

# The 3rd Mini-Symposium on Liquids (MSL2009) Physics and Chemistry of Soft Interfaces

## 講演概要

### "Interface-selective heterodyne-detected second-order nonlinear optical spectroscopy" 「界面選択的ヘテロダイン検出二次非線形分光の開発と応用」

山口祥一 Shoichi Yamaguchi

"Interface" is now one of the most important keywords in materials and life science. Among a lot of experimental techniques to investigate interfaces, the second-order nonlinear spectroscopy holds a special and unique position that cannot be replaced by the others. One can obtain electronic and vibrational spectra of interfaces noninvasively in the ambient atmosphere by using second harmonic generation (SHG) and vibrational sum frequency generation (VSFG), respectively, which provide essential information for identifying interfacial species, determining structure and orientation, and considering microscopic functions of the interfaces.

We recently developed electronic sum frequency generation (ESFG) that can provide electronic  $|\chi(2)|^2$  spectra with a much higher signal to noise ratio and far denser spectral data points than SHG [1]. SHG, VSFG, and ESFG measurements provide data representing  $|\chi(2)|^2$ , not  $\chi(2)$  itself, because of the homodyne nature of signal detection. This feature sometimes makes interpretation of data difficult, and even worse, it hides essential information inherent in  $\chi(2)$ . The most crucial information lost in the homodyne detection is the sign of  $\chi(2)$  that is directly related to the "up" versus "down" alignment of interfacial molecules.

Very recently, we have realized the heterodyne detection of ESFG and VSFG [2, 3]. These new methods, HD-ESFG and HD-VSFG, can provide electronic and vibrational complex  $\chi(2)$  spectra of interfacial molecules, respectively. We are now studying interesting topics such as absolute orientation of interfacial molecules, pH difference between the aqueous bulk and interface, and higher order structure of proteins adsorbed on interfaces, by using HD-ESFG and HD-VSFG.

#### References

- [1] S. Yamaguchi and T. Tahara, *Laser Photonics Rev.* 2 (2008) 74.
- [2] S. Yamaguchi and T. Tahara, *J. Chem. Phys.* 129 (2008) 101102.
- [3] S. Nihonyanagi, S. Yamaguchi, and T. Tahara, submitted to *J. Chem. Phys.*

### "Hierarchical structure induced by solvation effects of hydrophilic/hydrophobic ion pair in the mixture of water and 3-methylpyridine"

「溶媒和効果による水/有機溶媒混合系の階層的秩序」

貞包浩一朗 Koichiro Sadakane

Binary mixture of water and organic solvent have been used extensively to study universal aspects of critical behavior and phase separation dynamics. However, not enough attention has been paid to unique ion effects in such mixtures, where preferential hydration around each ion should affect the composition fluctuations [1]. Recently, we examined the effect of NaBPh<sub>4</sub>, which is a kind of salt composed of hydrophilic cation Na<sup>+</sup> and hydrophobic anion BPh<sub>4</sub><sup>-</sup>, on the phase behavior of the mixture of D<sub>2</sub>O and 3MP. By microscopic observation, a number of droplets with a size of 10 μm were observed at a room temperature when 85 mM of NaBPh<sub>4</sub> is dissolved in the mixture of D<sub>2</sub>O and 3MP. These droplets showed maltase cross patterns at a condition of crossnicole, using polarized light. The se patterns are known to be observed when the system forms the multi-lamellar vesicles [2]. Thus, this observation indicates a temperature induced phase transition from multi-lamellar vesicle structure to homogeneous structure. In order to understand the detailed structure of this system, we have carried out small-angle neutron scattering measurement. As a result, a sharp Bragg peak is observed together with second and third peaks. This profile is known to be observed in lamellar structures. We concluded that these hierarchical structure, i.e., lamellar at a length scale of μm and multi-lamellar vesicle at a length scale of nm, are induced by the strong interaction of ions at the interface of water and organic solvent.

- [1] J.N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, London, 1991).
- [2] L Ramos, D. Roux, P.D. Oimsted and M.E. Cates, *Europhys. Lett.*, 66, 888-894 (2004).

## "New aspects of age-old problems of capillary and wetting"

「古くて新しい表面張力と濡れの諸問題」

奥村剛 Ko Okumura

Capillary and wetting are phenomena observed in daily life quite frequently and familiar to children, for example, via soap bubbles.

Accordingly, various questions have been raised but many of them remain unanswered. In this talk, from such familiar topics, I would like to talk on some examples of a little success from our group along with previous efforts: (1) wetting on plant leaves (mainly with Chieko ISHINO), (2) dynamics of bubbles (with Ayako ERI), and (2) fusion of immiscible liquid drops (with Maria YOKOTA and Ayako ERI).

## "Hydrodynamics in multicomponent biomembranes"

「多成分生体膜における流体力学」

好村滋行 Shigeyuki Komura

We investigate the dynamics of critical fluctuations in binary fluid membranes using a two-dimensional hydrodynamic model with momentum decay to the surrounding water. In particular, the decay rate of concentration fluctuations is obtained analytically. In the limit of small wavenumber  $q$  with respect to the correlation length, the decay rate is proportional to  $q^2$ , as usual. In the large- $q$  limit, however, the effective diffusion coefficient increases only logarithmically with  $q$ .

## "Study on line tension of air/hexadecane/aqueous surfactant system"

「界面活性剤水溶液表面でのアルカンレンズの線張力に関する研究」

松原弘樹 Hiroki Matsubara

We measured the line tension of the air/hexadecane/aqueous solution of the dodecyltrimethylammonium bromide (DTAB) system as a function of the molality of DTAB aqueous solution at 298.15 K. The experimental values of the line tension were 10-10 to 10-12N, and they coincided with the theoretical estimates. Furthermore, it was found that the line tension changes in sign from positive to negative at around 0.750 mmol kg<sup>-1</sup>. This concentration is close to the point of transition from partial to frustrated-complete wetting. Taking into account the profiles of the free energy of the air/water surface, previously developed by Indekeu to understand the interrelationship between the wetting transition and line tension, it is suggested that the sign reversal of the line tension can be attributed to the transition from partial to frustrated-complete wetting.

## "How soft interfaces get wet"

「ソフト界面の濡れ方」

甲賀研一郎 Kenichiro Koga

We consider three fluid phases, alpha, beta, gamma, in equilibrium. One possible state of the system is that the beta phase wets the alpha-gamma interface and the other possibility is that the three phases meet at a line of common contact. With varying thermodynamic state there may be a transition between these two modes of three-phase equilibrium, termed a wetting transition. How intermolecular interactions of different strengths and ranges may lead to different orders of wetting transition has been much discussed in the literature. We introduce a mean-field density functional model of three-phase equilibrium that we show to have a first-order, second-order, and higher-order wetting transitions. With this model and earlier related models, we conjecture that the order of wetting transitions is related to the form of the wetting trajectory in the vicinity of the bulk phase that wets the alpha-gamma interface. Also we propose scaling assertions for the wetting and non-wetting trajectories that seem to hold in the vicinity of a continuous wetting transition.