Global /Local Innovations
for Next Generation of Automobiles,
Sendai International Center, October 27, 2015.

Nano-scopic Approach for Green Tribology

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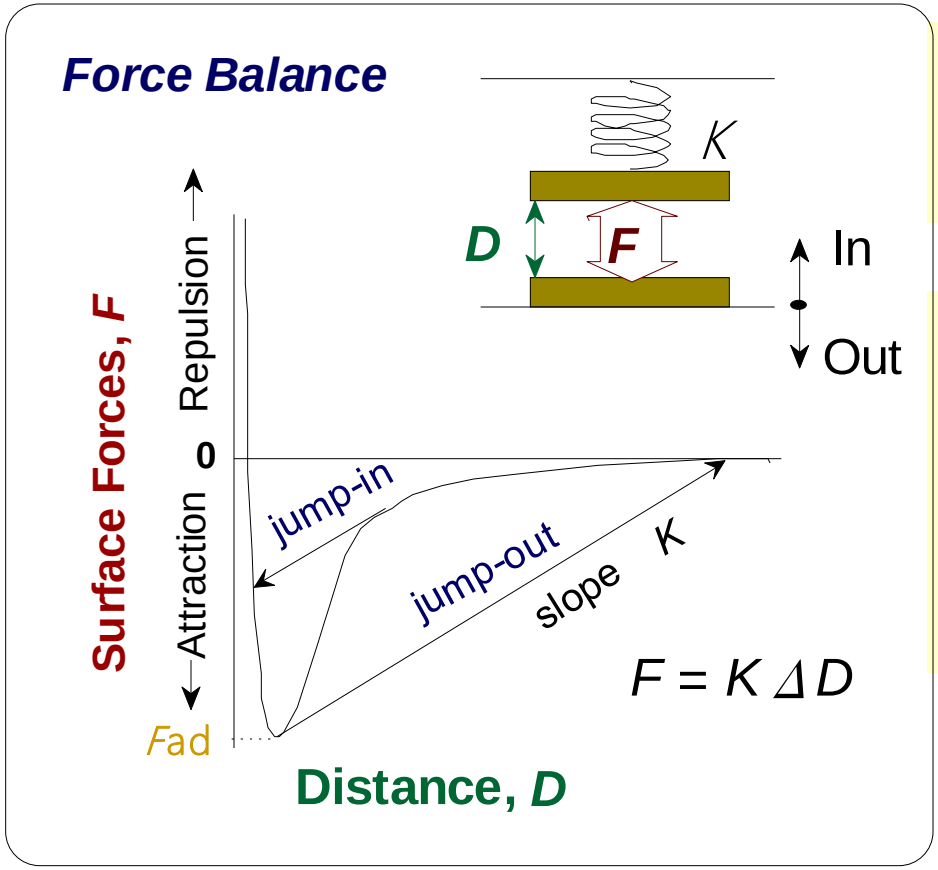
Surface Forces Measurements



Surface Forces Measurement

- **Best method for studying origins of interaction forces**

- **Possibility to investigate interfacial properties as a function of surface separations.**

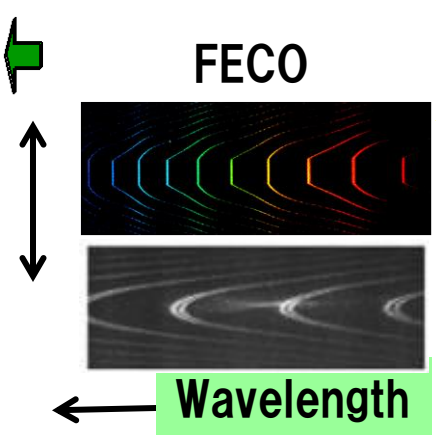
↓

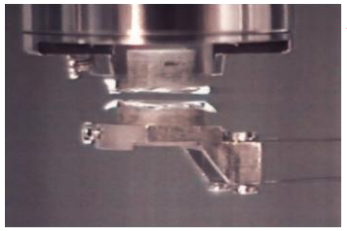
Precise control of surface separation.

Surface Forces Apparatus (SFA) can bridge "micro (meso)" and "nano"

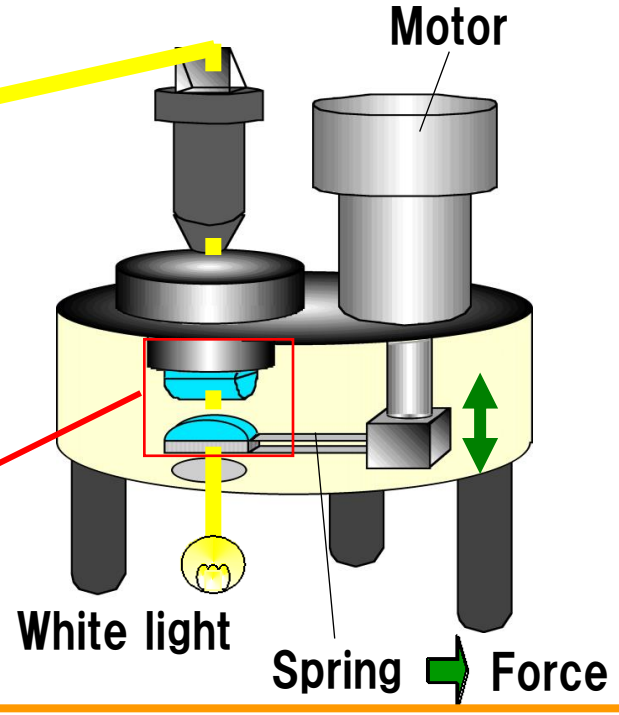
Distance (resolution 0.1 nm)

Geometric shape (contact diameter ~30 μm)

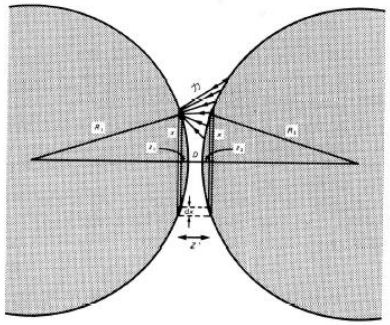




Crossed cylinder



Derjaguin Approximation (Derjaguin, 1934)



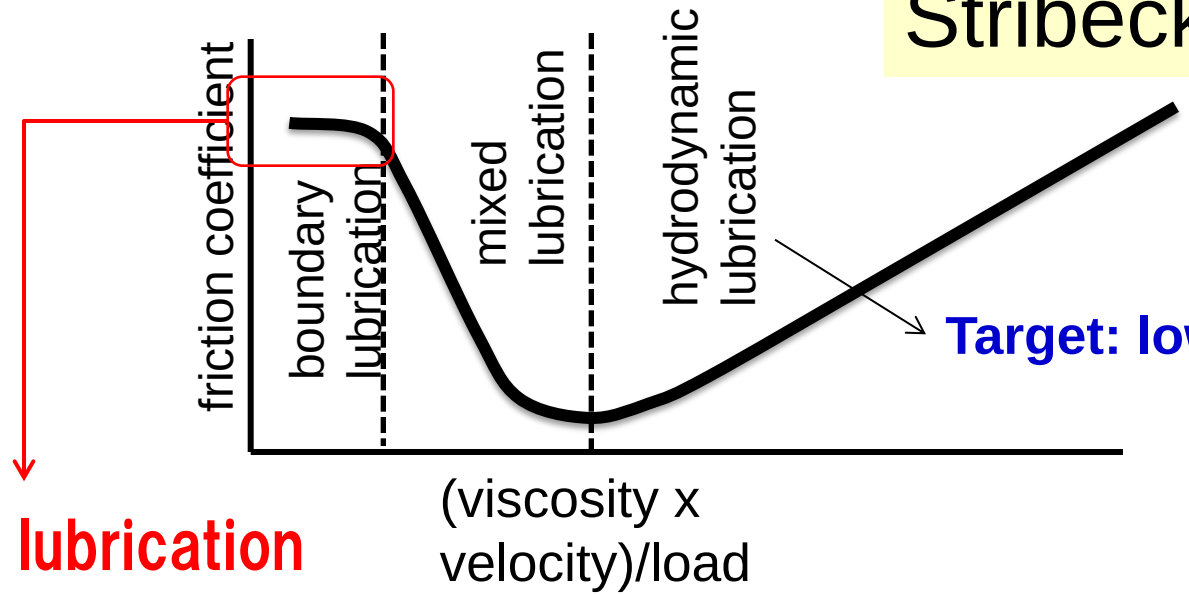
$$F(D)=2\pi[R_1R_2/(R_1+R_2)]W(D)$$

$F(D)$:Measured force

$W(D)$:Interaction between flat surfaces

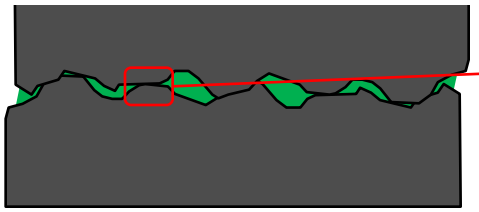
SFA and RSM study for Tribology

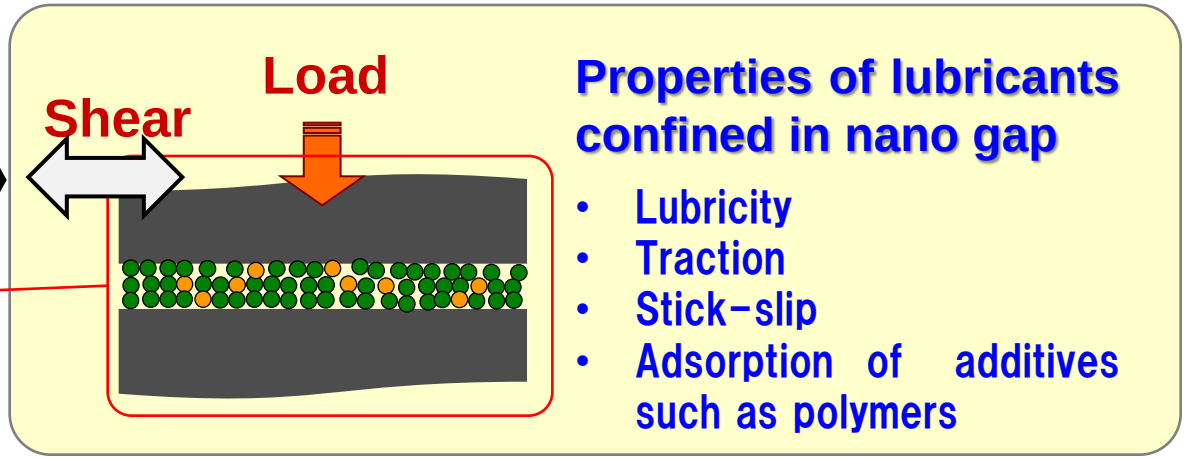
Stribeck curve



Boundary lubrication

- no lubricant?
- additive ?
- surface roughness
- substrate ?



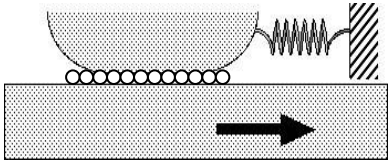


Resonance Shear Measurement Based on Surface Forces Measurement

Method for Nanorheology and Nanotribology
(Thickness dependence of nano-structuring of liquids)

Shear measurements based on SFA

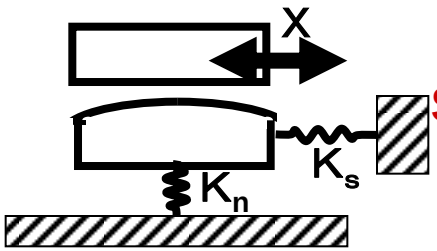
(a)



Stick-slip, Friction

Israelachvili et al (1988)

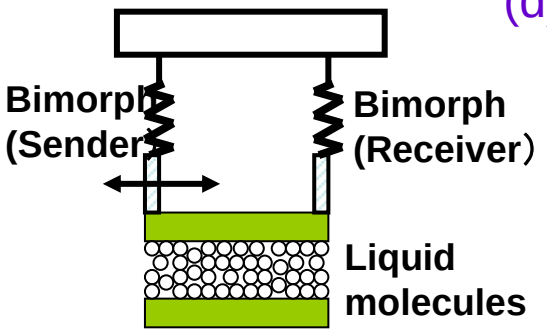
(b)



Stress

Klein et al (1998)
Klein et al (1991)

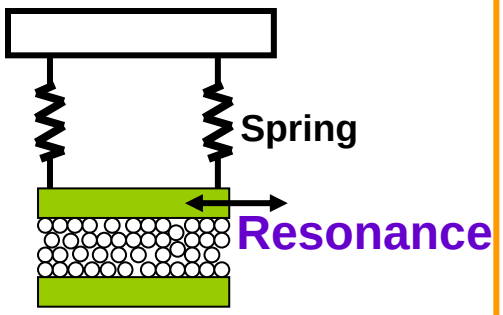
(c)



Viscosity

Granick et al (1990)

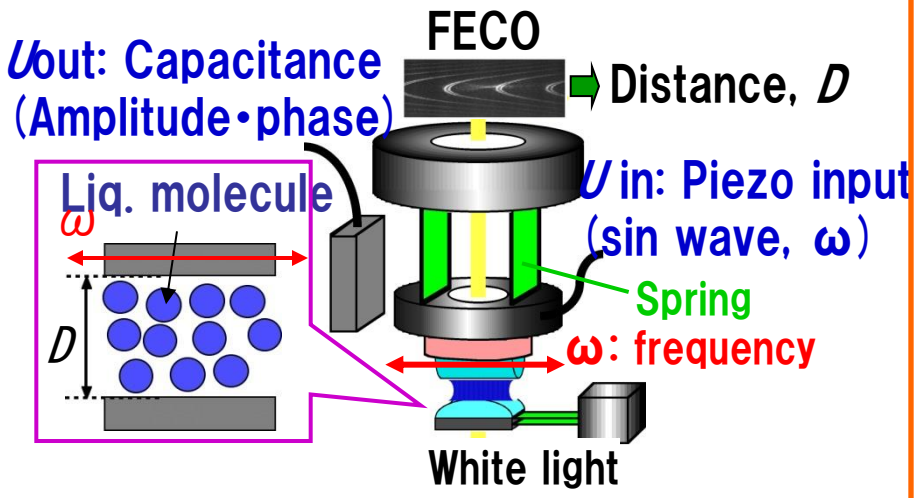
(d)



Viscosity,
Friction
Stick-slip

Kurihara et al (1997)

Apparatus



- **Fringes of equal chromatic order (FECO)**

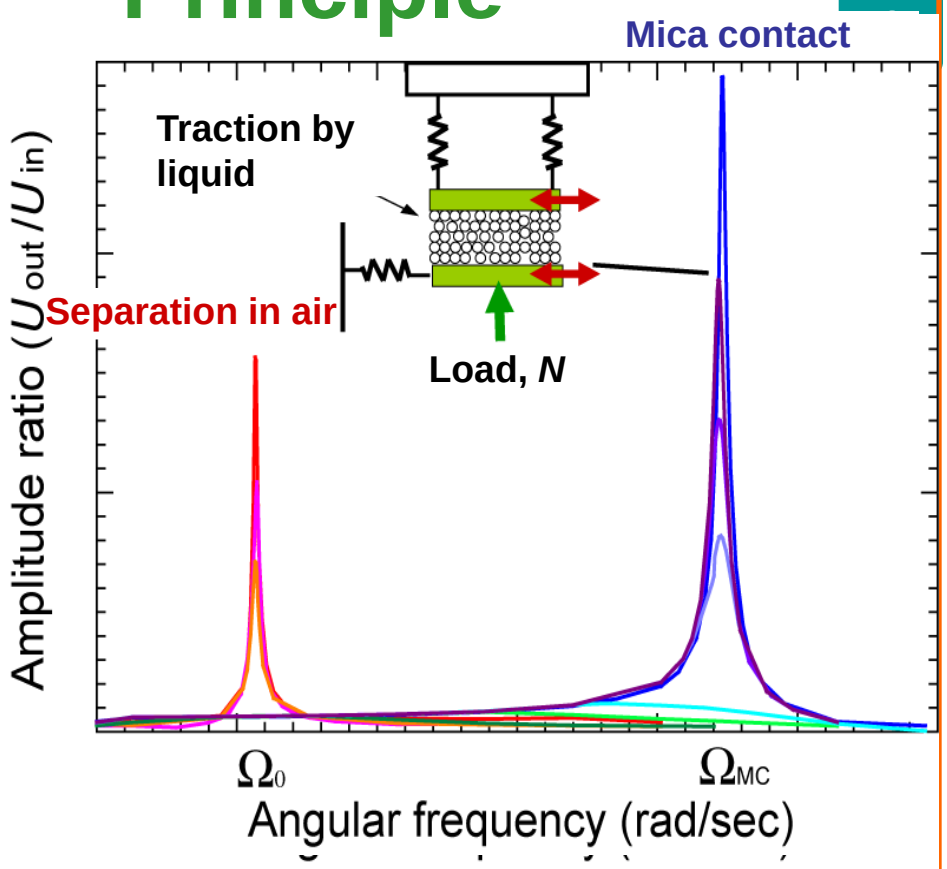
→ **Separation distance, *D***

(resolution: 0.1 nm)

- **Resonance: Peak frequency, amplitude**

→**Viscosity, friction, lubricity etc.**

Principle



- Large *D* → **Viscosity**
- Small *D*→**Friction and lubrication**

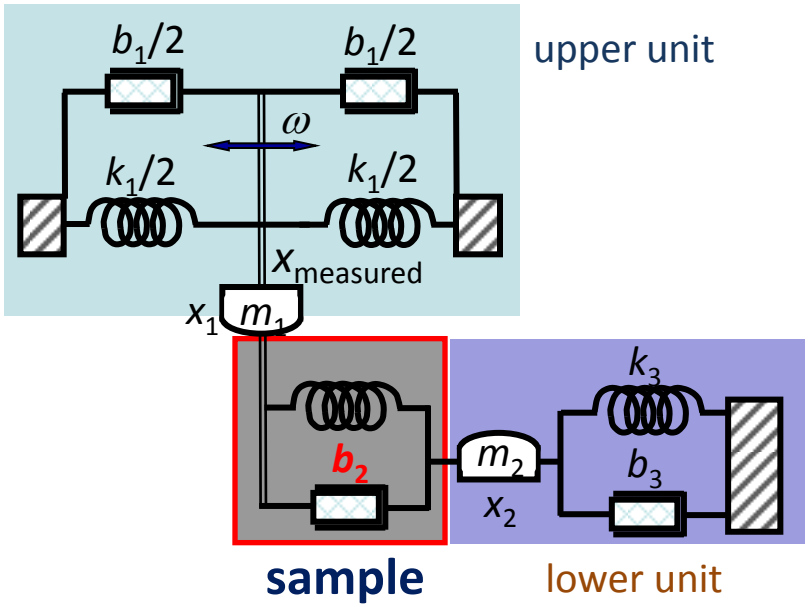
Dushkin C. D. and Kurihara K., *Colloid & Surf. A*, **129–130**, 131-139 (1997) .

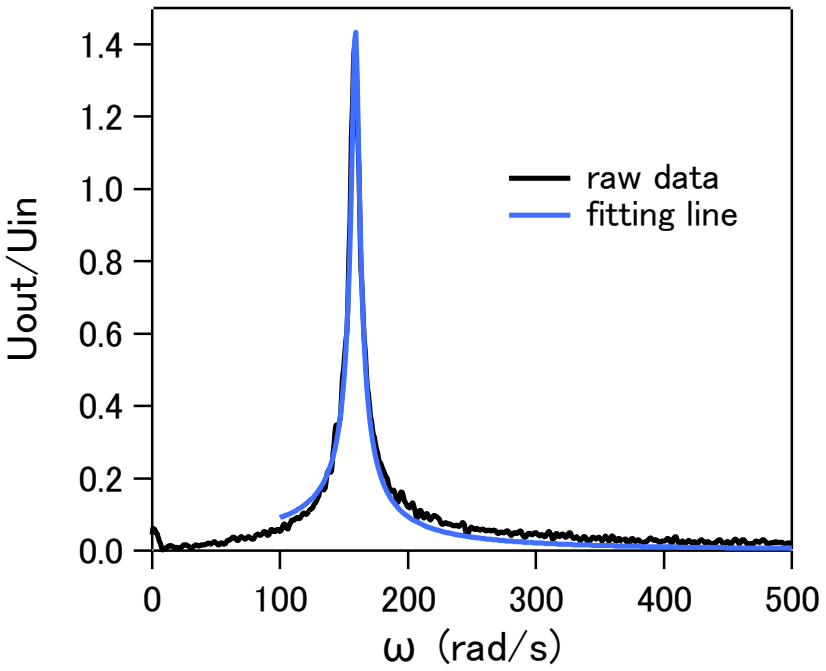
Dushkin C. D. and Kurihara K., *Rev. Sci. Instrum.*, **69**, 2095-2104 (1998).

Continuous monitoring of rheological and tribological properties is possible.

Physical model analysis of resonance curves

Physical model





Theoretical equation for resonance curves

$$\frac{U_{out}}{U_{in}} = \frac{C}{\alpha}\sqrt{\frac{\left(k_2+k_3-m_2\omega^2\right)^2+\omega^2\left(b_2+b_3\right)^2}{\left[\left(k_1/\alpha+k_2-m_1\omega^2\right)\left(k_2+k_3\right)-\omega^2\left(b_1+b_2\right)\left(b_2+b_3\right)-k_2^2+b_2^2\omega^2\right]^2+\omega^2\left[\left(k_1/\alpha+k_2-m_1\omega^2\right)\left(b_2+b_3\right)+\left(k_2+k_3-m_2\omega^2\right)\left(b_1+b_2\right)-2k_2b_2\right]^2}}$$

b_1,b_2 ,b_3:damping parameter, k_1,k_2 ,k_3 :spring constant, m_1, m_2,:effective mass, ω :angular frequency, X: displacement, α :$X_{measured}/X_1$, C :apparatus constant, U_{out}/U_{in} :Resonance amplitude

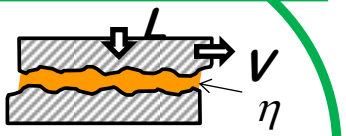
b_2 and viscosity(η_{eff}) for sample liquid can be determined

＊) M. Mizukami and K. Kurihara, *Rev. Sci. Instrum.*, **79**, 113705 (2008).

Practical lubricants

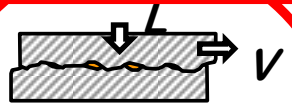
「low viscosity lubricants」: one of major targets

High energy efficiency



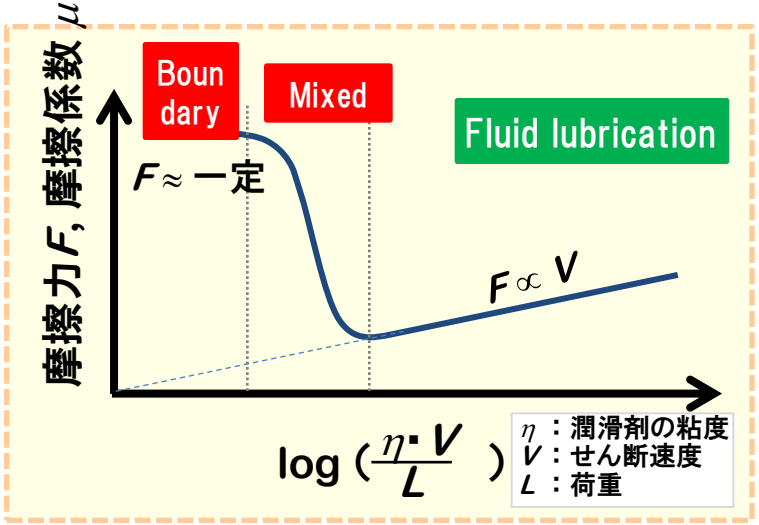
Low fluid resistance ⇒decreased μ

Poblem: yakitsuki/seizure



at boundary lubrication

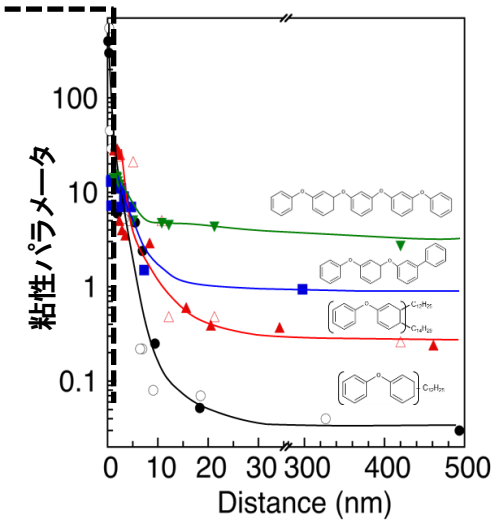
Increased μ & wear



Phenyl-ether lubricants

Nano-Space

MADE
⌄
DADE
⌄
m-4P2E
⌄
m-5P4E



Bulk viscosity

m-5P4E
⌄
m-4P2E
⌄
DADE
⌄
MADE

Effective viscosity parameter vs separation distance.

A mechanism for “Yakitsuki (Seizure)”

For decreasing the viscosity

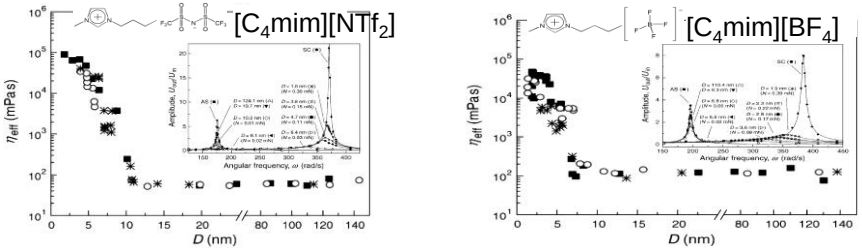
➡ Effective additive
Lubricant molecular design

J.Watanabe, M.Mizukami, K.Kurihara, *Tribol. Lett.* 56 (2014) pp. 501-508

Elucidation of lubrication at the molecular level

Ionic liquids between silica

K.Ueno, M.Kasuya, M.Watanabe, M.Mizukami, K.Kurihara, *Phys. Chem. Chem. Phys.* **12**, 4066-4071 (2010).



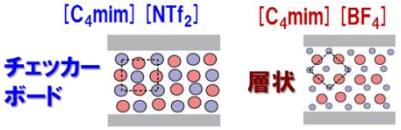
η_{eff} of the ionic liquids confined between silica surfaces at various D.

・effective viscosity

nano: [C_4mim] [NTf_2] > [C_4mim] [BF_4], bulk: [C_4mim] [NTf_2] < [C_4mim] [BF_4]

→ explain smaller friction by C_4mim] [BF_4]

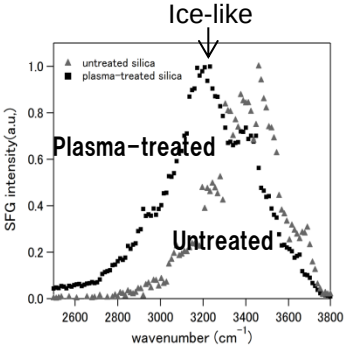
Molecular dynamics simulation



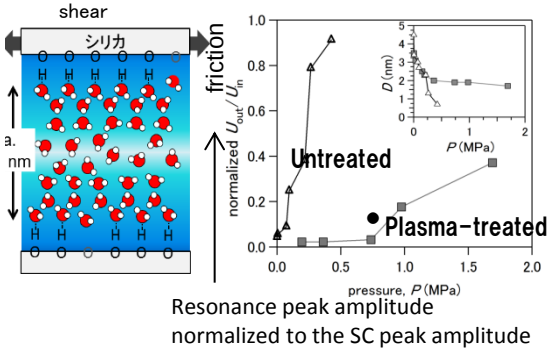
F. Federici Canova, H.Matsubara, M.Mizukami, K.Kurihara, A.L.Shluger, *Phys. Chem. Chem. Phys.* **16**, 8247 (2014)

Friction: Large, Small

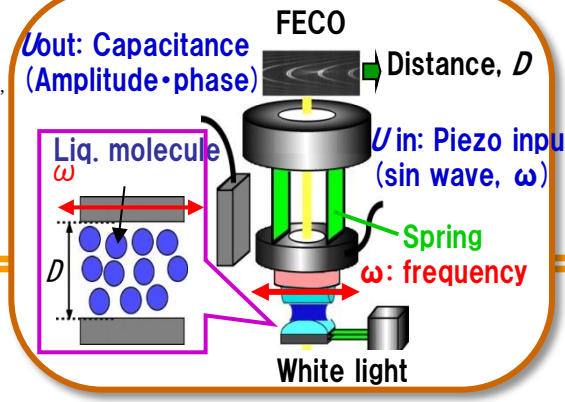
Water lubrication and SiOH density



Vibrational SFG spectra of water on silica prism surfaces. (SSP polarization)



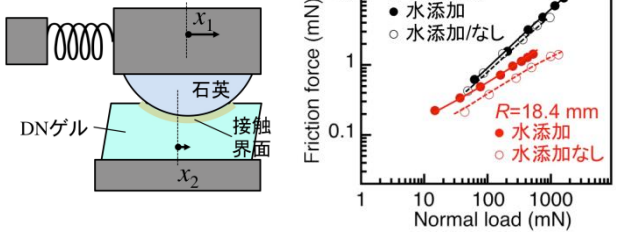
Resonance peak amplitude normalized to the SC peak amplitude under various pressure on thin films of water (P = L/contact *area*)



Plasma-treated silica (higher Si-OH density) showed higher lubricity and stability against pressure which might due to ice-like structure of water.

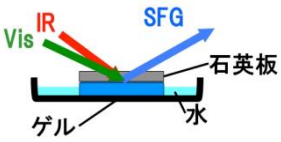
M. Kasuya, M. Hino, H. Yamada, M. Mizukami, H. Mori, S. Kajita, T. Ohmori, A. Suzuki, Kazue Kurihara, *J. Phys. Chem. C* **117**, 13540-13546 (2013).

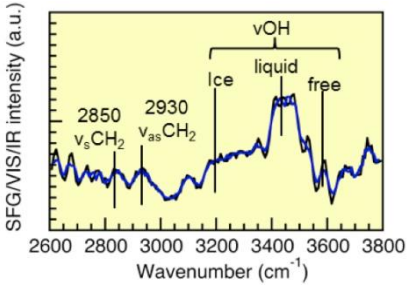
Friction of gel



Friction between gel-silica interface by RSM

We could quantitatively evaluate varioud contributions (deformation, charge etc.) to friction.





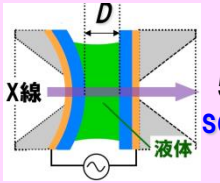
SFG spectrum of water-gel interface

H.Ren, M. Mizukami, T. Tanabe, H. Furukawa, K. Kurihara, Soft Matter, **11**, 6192(2015).

Characterization of Interfaces by SFA and RSM

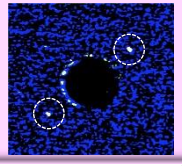
Characterization of confined liquids

X-ray diffraction from thin liquid films

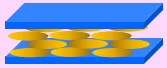


Thickness:
500 nm (previous) → several nm (this worl)

・structural relaxation



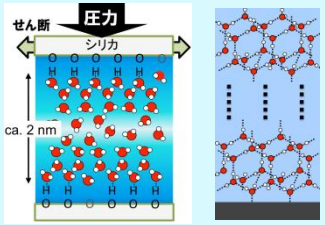
・Confined effect on *E*-induced orientation



Interfacial water

At various phys. dhem. conditions

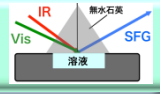
Silanol density　　Water cont.



Tribology

Lubrication in the presence of additives

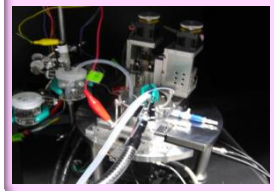
SFG spectroscopy

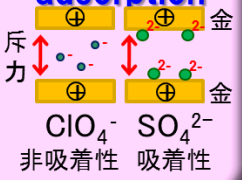


Novel SFA's

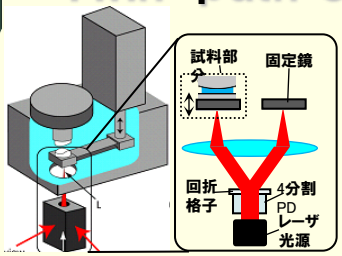
Electrochemical SFA

Evaluation of electrodes: Effective potential and ion adsorption

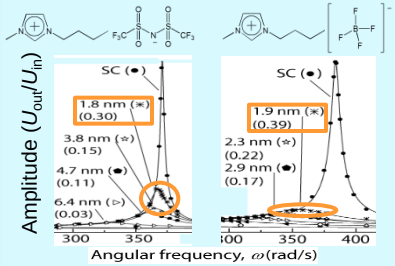




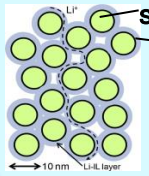
Twin-path SFA



RSM and macro-properties

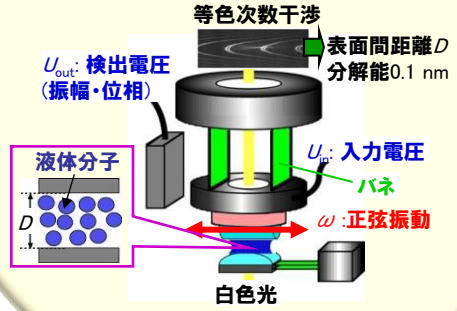


Dispersion rheology



Li-ion battery

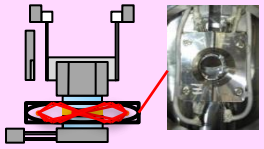
RSM



Temp. control

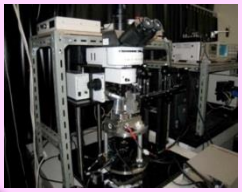
IR heater

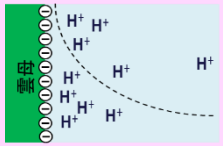
Room tenp. ～100℃, ±0.15℃



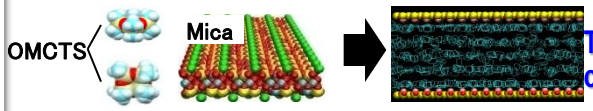
Fluorescence SFA

PH and viscosity of confined liquids





Large-scale simulation with molecular model



To understand confinement effect

Nano-scopic characterization of tribological phenomena can provide new insights in the phenomena, leading to develop new lubricant materials based on more rational design for Green Tribology.


THANK YOU FOR YOUR ATTENTION
April , 2014