SURFACE FORCES BETWEEN MICA SURFACES IN UNDERSATURATED VAPOR OF HYDROCARBON LIQUIDS

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An apparatus which can measure surface forces between solid surfaces accurately in an atmosphere controlled chamber is developed. Adhesion forces and nanomeniscus forces between crossed-cylindrical mica surfaces were measured in undersaturated vapor of hydrocarbon liquids. It is found that the adhesion force under dry condition agrees well with the JKR theory and the nanomeniscus forces in relatively high vapor pressure show bulk meniscus force. The surface forces change gradually from dry condition (JKR prediction) to bulk meniscus force according to increases in the relative vapor pressure of sample liquids. It is also found that bulk meniscus of liquids which have cyclic hydrocarbon chain appears at lower relative vapor pressure than linear hydrocarbons.

Keywords: Adhesion Force, Nanomeniscus Force, SFA, Relative Vapor Pressure, Molecular Shape

1. INTRODUCTION

Miniaturization of machine elements, especially of information systems or micromachine systems, has become remarkable with the progress in micromachining technology in recent years. In these micromechanical systems, surface forces such as adhesion force [1], meniscus force [2] or van der Waals force [3, 4], which have been neglected in the conventional and relatively large mechanical systems, become important and have considerable effects on their dynamic characteristics. For example, adhesion force (mainly caused by the van der Waals force) between machine elements or the meniscus force generated by adsorbed water from the air often disturbs the functioning of a micromachine. Also, in a hard disk drive system, adhesion between a head slider and a disk surface in the contact start/stop (CSS) is a serious problem.

In this study, a surface force apparatus (SFA) -type setup which can measure surface forces between solid surfaces acculately in an atmosphere controlled chamber is developed. Adhesion forces and nano-meniscus forces between crossedcylinder mica surfaces are measured accurately in undersaturated vapor of several kinds of hydrocarbon liquid by using the apparatus.

2. EXPERIMENTS

2.1 Apparatus

Figure 1 (a) shows main part of a SFA-type apparatus the authors developed. Adhering surfaces (A and B) are in a crossed cylinder configuration which is equivalent to a plane and a sphere configuration. These cylinders are supported by parallel leaf springs. Spring type I is used to measure normal force between

the solid surfaces and type T is for measuring tangential force. In this study, spring type I is used since surface forces which is normal to the surfaces are measured. The spring constant of type I is 1270 N/m. The normal force can be obtained by measuring



(b) mica surface glued on a cylindrical glass lens

Fig. 1 Mica surfaces, leaf springs, displacement sensors

the deflection of the spring type I. The deflection is measured by the displacement sensor No. 1 and 2 which are high resolution noncontact capacitive displacement sensors.

Figure 1 (b) is an enlargement of the cylindrical solid. Cleaved mica is glued on a cylindrical glass lens whose radius of curvature *R* is 8.5 mm. Note that the mica sheet and adhesive shown in Fig. 1 (b) are very thin ($\sim 20\mu$ m).

The main unit shown in Fig. 1 (a) is put on stages, which is shown in Fig. 2. The cylinder A is put on an elastic stage which is driven by a piezoelectric actuator and can realize fine movement in X direction. The cylinder B is put on a microstage for coarse movement.

This unit shown in Fig. 2 is put in a vacuum chamber in which the vapor pressure of a liquid can be controlled and the total system for measuring surface force as a function of relative vapor pressure is shown in Fig. 3. Temperature of a sample liquid is controlled by a temperature controll pool, and vapor of the sample liquid is introduced into the chamber through a valve. The chamber has a pressure gauge and a thermocouple.

The apparatus is put on a vibration isolator and in a clean booth.

2.2 Properties of specimens

In this study, mica and 5 hydrocarbon liquids are used. Properties of mica are shown in Table 1 [5, 6]. Surface roughness of cleaved mica surface is measured by an AFM and it is



Fig. 3 Experimental system

Table 1Properties of mica [5, 6]

Surface Geometry				
Surface roughness : $R_a = 0.048$ nm				
Peak radius of curvature : $\beta = 18 \ \mu m$				
Standard deviation of peak height : $\sigma_p = 0.048$ nm				
Mechanical Properties				
Young's Modulus : E = 34.5 GPa				
Poisson's ratio : $v = 0.205$				
Vicker's hardness : HV = 1.43 GPa				
Surface energy : $\gamma_s = 47.7 \text{ mJ/m}^2$				
Contact State Parameters				
Plasticity index : $\Psi = 0.0206$				
Adhesion parameter : $\theta = 0.0118 - 0.0174$				
Contact theory index : $\mu = 101 - 115$				

found that the cleaved mica has molecularly smooth surface.

Using these properties, i.e., surface geometry, mechanical properties and surface energy, contact state parameters are estimated.

Plasticity index Ψ [7] shows that the contact is elastic or plastic. If the plasticity index is less than 0.6, the contact is elastic, and if larger than 1, the contact is plastic. For mica surface, the value of the plasticity index is 0.0206 which indicates the contact is elastic.

Adhesion parameter θ [8] represents effect of surface roughness on adhesion between solid surfaces. The contact is adhesive when the adhesion parameter is less than 10, but the adhesion is hardly observed when it is larger than 10. For mica surfaces, 0.0118 - 0.0174 is obtained which means effect of surface roughness is very small and the contact is adhesive.

Contact theory index μ [9] tells what contact theory can be applied. For mica surface, the index is 101 - 115, which indicates JKR theory [10] is applicable.

Properties of hydrocarbon liquids are shown in Table 2 [11]. Three linear alkanes and two cyclic alkanes are selected.

2.3 Experimental method and conditions

After preparing cylindrical mica surfaces shown in Fig. 1 (b) and attaching them to the parallel leaf springs shown in Fig. 1 (a), the chamber in Fig. 3 is vacuumized to less than 0.1 Torr. The mica surfaces are baked at 200 °C and 5 minutes in order to remove adsorbed film, mainly water film since the mica surface is hydrophilic surface. Turning the heater off and cooling the surfaces down to room temperature. Vapor of a sample liquid is introduced and holding three minutes. Then, the mica surfaces are made contact with each other at the speed of 1 μ m/s using the microstage shown in Fig. 2 until the contact load (initial load) becomes 0.5 mN and keeping the initial load for 3 minutes. Load-Time relation is shown in Fig. 4 schematically. Then unloading and separating the surfaces from each other at the speed of 0.44 μ m/s. Abrupt separation is observed and surface

Liquid	Linear Alkanes			Cyclic Alkanes	
	<i>n</i> -hexane	<i>n</i> -octane	<i>n</i> -decane	cyclopentane	cyclohexane
Chemical formula	$C_{6}H_{14}$	C ₈ H ₁₈	$C_{10}H_{22}$	C5H10	C ₆ H ₁₂
Molecular weight, <i>M</i> , kg/mol	8.62×10 ⁻²	1.14×10 ⁻¹	1.42×10 ⁻¹	7.01×10 ⁻²	8.42×10 ⁻²
Density, ρ , kg/m ³	659	703	730	745	774
Molar volume, V, m ³ /mol	1.31×10 ⁻⁴	1.63×10 ⁻⁴	1.95×10 ⁻⁴	9.41×10-5	1.09×10 ⁻⁴
Surface energy, γ_L , mJ/m ²	17.5	20.7	22.9	21.3	24.2
Effective molecular diameter, σ_{e} , nm	0.61	0.70	0.78	0.49	0.60

Table 2Properties of liquids [11]



Fig. 4 Load-Time relation in experiments

force can be obtained.

The effects of initial load, holding time of the initial load and unloading speed on the adhesion force were investigated in the past study [12]. It was confirmed that the initial load, the holding time of the initial load and the unloading speed hardly affects the adhesion force in the range of 0.25 - 2 mN, more than 50 sec, $0.22 - 1.32 \mu$ m/s, respectively. Therefore, the conditions which are adopted in this study are considered to be proper to measure the adhesion force as a function of relative vapor pressure.

3. RESULTS AND DISCUSSIONS

Figure 5 shows relation between adhesion force F_{ad} and relative vapor pressure p/p_s for linear alkanes, where p_s means saturated vapor pressure. Under dry condition, i.e., at the point $p/p_s = 0$ (\triangleleft), the adhesion force agrees well with one predicted by JKR theory (dotted line) [10]. It is found that the adhesion forces decrease gradually and then become constant according to increase in the relative vapor pressure. The constant value of the adhesion force in the region of high relative vapor pressure corresponds with the bulk meniscus force generated by the Laplace pressure at the surface energy of each sample liquid, which means that the meniscus shows macroscopic bulk property. It is also found that the SFA-type apparatus the authors developed can measure the surface forces in detail as a function of the relative vapor pressure.



Fig. 5 Relation between adhesion force F_{ad} and relative vapor pressure p/p_{s} for linear alkanes



Fig. 6 Relation between adhesion force F_{ad} and relative vapor pressure p/p_s for cyclic alkanes

Relation between adhesion force F_{ad} and relative vapor pressure p/p_s for cyclic alkanes is shown in Fig. 6. Gradual change from dry adhesion to bulk meniscus is again observed. However, the adhesion force of cyclic alkane approaches much faster to bulk meniscus force than that of linear alkanes. Linear alkanes require the relative vapor pressure of 50 - 70 % to show their bulk property, which is seen from Fig. 5, but bulk meniscus of cyclic alkanes appears at about 30 %, which corresponds to the past study in case of *n*-hexane and cyclohexane [13]. It is considered that in nanomeniscus generated at the solid interface, molecules of a linear alkane are entangled and more difficult to flow like bulk liquid than those of a cyclic alkane.

In Figs. 5 and 6, net values of adhesion force are shown. In order to compare adhesion forces with each other in the same scale, nondimensional adhesion force F_{ad}^{*} is introduced as the following expression:

$$F_{ad}^* = \frac{F_{ad} - 4\pi R \gamma_L}{3\pi R \gamma_s - 4\pi R \gamma_L} + 1 \tag{1}$$

where F_{ad} is measured adhesion force, *R* radius of curvature of the cylindrical surface (8.5 mm), γ_L surface energy of a sample liquid, γ_s surface energy of a solid (47.7 mJ/m² for mica). Note that under dry condition, i.e., when F_{ad} agrees with JKR theory $(3\pi R\gamma_s)$, the value of F_{ad}^{**} is 2, on the other hand, when F_{ad} agrees with bulk meniscus force $(3\pi R\gamma_s)$, F_{ad}^{**} becomes 1.

Furthermore, in order to estimate radius of curvature of nanomeniscus assuming bulk liquid at any relative vapor pressure, the Kelvin radius r_{κ} [11] is introduced:

$$r_{K} = -\frac{\gamma_{L}V}{R_{G}T\ln(p/p_{s})}$$
(2)

where V is molar volume of a liquid, R_{g} the gas constant, T temperature in Kelvin. The Kelvin radius means radius of curvature of meniscus at corresponding relative vapor pressure. The Kelvin radius is nondimensionalized by effective molecular diameter σ_{e} shown in Table 2, i.e., r_{k}/σ_{e} .

Figure 7 shows relation between the nondimensional adhesion force F_{ad}^* and the nondimensional Kelvin radius r_k/σ_e . All adhesion forces are in the range from 1 to 2. Since the Kelvin radius has its meanings at $F_{ad}^* = 1$, it is interesting to investigate at which point, i.e., at what value of the Kelvin radius, bulk property of nanomeniscus appears. The authors decided a criterion of transition to bulk property at $F_{ad}^* = 1.05$ and call the Kelvin radius at the critical point of the transition critical Kelvin radius r_{kc} .

The nondimensionalized critical Kelvin radii r_{kc}/σ_e of each sample liquid are shown in Fig. 8. In case of linear alkanes, longer hydrocarbon chain requires larger Kelvin radius, i.e., larger nanomeniscus radius to show bulk meniscus property, which suggests that entanglement of molecules affects the nanomeniscus force as mentioned above. On the other hand, cyclic alkanes show bulk property at relatively small meniscus radius and the nondimensionalized critical Kelvin radius scarcely changes.

The experimental data of critical Kelvin radii are shown in Table 3. It is found that bulk property of nanomeniscus appears at very small radius of curvature. Especially in case of cyclic



Fig. 7 Nondimensional adhesion force and nondimensional Kelvin radius



Fig. 8 Nondimensionalized critical Kelvin radius r_{Kc}/σ_e of each sample liquid. Showing transition from molecular adsorbed film to bulk nanomeniscus.

Table 3 The critical Kelvin radius $r_{\kappa c}$ in dimensional form. Cyclic alkane shows bulk property at very small nanomeniscus radius.

Liquid	$r_{_{Kc}}/\sigma_{_{e}}$	σ_{e} , nm (see Table 2)	$r_{_{Kc}}$, nm
<i>n</i> -hexane	2.02	0.61	1.23
<i>n</i> -octane	2.82	0.70	1.97
<i>n</i> -decane	3.29	0.78	2.57
cyclopentane	1.21	0.49	0.59
cyclohexane	1.24	0.60	0.74

alkanes, it appears in sub-nanometer meniscus. In case of cyclohexane, it is reported that bulk meniscus force appears about at the same radius of curvature as molecular diameter [11]. The experimental result of this study reconfirms the past result with respect to cyclohexane.

SUMMARY

An apparatus which can measure surface forces between solid surfaces accurately in an atomosphere controlled chamber is developed. Using the apparatus, adhesion forces and nanomeniscus forces between crossed-cylinder mica surfaces are measured in undersaturated vapor of hydrocarbon liquids. The SFA-type apparatus the authors developed could measure the surface forces in detail as a function of the relative vapor pressure and the followings are found.

- (i) Adhesion force of mica surfaces under dry condition can be predicted by JKR theory.
- (ii) The adhesion forces change gradually with respect to relative vapor pressure of hydrocarbon liquids.
- (iii) Bulk property of nanomeniscus of cyclic alkanes appears at lower relative vapor pressure than linear alkanes.

Nondimensional adhesion force and nondimensional Kelvin radius are introduced in order to analyze the experimental results and critical Kelvin radius is defined to investigate the transition to bulk property. The followings are found.

- (iv) In case of linear alkanes, longer hydrocarbon chain requires larger nondimensionalized critical Kelvin radius to show bulk meniscus property.
- (v) In case of cyclic alkanes, the nondimensionalized critical Kelvin radius scarcely change.
- (vi) Bulk property of nanomeniscus appears at very small (nanometer scale) radius of curvature, especially in case of cyclic alkanes, it appears in sub-nanometer meniscus.

It is considered that entanglement of molecules of linear alknaes affects the meniscus force.

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