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Highlights of Research Activities (Kazue Kurihara)

Kazue Kurihara is internationally well-known for her research on the surface forces measurement which she has made tireless efforts to broaden the scope of the measurement for materials science including instrumentation. She also offered her services for the science communities for both domestic and international ones including IASIS (International Association of Colloid and Interface Scientists) for which she was a president from 2012 to 2015. She is always happy to help colleagues and promote science.

Kurihara, who is currently a research professor of the Tohoku University, is a distinguished scientist of multidisciplinary background from synthetic chemistry to applied physics, while keeping her major interest in colloid and interface science. Unlike the most of her colleagues in Japan who stay at the same institution for life, she worked at various top groups in the field of colloid and interface science during her early career, which provided her with the opportunity to do multidisciplinary research and to be linked to the international network. She worked at Texas A&M and Clarkson University as a post-doc at the Prof. Janos Fendler's group after graduating from the University of Tokyo. She then returned to Japan and worked with Prof. Iwao Tabushi, an expert in the host-guest chemistry, of Kyoto University, went to Stockholm at the Institute of Surface Chemistry as a visiting scientist when Prof. Per Stenius was the director, where she learnt basics of the surface forces measurement. In 1987, she returned Japan to work as a group leader for the five years molecular architecture project directed by Prof. Toyoki Kunitake of Kyushu University where she could start her surface forces measurement. During these years, she studied various functions of molecular assemblies such as micelles liposomes, vesicles, microemulsions and monolayers, and demonstrated many interesting results, which include the first demonstrations of photo-induced formation of gold nanoparticles in microemulsions in 1983 and of molecular recognition employing hydrogen bonding at surface monolayers on water in 1991.

In 1992, she was promoted to an associate professor at the applied physics department of the Nagoya University, then in 1997 to a full professor at the institute of chemical reaction science (later became the institute of multidisciplinary research for advanced materials), the Tohoku University. At Nagoya, she determined to focus on the surface forces measurement and hoped to extend the scope of the surface forces measurement with her multidisciplinary background. With the support of the machine shop of the department, she started to construct the apparatus by herself, and has made original contributions to the measurement since.

Surface forces measurement employing surface forces apparatus (SFA) is known as a very demanding technique, so the field has perhaps not sufficiently grown in spite of its importance and advantages. Kurihara has made efforts to remove various existed limitations of the conventional surface forces measurement such as sample availability (e.g. smooth silica substrates prepared only by sputtering without suing glue to remove the limitation that previously only transparent mica was a practical substrate), temperature control, and to extend the potential of the measurement both in instrumentation, sample preparation and characterization.

She developed (1) twin path SFA, an only practical SFA for opaque samples, which was a basic setting for electrochemical SFA and SFA fluorescence spectroscopy; (2) a high (till 140 ℃) and low temperature (till -15 ℃) SFA, the latter was used for studying ice: and (3) the resonance shear measurement (RSM) which monitors the shear response for studying confined liquids, surface deformation of gel and rubber. She has constructed these apparatuses using the university machine shops. Besides, she offered the design to ADVANCE RIKO Co. Ltd., which now commercially provides the twin-path SFA & RSM. This machine was sold to several major Japanese companies (Hitachi, Ltd. and Idemitsu Kosan Co. Ltd. etc.) and helped their R&D's. By taking advantages from her early research experiences on molecular self-assemblies for surface modification and characterization, she used the technique for studying the solid-liquid interfaces and observed intriguing phenomena, which include hydrogen-bonded organization of liquids at the interfaces. She also extensively studied confined liquids, and at earlier time biologically relevant systems such as polyelectrolytes and enzymes. These achievements were possible only by someone like her who has multidisciplinary background. Her colleague once called her “trail blazer”, and another mentioned her study the result by “heroic efforts”. Her major achievements are listed at the end of this note.

Kurihara has published to date 225 peer-reviewed research articles and reviews, and 41 book chapters while constructing many apparatus by herself. Her achievements have been internationally recognized by various awards including 2022

IACIS Lectureship Award, 2016 SPSJ Award for Outstanding Achievement in Polymer Science and Technology, The Society of Polymer Science, 2013 IUPAC Distinguished Women in Chemistry or Chemical Engineering Award, and the A.E. Alexander Lectureship Award 2011 from the Australian Society of Colloid and Interfaces. She was an elected member of the science council of Japan since 2005.

< Major Research Achievements>

Twin-path Surface Force Apparatus (Twin-path SFA)

Kurihara developed a new surface forces apparatus (SFA) called Twin-path Surface Forces Apparatus using modified two-beam interferometry for the distance determination [29 in the list]. This apparatus can be used to study opaque samples such as metals, and has removed the limitation of the conventional SFA: the sample substrates need to be transparent, so only mica has been practically used. This SFA has the potential for dramatically expanding the scope of the surface forces measurement: the measurements on new samples using both of various substrates and various surface modification methods including thiol derivatives on gold substrates [17].

Electrochemical SFA (Ec-SFA) based on the twin-path SFA can study the double layer force between identical electrodes unlike the previous Ec-SFA for which one surface need to be transparent mica. It was used to study selective adsorption of anion [12, 25] and quantitative evaluation of strongly and loosely bound counterions of the electric double layer on Au electrode [17], proton adsorption and hydrogen evolution on Pt electrode [9]. Recently, she observed an intriguing phenomenon, the sudden current increase, when the electrodes approached below 5 nm. The increase is two orders greater than the conventional feedback current, and interpreted by organized redox species between the electrode [1].

The twin-path SFA can be placed under the fluorescence microscope to perform fluorescence spectroscopy. Using appropriate fluorescence dye probes, this spectroscopic SFA can the local viscosity of the confined liquid [24] and the interfacial pH of mica and silica [2, 23].

For these studied, Kurihara prepared various smooth substrates including metals. She also developed a method to prepare transparent smooth silica substrates for FECO (fringes equal chromatic order used for distance determination) by only sputtering [10], which can be used for chemical modification and interaction measurements in organic solvents [5, 6] because no polymer glue is necessary.

Temperature control is another difficult task for SFA. Kurihara has constructed a low temperature control device (till - 15 ℃) for ice studies [3, 4, 7] and a high temperature one (till 140 ℃) [not in English publication] with a small deviation of ± 0.2 ℃.

Resonance Shear Measurement (RSM)

Shear force measurement is one of the active areas in the surface forces measurements with taking advantages of large surface areas (ca. 30 μm in diameter at their contact) used and the sensitive control of the surface separation. Kurihara's original contribution to the shear measurement is the development of the resonance method [40], which has various advantages: the high sensitivity to changes in rheological and tribological properties of samples and easy operation. The RSM was used for characterizing aqueous NaCl solution between mica surfaces [33]. The results show the effective viscosity of water for the separation less than 1 nm is 2-4 orders of magnitude larger than the bulk value while it exhibits high lubrication effect. This study by RSM has provided a comprehensive picture for the dynamics of confined water thinner than a few nanometers, which was the controversial problem at the time of the study.

Recently, the RSM has been used to resolve the friction of gel [14] and polymer brushes [5] to the contribution of deformation, viscosity and surface interactions. This will enable us to design better lubricants at the molecular level.

Characterization of Confined Liquids between Solid Substrates

Liquids confined in nano-spaces exhibit different properties from those in the bulk. They attract increasing attention from their importance in basic science and applications including micro- and nano-devices and tribology. Kurihara's studies using RSM revealed interesting, previously unknown behavior of confined liquids as follows: (1) the effect of confinement preventing the nematic liquid crystal, 4-cyano-4'-hexylbiphenyl, from the electric field induced orientation [19]; (2) Different viscosity and lubricity observed for water confined between silica surfaces of the different silanol densities [20]; (3) Different viscosity values of ionic liquids nano-confined between silica surfaces depending on the kind of anions [26], of which molecular mechanism was interpreted by simulation [15, 18] and X-ray diffraction[8]: (4) Increase in the viscosity of confined dioctylphthalate, which provides a new model explaining the role of the viscosifier, alkyl-coated $CaCO_3$ particles [30].

The RSM method is also used for characterizing model and practical lubricants in confined spaces, providing new molecular-level of insights into macroscopic behavior of lubrication [11, 16, 27].

Kurihara's various efforts for understanding confined liquids include: the X-lay diffraction study of a liquid crystal in the thickness down to ca. 2 nm [8]; realistic simulation reflecting the molecular natures of confined liquids by collaboration with the simulation specialists [15, 18, 21].

Surface Molecular Macrocluster Formed by Adsorption from Binary Liquids

Kurihara has found hydrogen bonded organizations of simple molecules such as alcohols [34, 36, 37], acids[39], phenol [31], amides[28, 35], and water [22] adsorbed on silica surfaces from their binary mixtures with cyclohexane. This surface molecular assembly is named "surface molecular macrocluster". The long-range attraction associated with such adsorption, of which thickness is typically 10 to 30 nm for alcohol, has revealed the larger interfacial energy due to the oriented molecules than the value for the bulk phase separation although such adsorption can occur in completely miscible binary liquids. The long ranged attraction is modulated by the kind of adsorbed molecules and the dynamics between the interfacial and the bulk phase. The force can be used to reveal unknown phenomena and distinguish the presence of different organizations [10, 22].

Characterization of Polyelectrolyte Brushes and Biologically Relevant Molecules

Her early studies have been conducted extensively using the Langmuir Blodgett films for surface modification. They include systematic measurements on polyelectrolyte brushes depending on their chain length and density [40, 43, 46], and the pH and salt concentrations of the medium [38]; molecular recognition involved in nucleic acid base paring [42] and enzyme reaction [32].

List of Relevant Publications

1. Nano-confined Electrochemical Reaction Studied by Electrochemical Surface Forces Apparatus, M. Kasuya, D. Kubota, S. Fujii and K. Kurihara, *Faraday Discussion*, 233, 206 - 221 (2022).
2. Evaluation of Interfacial pH Using Surface Forces Apparatus Fluorescence Spectroscopy, M. Kasuya, Y, Sano, M. Kawashima, and K. Kurihara, *Langmuir*, **37**(16), 5073-5080 (2021).
3. Ice premelting layer of ice–rubber friction studied using resonance shear measurement, F. Lecadre, M. Kasuya, S. Hemette, A. Harano, Y. Kanno, K. Kurihara, *Soft Matter*, **16**(39), 8677-

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10. Preparation of Stable Silica Surfaces for Surface Forces Measurement, H.-Y. Ren, M. Mizukami, K. Kurihara, *Rev. Sci. Instrum.*, **88**(9), 095198 (2017).
11. Nanotribological Characterization of Lubricants between Smooth Iron Surfaces, M. Kasuya, K. Tomita, M. Hino, M. Mizukami, H. Mori, S. Kajita, T. Ohmori, A. Suzuki, K. Kurihara, *Langmuir*, **33**(16), 3941–3948 (2017).
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13. Lubrication Properties of Ammonium-Based Ionic Liquids Confined between Silica Surfaces Using Resonance Shear Measurements, T. Kamijo, H. Arafune, T. Morinaga, S. Honma, T. Sato, M. Hino, M. Mizukami and K. Kurihara, *Langmuir*, **31**(49), 13265-13270 (2015).
14. Friction of polymer hydrogels studied by resonance shear measurements, H.-Y. Ren, M. Mizukami, T. Tanabe, H. Furukawa and K. Kurihara, *Soft Matter*, **11**, 6192-6200 (2015).
15. Structural stability and polarisation of ionic liquid films on silica surfaces, F. F. Canova, M. Mizukami, T. Imamura, K. Kuriharaa and A. L. Shluger, *Phys. Chem. Chem. Phys*, **17**, 17661-17669 (2015).
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