molecular dynamics simulation and the particle insertion method. Two systems (solute/solvent) are considered : methane/water and Lennard-jones particle/Lennard-jones particle. We obtained the density profile of the solute (scaled by the bulk gas density) along the z axis which is perpendicular to the interface.

We found that the temperature dependence of the local density of the solute is closely related to the temperature dependence of the local density of the solvent, which is analogous to the case of a bulk solution where a thermodynamic relation between the temperature dependence of the solubility and that of the volume of the solution can be derived.

P30. *Norio Yoshida* (Kyushu Univ.)

#### **Density fluctuation of fluids at supercritical region: realization of the "Ridge" by the statistical mechanics of liquids**

Supercritical fluids have been attracting persistent attentions both from industrial and academic societies due not only to versatility in the application but also to their interesting physicochemical properties. One of those properties which distinguish the supercritical fluid from the fluids at normal region, or vapor and liquids, is the density fluctuation which is extraordinarily large. Concerning the density fluctuation in supercritical fluids, an interesting characterization has been made by Nishikawa and coworkers based on the small angle X-ray

scattering measurement. According to their analysis, the density fluctuations at different temperatures plotted against density form two regions separated by a line which is referred to as a ridge. They have suggested that the higher density side of the ridge is more liquid-like, whereas the lower density side is more vapor-like. However, there are no information concerning the microscopic structure of fluids at both sides of the ridge. In this study, we present a theoretical analysis of the density fluctuation of fluids at supercritical region, based on the statistical mechanics of liquids, or the reference interaction site model (RISM) theory. It is our purpose to identify the ridge, theoretically, and to clarify the microscopic structure of fluids at both sides of the line.