

On the Appearance of Molecular Effects in Different Tribological Systems

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1. Backgrounds and Objectives

Machine elements are being downsized in recent years with the advance of micromachining technology.

The separation between surfaces that move relative to each other becomes smaller and smaller.

The surface forces, *e.g.*, van der Waals force, meniscus force or structural force, have relatively large effects in the microelectromechanical systems (MEMS), powder systems, colloidal systems and so on.

Knowledge concerning the characteristics of surface forces is considered to be indispensable as the basis of key technologies in the near future.

In this study...

A surface force apparatus (SFA) - type setup which can accurately measure the surface forces between solid surfaces in an atmosphere-controlled chamber has been developed. Using this apparatus,

(1) the surface forces including the nanomeniscus forces in the undersaturated vapor of several kinds of liquids and

(2) the hydrodynamic film thickness of liquid lubricant under shear

were measured. The appearance of molecular effects in these tribological systems is discussed.

2. Experimental Setup

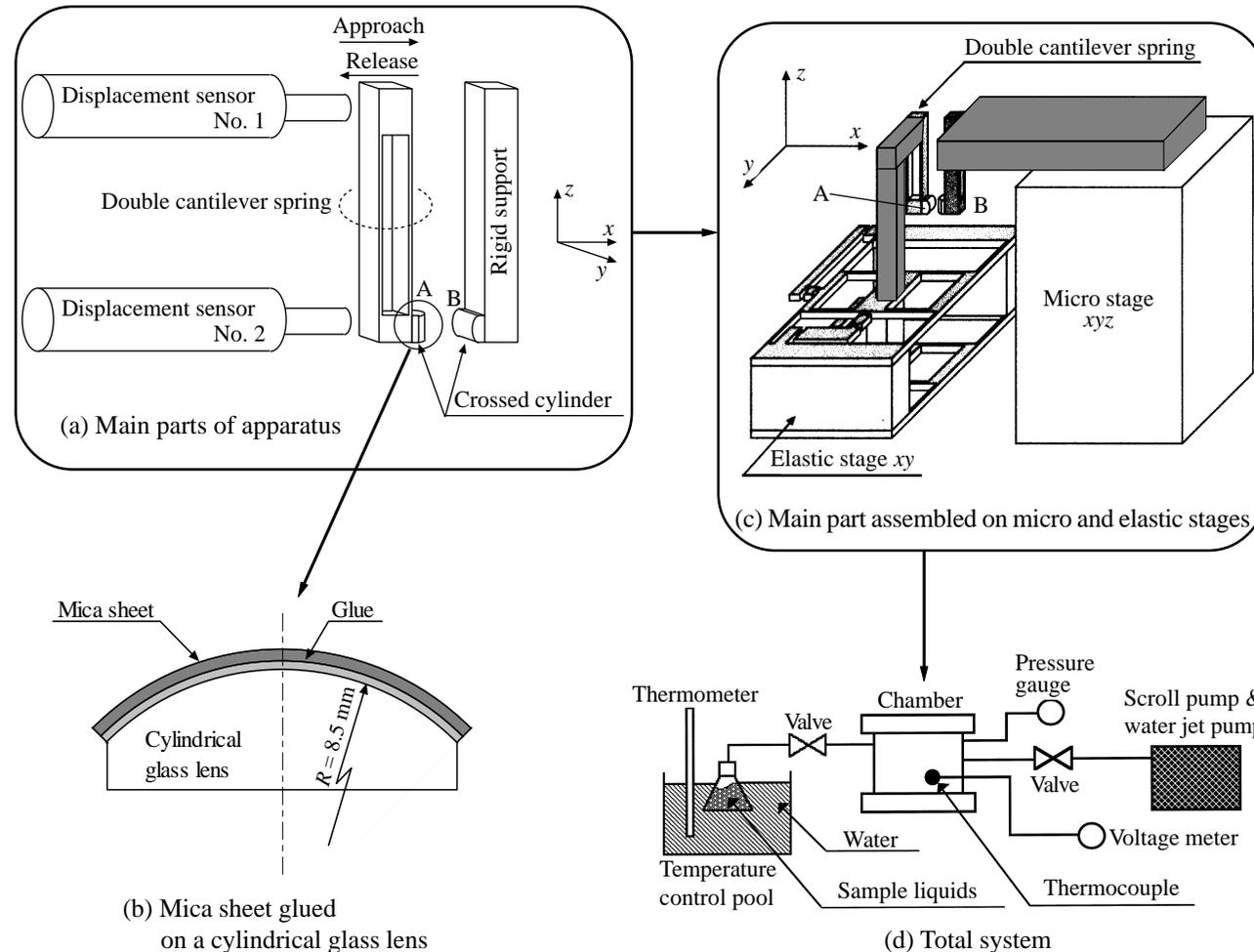


Fig. 1 SFA-type apparatus

Figure 1 (a)

Crossed cylinder configuration

$$k_{\text{double cantilever spring}} = 1270 \text{ N/m}$$

Resolution of the displacement sensors: $< 1 \text{ nm}$

Resolution of the normal force detection: about 1 mN .

Figure 1 (b)

Enlargement of a cylinder.

Cleaved mica: glued by epoxy resin
Radius of curvature of cylindrical glass lens, $R = 8.5 \text{ mm}$.

Figure 1 (c)

Cylinder A is on an elastic stage driven by a piezoelectric actuator. Cylinder B is on a microstage for coarse movement.

Figure 1 (d)

Located in a vacuum chamber. The vapor pressure of a liquid can be controlled.

The apparatus is located on a vibration isolation system in a clean booth.

3. Specimens

Table 1 Properties of mica

<p><u>Surface geometry</u></p> <p>Surface roughness : $R_a = 0.048$ nm Average radius of curvature of peak of surface roughness : $\beta = 18$ μm Standard deviation of peak height : $\sigma_p = 0.048$ nm</p>
<p><u>Mechanical properties</u></p> <p>Young's modulus : $E = 34.5$ GPa Poisson's ratio : $\nu = 0.205$ Vicker's hardness : $HV = 1.43$ GPa</p>
<p>Surface energy : $\gamma_s = 47.7 \pm 0.9$ mJ/m²</p>
<p><u>Contact state parameters</u></p> <p>Plasticity index : $\Psi = 0.0206$ Adhesion parameter : $\theta_{ad} = 0.0118$ Elasticity parameter : $\mu = 101$</p>

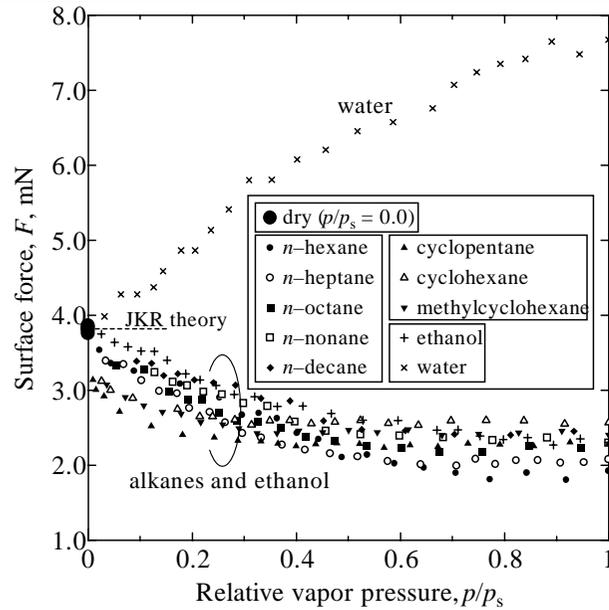
Table 2 Properties of liquids used in nanomeniscus force measurements

Liquid	Chemical formula	Molecular weight M , kg/mol	Density ρ , kg/m ³	Molar volume V , m ³ /mol	Surface energy γ_s , mJ/m ²	Effective molecular diameter σ_e , nm
<i>n</i> -hexane	C ₆ H ₁₄	8.62×10^{-2}	659	1.31×10^{-4}	17.5	0.61
<i>n</i> -heptane	C ₇ H ₁₆	1.00×10^{-1}	684	1.47×10^{-4}	19.2	0.65
<i>n</i> -octane	C ₈ H ₁₈	1.14×10^{-1}	703	1.63×10^{-4}	20.7	0.70
<i>n</i> -nonane	C ₉ H ₂₀	1.28×10^{-1}	722	1.78×10^{-4}	22.0	0.74
<i>n</i> -decane	C ₁₀ H ₂₂	1.42×10^{-1}	730	1.95×10^{-4}	22.9	0.78
cyclopentane	C ₅ H ₁₀	7.01×10^{-2}	745	9.41×10^{-5}	21.3	0.50
cyclohexane	C ₆ H ₁₂	8.42×10^{-2}	774	1.09×10^{-4}	24.2	0.60
methylcyclohexane	C ₆ H ₁₁ CH ₃	9.82×10^{-2}	769	1.28×10^{-4}	22.8	0.74
ethanol	CH ₃ CH ₂ OH	4.61×10^{-2}	794	5.80×10^{-5}	21.6	0.45
water	H ₂ O	1.80×10^{-2}	1000	1.80×10^{-5}	71.1	0.28

Table 3 Properties of liquids used in ultrathin liquid Film thickness measurements

Liquid	OMCTS	Cyclohexane	<i>n</i> -hexadecane
chemical formula	[(CH ₃) ₂ SiO] ₄ ^d	(CH ₂) ₆ ^e	CH ₃ (CH ₂) ₁₄ CH ₃ ^f
diameter σ	1 nm ^d	0.6 nm ^e	0.4 nm ^f
refractive index n	1.40 ^d	1.43 ^e	1.42 ^f
absorption frequency ω	1.60×10^{16} rad/s ^d	1.82×10^{16} rad/s ^f	1.82×10^{16} rad/s ^f
dielectric constant ϵ_0	2.30 ^d	2.02 ^e	2.05 ^f
viscosity η_0	2.35 mPa · s ^d	0.980 mPa · s ^e	3.35 mPa · s ^f

4. Results of Nanomeniscus Force Measurements 1: Surface Forces



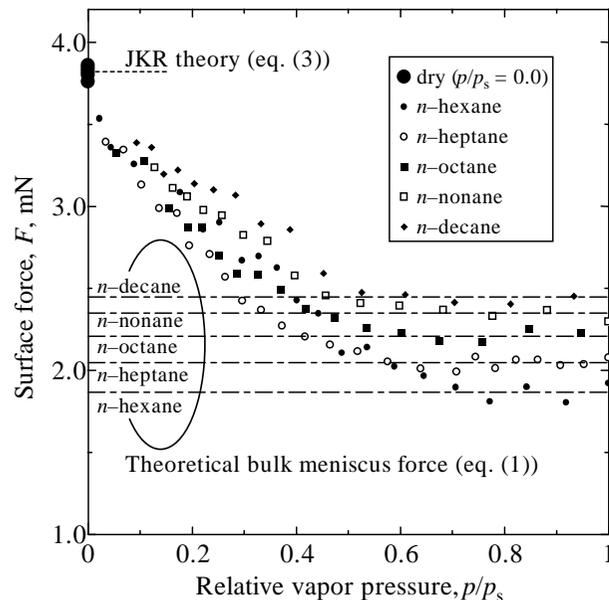
(a) All liquids

Surface forces as a function of the relative vapor pressure (p/p_s).

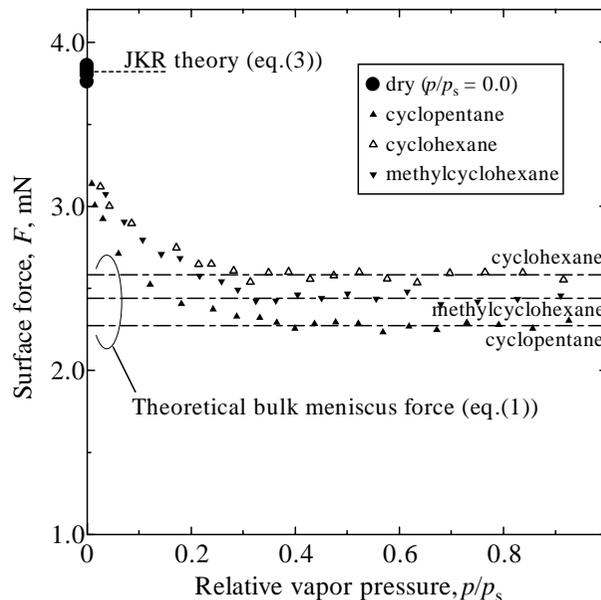
(a) Experimental data of all liquids; Theoretical adhesion force under dry condition shown by dotted line is obtained from the **JKR Theory**, *i.e.*, $F = 3\pi R\gamma_s$.

In (b) - (c), the **theoretical bulk meniscus forces predicted by the Laplace pressure** are also shown; Note that the experimental data are the same as (a).

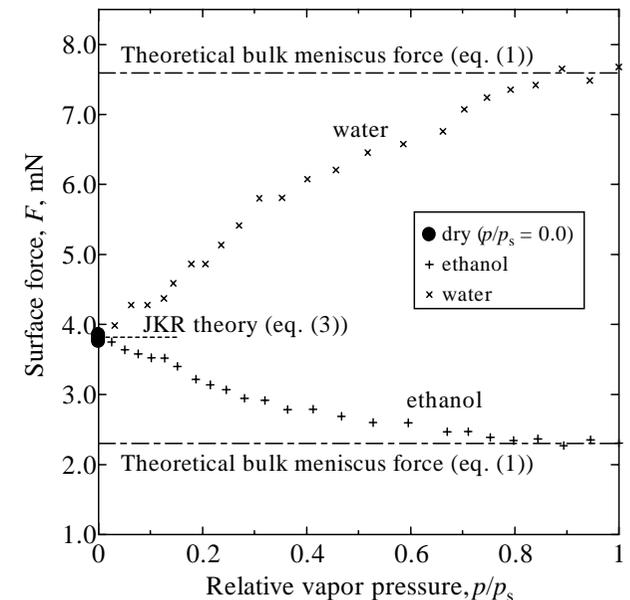
The surface forces **gradually change** from those under dry conditions to a constant asymptote with increasing relative vapor pressure.



(b) Linear alkanes



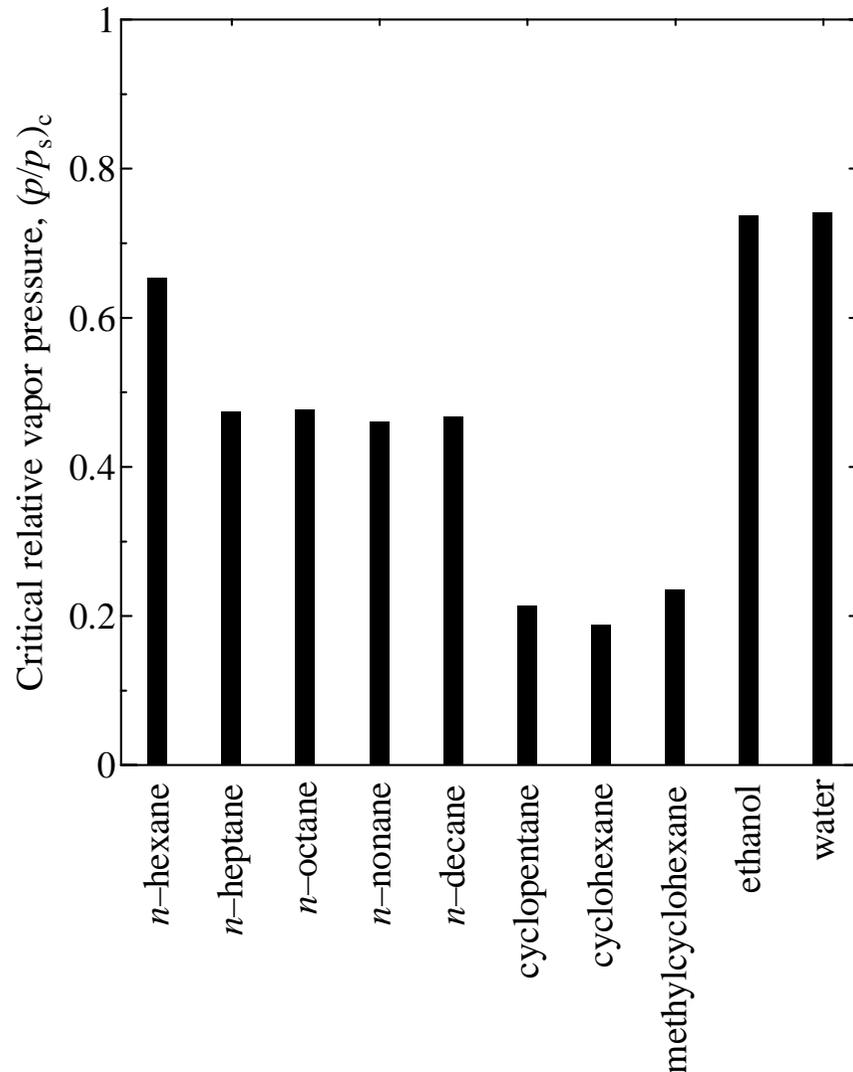
(c) Cycloalkanes



(d) Polar liquids

5. Results of Nanomeniscus Force Measurements 2:

Critical relative vapor pressure, $(p/p_s)_c$



The critical relative vapor pressure means that the nanomeniscus shows macroscopic characteristics when the relative vapor pressure is greater than the critical relative vapor pressure, *i.e.*, $p/p_s > (p/p_s)_c$.

It is found that

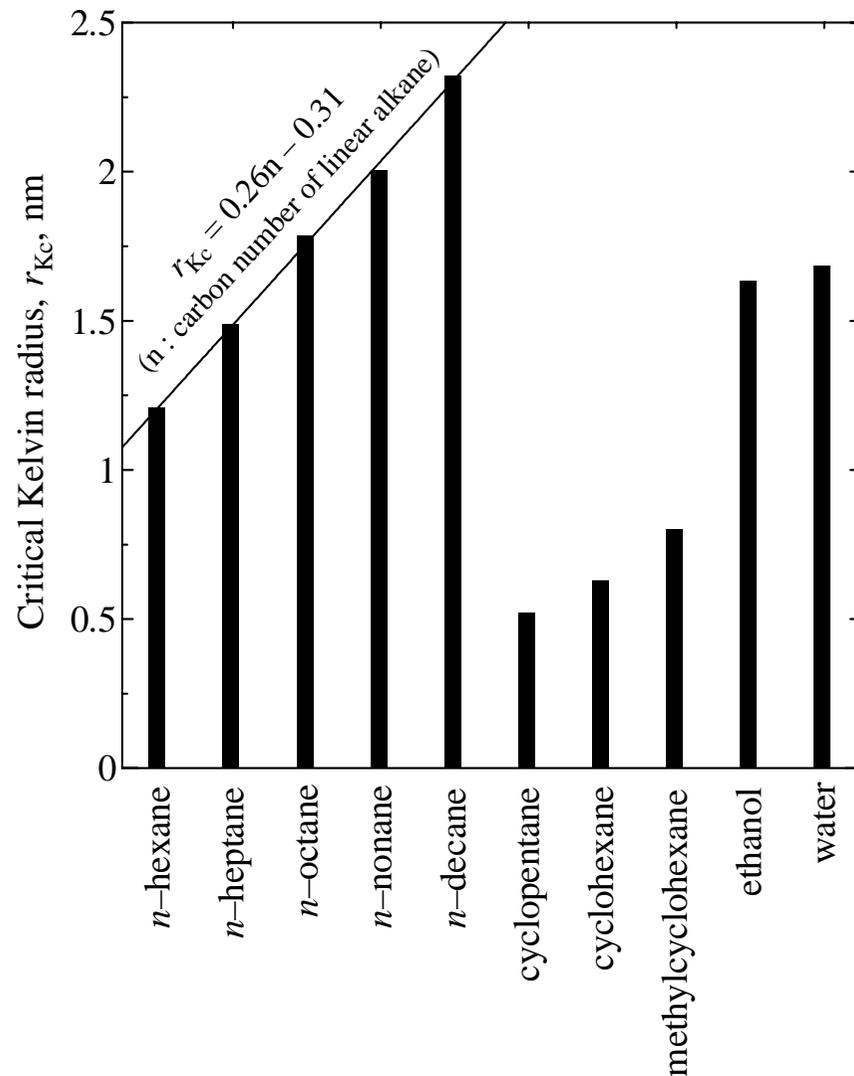
$$(p/p_s)_c^{\text{cycloalkanes}} < (p/p_s)_c^{\text{linear alkanes}} < (p/p_s)_c^{\text{polar liquids}}$$

The thicknesses of the adsorbed film of the cyclohexane and water at the critical relative vapor pressure have been estimated to be about 0.2 and 0.4 nm, respectively, in a previous study*. This means a free mica surface will be imperfectly covered by cyclohexane molecules and will be covered by one or two molecular layers of water at the critical relative vapor pressure, $(p/p_s)_c$.

* Beaglehole, D. and Christenson, H. K., J. Phys. Chem., 1992, **96**, 3395-3403.

6. Results of Nanomeniscus Force Measurements 3:

Critical Kelvin radius, r_{Kc}



The radius of curvature of the nanomeniscus **at which the nanomeniscus begins to show macroscopic characteristics** can be estimated from the **Kelvin equation**

$$r_K = -\gamma_L V / (R_G T \ln(p/p_s))$$

by substituting the critical relative vapor pressure, $(p/p_s)_c$, for the relative vapor pressure, (p/p_s) . This Kelvin radius is defined as the critical Kelvin radius, r_{Kc} .

The critical Kelvin radii of **linear alkanes** vary linearly with respect to the carbon number, n , of a molecule:

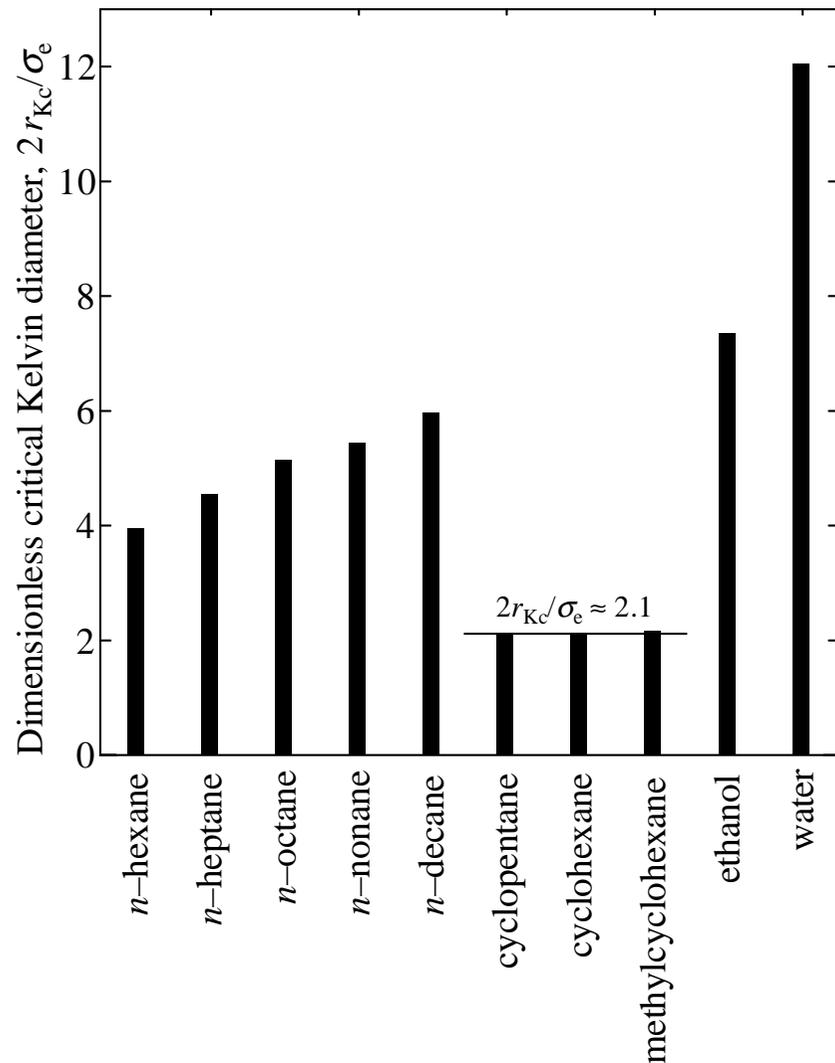
$$r_{Kc} = 0.26n - 0.31,$$

in which the r_{Kc} is measured in nanometers.

The critical Kelvin radius is very small for the cycloalkanes, and close to the effective molecular diameter, σ_e (see Table 2). Furthermore, r_{Kc} for water and ethanol is large compared to their σ_e .

7. Results of Nanomeniscus Force Measurements 4:

Dimensionless Critical Kelvin Diameter, $2r_{Kc}/\sigma_e$



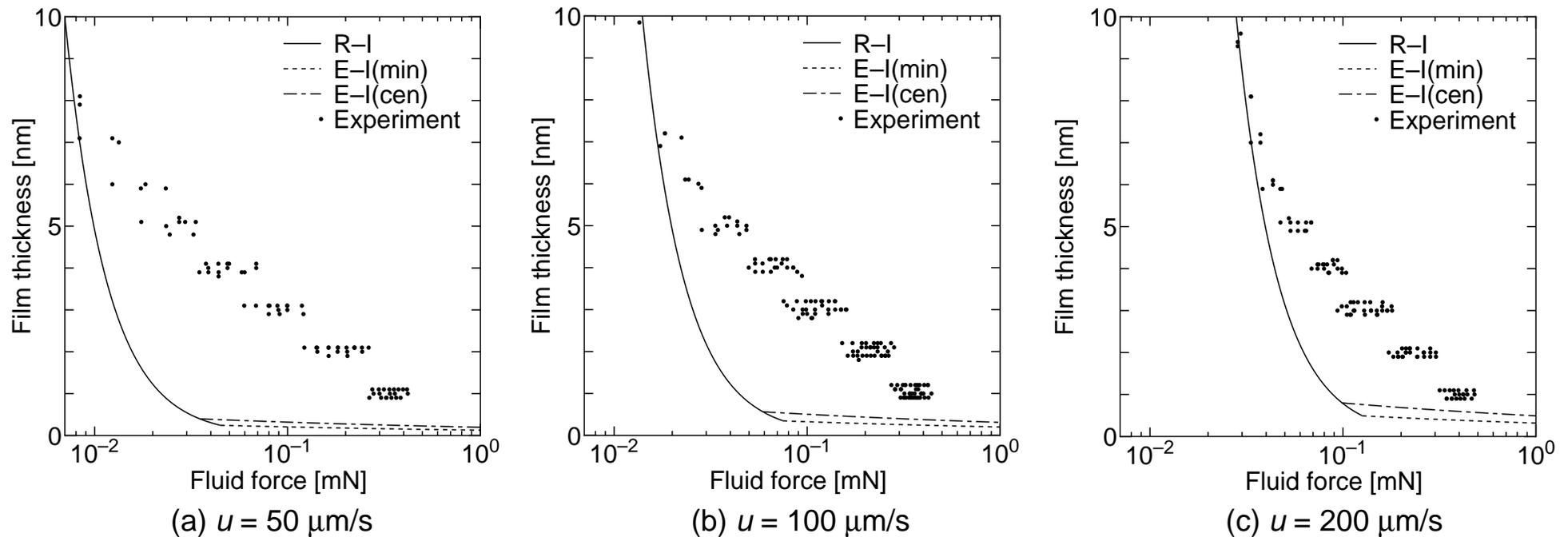
A comparison of the critical Kelvin diameter, $2r_{Kc}$, and the effective molecular diameter, σ_e , *i.e.*, the dimensionless critical Kelvin diameter, $2r_{Kc}/\sigma_e$, is shown in this figure.

The dimensionless critical Kelvin diameter increases according to the increase in the carbon number for the linear alkanes.

For the cycloalkanes, the dimensionless critical Kelvin diameter is found to be almost constant: $2r_{Kc}/\sigma_e \approx 2.1$.

This value suggests that the nanomeniscus shows macroscopic characteristics when a single molecular layer of a cycloalkane is arranged on each mica surface.

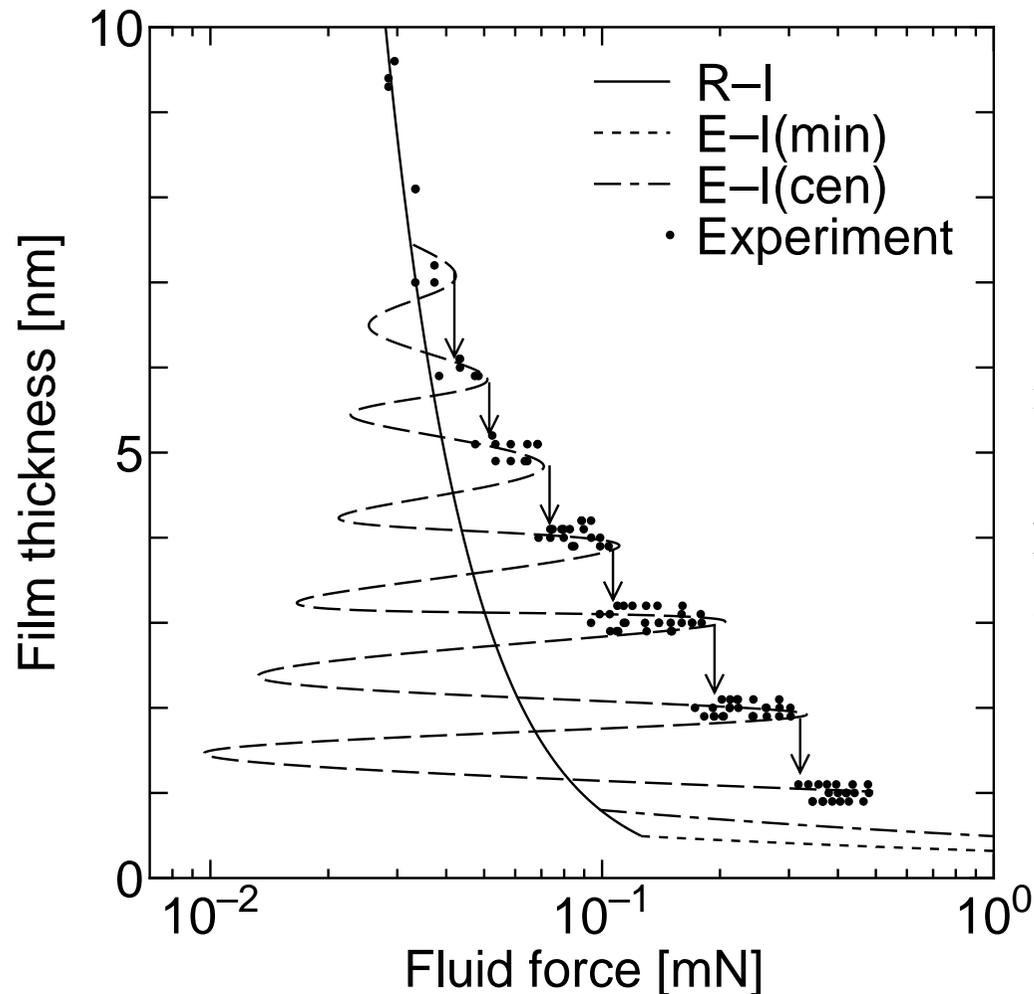
8. Results of Ultrathin Liquid Film Thickness Measurements 1: OMCTS



Shearing the cylindrical surfaces, the **lubrication film thicknesses** were measured. The fluid force shown in the horizontal axis means the load between cylindrical surfaces. The black dots show experimental results. Solid line, dotted line, and dot-dashed line show the theoretical film thickness of rigid-iso-viscous, elastic-iso-viscous (minimum), and elastic-iso-viscous (center), respectively, those are obtained by the elastohydrodynamic lubrication theory.

The measured film thickness begins to deviate from the theory at about 7 - 8 nm and discretization of the film thickness due to the structural force is observed.

9. Results of Ultrathin Liquid Film Thickness Measurements 2: Mechanism of the Discretization of the Film Thickness due to the Structural Force



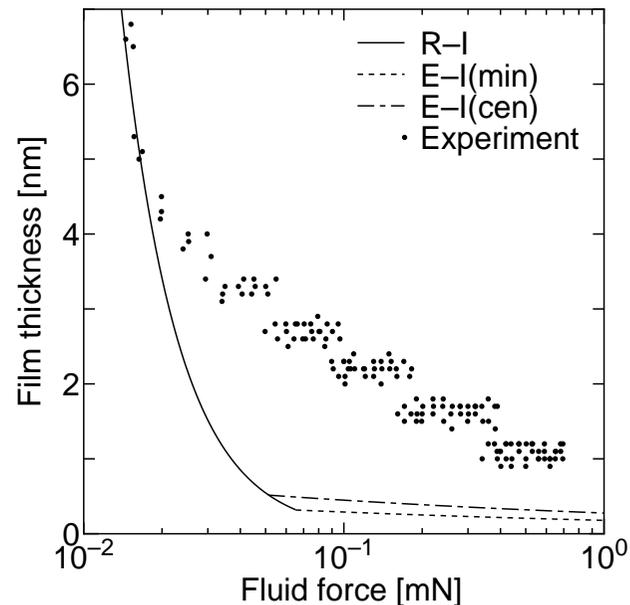
Mechanism of the discretization is illustrated schematically.

The interval of the discretized film thickness is about 1 nm, which corresponds roughly to the molecular diameter of OMCTS.

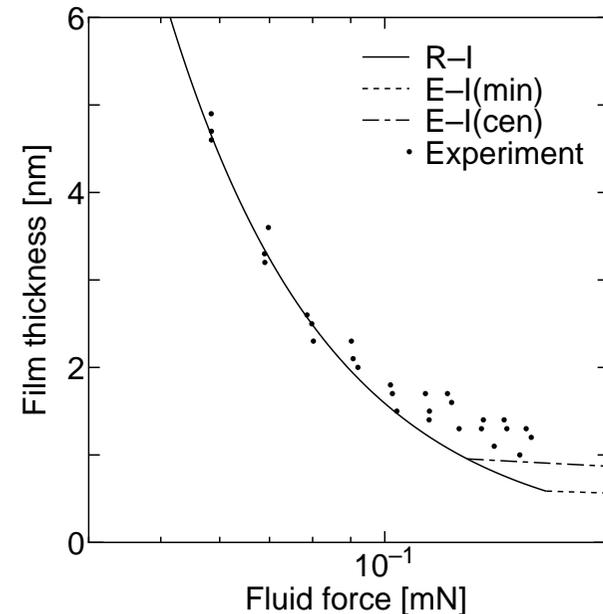
The **stable film thickness** considering both the hydrodynamic and structural forces **can be observed in experiments**.

10. Results of Ultrathin Liquid Film Thickness Measurements 3:

Cyclohexane and *n*-Hexadecane



(a) cyclohexane ($u = 200 \mu\text{m/s}$)



(b) *n*-hexadecane ($u = 200 \mu\text{m/s}$)

(a) The film discretization is again observed. The interval of the film discretization is 0.5 - 0.6 nm, which is roughly the same value as the molecular diameter of cyclohexane obtained by hard-sphere approximation.

The discretization appears at about 5 nm.

(b) The discretization of the film thickness is **not observed in this case**. This may be because long chain molecules of *n*-hexadecane have flexibility and are entangled in each other in the vicinity of a solid surface.

11. Appearance of Molecular Effects in Both Tribological Systems

Table Critical scale nondimensionalized by molecular diameter σ_e of liquid

Experimental system has free surface of liquid (Nanomeniscus force measurement)	Experimental system does not have free surface of liquid, <i>i.e.</i> , liquid is confined between solid walls (Ultrathin liquid film thickness measurement)
spherical molecule 2	spherical molecule 7 - 8
linear molecule 4 - 6	linear molecule < 5
with functional group 8 <	with functional group -

Critical scales nondimensionalized by the molecular diameter σ_e of liquid are shown in the upper table. **The critical scale means that molecular effects begin to appear, in other words, continuum theories cannot be applied when we measure or observe dimensions less than the critical scale in an experimental system.**

Comparing two tribological systems, it is found that there is **an opposite relation between spherical molecule and linear molecule**. The authors consider that this difference can be attributed to whether or not the liquid is perfectly confined between two solid surfaces, *i.e.*, whether or not the experimental system involves a free liquid surface. Consequently, **the effects of discrete molecules are considered different in each experimental system.**

12. Summary

A SFA - type setup, which can accurately measure the surface forces between solid surfaces in an atmosphere-controlled chamber, was presented. The surface forces including the nanomeniscus forces in the undersaturated vapor of several kinds of liquids and the film thickness of liquid lubricant were measured using this apparatus. It is found by comparing the experimental results that the appearance of molecular effects in these tribological systems has different tendency. The authors considered that this difference is due to the free surface of liquid.

References

- [1] H. Matsuoka, T. Kato and S. Fukui, "Nanomeniscus Forces in Undersaturated Vapors: Observable Limit of Macroscopic Characteristics," *Langmuir*, Vol. 18, No. 18, 2002, pp. 6796-6801.
- [2] H. Matsuoka and T. Kato, "Experimental Study of Ultrathin Liquid Lubrication Film Thickness at the Molecular Scale," *IMEchE, Journal of Engineering Tribology*, Vol.211, Part J, 1997, pp. 139-150.
- [3] H. Matsuoka and T. Kato, "An Ultrathin Liquid Film Lubrication Theory - Calculation Method of Solvation Pressure and Its Application to the EHL Problem," *Transactions of the ASME, Journal of Tribology*, Vol.119, No.1, 1997, pp. 217-226.