Nanomeniscus Forces in Undersaturated Vapors: Observable Limit of Macroscopic Characteristics

Hiroshige Matsuoka^{*} and Shigehisa Fukui

Department of Applied Mathematics and Physics, Faculty of Engineering, Tottori University, 4-101 Minami, Koyama, Tottori 680-8552, Japan

Takahisa Kato

Institute of Mechanical Systems Engineering, Tsukuba East Center, National Institute of Advanced Industrial Science and Technology (AIST), 1-2-1 Namiki, Tsukuba, Ibaraki 305-8564, Japan

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An apparatus which can accurately measure surface forces between solid surfaces in an atmospherecontrolled chamber has been developed. The surface forces between crossed-cylindrical mica surfaces were measured in undersaturated vapors of various liquids (hydrocarbons, alcohols, and water) using this apparatus. The surface forces changed gradually with an increase in the relative vapor pressure of liquid from those under dry conditions to macroscopic meniscus forces. To investigate the formation of the meniscus bridge between solid surfaces, the authors introduce the critical relative vapor pressure, $(p/p_s)_c$, at which the surface adhesive force approaches the macroscopic meniscus force. The Kelvin radius at this critical relative vapor pressure was on the nanometer level and was found to be dependent on the structure, molecular weight, and electrostatic nature of the molecules.

Introduction

The nanomeniscus bridge generated between solid surfaces or particles due to condensation and adsorption of liquid vapors from an atmosphere is one of the most fundamental and interesting phenomena in many engineering and scientific fields.^{1,2} Nanomeniscus causes an attractive (rarely repulsive) force between solid surfaces which is often called the meniscus force or adhesion force^{3–6} that can change the statics and dynamics of an engineering system. For example, the behavior of MEMS (microelectromechanical system) elements is affected significantly by the nanomeniscus force, which has been neglected in relatively large conventional mechanical systems; in particular, the nanomeniscus force was found to have important effects on the dynamic behavior of a head-slider/ suspension assembly of hard disk systems.^{7–9}

We examine the effect of the relative vapor pressure of volatile liquids on the nanomeniscus force between two macroscopic solid surfaces. In previous studies of this effect, McFarlane and Tabor¹⁰ confirmed that the adhesion force between a glass sphere and a glass plane in a

* To whom correspondence should be addressed. Tel & Fax: +81-857-31-5759. E-mail: hiro@damp.tottori-u.ac.jp.

Fisher, L. R.; Israelachvili, J. N. *Colloids Surf.* **1981**, *3*, 303–319.
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saturated vapor of several kinds of liquids was given by

$$F = 4\pi R \gamma_{\rm L} \cos \theta \tag{1}$$

where *F* denotes the adhesion (or meniscus) force, *R* is the radius of curvature of the sphere, γ_L is the surface energy of a liquid, and θ is the contact angle of the liquid to solid, which is derived from the Laplace pressure.⁵ The nanomeniscus can be considered to have macroscopic characteristics when the measured force corresponds to the value given by eq 1. Fisher and Israelachvili¹ showed that the adhesion force is given by eq 1 when the relative vapor pressure is greater than 0.1-0.2 which approximately corresponds to the meniscus radius, estimated using the Kelvin equation (eq 2), equalling the molecular diameter of the liquid,

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

where $r_{\rm K}$ is the Kelvin radius which is the radius of curvature of the meniscus, *V* is the molar volume of the liquid, $R_{\rm G}$ is the gas constant, *T* is the absolute temperature, *p* is the vapor pressure of the liquid, and $p_{\rm s}$ is the saturated vapor pressure (i.e., $p/p_{\rm s}$ denotes the relative vapor pressure). The geometry of a meniscus between solid surfaces and a more detailed explanation of eq 2 are found in ref 11. Note that the data given in ref 1 have later been reexamined by Christenson¹² using a double cantilever spring and a nontilting spring. In these previous studies,^{1,12} a much higher relative vapor pressure of water compared with that of other, nonpolar and simple liquids was required for the macroscopic meniscus force given by eq 1 to develop. The Kelvin eq 2 was verified experimentally

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Figure 1. Schematic illustration of experimental apparatus.

down to a meniscus radius of about 4 nm, 13 and the curvature dependence of the surface energy 14 has also been investigated. 13

In this study, a surface force apparatus (SFA) type setup,^{1,5} which can accurately measure the surface forces between solid surfaces in an atmosphere-controlled chamber, has been developed. The surface forces between crossed-cylinder mica surfaces have been accurately measured in the undersaturated vapor of several kinds of liquids using this apparatus, and the dependence on relative vapor pressure has been obtained more accurately than in previous studies. The effects of the type of liquid, carbon number of the liquid molecule, and molecular shape on the observable limit of the macroscopic characteristics of nanomeniscus forces are discussed. Note that the term "surface force" includes both the adhesion force and the (nano)meniscus force and that the meniscus with a radius of curvature, that is, Kelvin radius, on the nanometer level is called the "nanomeniscus" in this study.

Experimental Section

Apparatus. Figure 1a shows the main part of the SFA-type apparatus. The adhering surfaces (A and B) are in a crossed-cylinder configuration which is equivalent to a plane and sphere configuration. The cylindrical surface A is supported by a double cantilever spring which is used to measure the normal force between the solid surfaces. The spring constant of the double cantilever spring is 1270 N/m; the normal force can be obtained by measuring the deflection of this spring. The deflection is measured by displacement sensors nos. 1 and 2, which are high-resolution noncontact capacitive displacement sensors. Since the resolution of the displacement sensors is less than 1 nm, the resolution of the normal force detection is about 1 μ N. The cylindrical surface B is supported by a rigid arm.

Figure 1b is an enlargement of one of the cylinders. Cleaved mica is glued by epoxy resin on a cylindrical glass lens whose radius of curvature, *R*, is 8.5 mm.

The main unit shown in Figure 1a is mounted on stages, as shown in Figure 1c: cylinder A is on an elastic stage which is driven by a piezoelectric actuator and can realize fine movement in the x direction; cylinder B is on a microstage for coarse movement. The displacement sensors shown in Figure 1a are omitted from Figure 1c.

The assembly shown in Figure 1c is located in a vacuum chamber in which the vapor pressure of a liquid can be controlled, giving the complete system for measuring the surface forces as a function of the relative vapor pressure shown in Figure 1d. The temperature of a liquid sample is controlled by the temperature control pool, and the vapor of the sample liquid is introduced into the chamber through a valve. The chamber has a pressure gauge and a thermocouple. The complete apparatus is located on a vibration isolation system in a clean booth.

Properties of Specimens. In this study, mica is used as the solid specimen and several kinds of volatile liquids are used.

The properties of the mica are shown in Table $1.^{15-17}$ The surface geometry of the cleaved mica surface is measured using atomic force microscopy (AFM), and the cleaved mica surfaces used in these experiments were molecularly smooth.

From the contact mechanics theory, $^{18-23}$ the Johnson–Kendall–Roberts (JKR) theory 21 is applicable for the contact of the mica surfaces. The adhesion force (pull-off force) derived from

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Table 1. Properties of Mica^a

 $\begin{array}{l} \text{Surface Geometry} \\ \text{surface roughness: } R_{\mathrm{a}} = 0.048 \ \mathrm{nm} \\ \text{average radius of curvature of peak of surface roughness:} \\ \beta = 18 \ \mu \mathrm{m} \\ \text{standard deviation of peak height: } \sigma_{\mathrm{p}} = 0.048 \ \mathrm{nm} \end{array}$

 $\begin{array}{l} \mbox{Mechanical Properties}\\ \mbox{Young's modulus: $E=34.5$ GPa}\\ \mbox{Poisson's ratio: $\nu=0.205$}\\ \mbox{Vicker's hardness: $HV=1.43$ GPa}\\ \mbox{surface energy: $\gamma_{\rm s}=47.7\pm0.9$ mJ/m²} \end{array}$

Contact State Parameters plasticity index: $\Psi = 0.0206$ adhesion parameter: $\theta_{ad} = 0.0118$ elasticity parameter: $\mu = 101$

^{*a*} References 15–17.

the JKR theory is given by

$$F = 3\pi R \gamma_{\rm s} \tag{3}$$

where γ_s is the surface energy of the solid.

We selected 10 kinds of liquids: 5 linear alkanes, 3 cycloalkanes, ethanol, and water. The properties of these liquids are shown in Table 2.^{5,24,25} Note that the contact angle, θ , appearing in eq 1 of all the liquids to the mica surface was almost zero when measured in air; especially, the contact angle of water is close to zero since the mica surface is hydrophilic, though the surface energy of water is larger than that of the mica.

Experimental Method and Conditions. After preparing the cylindrical mica surfaces shown in Figure 1b and attaching them to the double cantilever spring and the rigid support shown in Figure 1a, the chamber in Figure 1d is evacuated to less than 0.1 Torr. The mica surfaces are baked at 200 °C and held for 5 min in order to remove any adsorbed liquid film on the mica surfaces, which is mainly water since the mica surface is hydrophilic. After the heater is turned off and the surfaces are cooled to room temperature while pumping, the vapor of a sample liquid is introduced and held for 3 min. The mica surfaces then approach each other at a speed of 1 μ m/s using the microstage shown in Figure 1c until the contact load (initial load) becomes 0.5 mN, and the initial load is then held for 3 min. The surfaces were separated and unloaded at a speed of 0.44 μ m/s using the elastic stage. An abrupt separation is observed, and the surface force can be obtained from the difference between the displacement sensors nos. 1 and 2.

The effects of the initial load, hold time of the initial load, and unloading speed on the surface force were investigated in a previous study.²⁶ It was confirmed that the initial load, the holding time of the initial load, and the unloading speed only affect the surface force slightly in the range of 0.25-2 mN, for hold times greater than 50 s and unloading speeds of $0.22-1.32 \ \mu$ m/s.

Results and Discussion

Surface Forces as a Function of Relative Vapor Pressure. Figure 2a shows the relation between the surface force, *F*, and relative vapor pressure, p/p_s , for all liquids used in this study. Under dry conditions $(p/p_s =$ 0.0), the surface forces denoted by the big black dots agree well with the theoretical value predicted by the JKR theory, that is, eq 3 (dotted line in Figure 2a). Ťhe surface forces gradually change from those under dry conditions to a constant asymptote with increasing relative vapor pressure. In previous experiments,¹² it has been observed that some liquid molecules are sandwiched between the mica surfaces even in an undersaturated vapor atmosphere. The intervening layer of liquid molecules between the mica surfaces increases with increasing relative vapor pressure, and consequently, the surface forces show the gradual change observed in Figure 2a as direct contact between the mica surfaces is prevented. In the case of water, the surface forces gradually increase, while in the other cases they decrease. This is because the surface energy of water is greater than that of mica while the surface energies of other liquids are lower than that of mica (see Tables 1 and 2) and because the mica surface is hydrophilic.

Figure 2b-d shows the same experimental data as Figure 2a for the different liquids, and the theoretical prediction of macroscopic meniscus forces of each liquid based on eq 1 are also shown (dotted-dashed line). Note that the contact angle, θ , is assumed to be zero. The constant values of the surface forces in the region of high relative vapor pressure correspond to the macroscopic meniscus forces generated by the Laplace pressure of each liquid, as given by eq 1, which means that the nanomeniscus forms at the interface and shows macroscopic bulk characteristics for relative vapor pressures above a certain value. The relative vapor pressures at which the nanomeniscus force begins to deviate from the macroscopic prediction of eq 1 are different for each liquid. It is considered that in the transition region from dry adhesion to nanomeniscus formation, the intervening layer of liquid molecules mentioned above plays a significant role and a partial nanomeniscus (imperfect liquid ring) around the periphery of mica-mica contact will be generated. Also, the surface forces decrease more sharply for the cycloalkanes than for the linear alkanes, and the surface forces for polar liquids decrease the most gradually. We now consider this transition.

Critical Relative Vapor Pressure, $(p/p_s)_c$. It is interesting to investigate the relative vapor pressure or nanomeniscus radius of curvature at which the nanomeniscus shows macroscopic characteristics by application of macroscopic theory. The authors adopt the criterion

$$\left|\frac{4\pi R\gamma_{\rm L} - F}{4\pi R\gamma_{\rm I}}\right| < 0.05 \tag{4}$$

that is, it is assumed that a macroscopic meniscus is formed at the point where the difference between the measured

Table 2. Properties of Liquids^a

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liquid	chemical formula	molecular weight <i>M</i> , kg/mol	density ρ, kg/m ³	molar volume <i>V</i> , m ³ /mol	surface energy $\gamma_{\rm L}$, mJ/m ²	effective molecular diameter $\sigma_{\rm e}$, nm
<i>n</i> -hexane	C ₆ H ₁₄	$8.62 imes 10^{-2}$	659	$1.31 imes 10^{-4}$	17.5	0.61
<i>n</i> -heptane	C7H16	$1.00 imes 10^{-1}$	684	$1.47 imes10^{-4}$	19.2	0.65
<i>n</i> -octane	$C_{8}H_{18}$	$1.14 imes10^{-1}$	703	$1.63 imes10^{-4}$	20.7	0.70
<i>n</i> -nonane	$C_{9}H_{20}$	$1.28 imes10^{-1}$	722	$1.78 imes10^{-4}$	22.0	0.74
<i>n</i> -decane	$C_{10}H_{22}$	$1.42 imes 10^{-1}$	730	$1.95 imes10^{-4}$	22.9	0.78
cyclopentane	C_5H_{10}	$7.01 imes10^{-2}$	745	$9.41 imes 10^{-5}$	21.3	0.50
cyclohexane	$C_{6}H_{12}$	$8.42 imes10^{-2}$	774	$1.09 imes10^{-4}$	24.2	0.60
methylcyclohexane	C ₆ H ₁₁ CH ₃	$9.82 imes 10^{-2}$	769	$1.28 imes 10^{-4}$	22.8	0.74
ethanol	CH ₃ CH ₂ OH	$4.61 imes10^{-2}$	794	$5.80 imes 10^{-5}$	21.6	0.45
water	H ₂ O	$1.80 imes10^{-2}$	1000	$1.80 imes10^{-5}$	71.1	0.28

^a References 5, 24, and 25.



Figure 2. Variation of surface force with relative vapor pressure. (a) Experimental data of all liquids; the theoretical adhesion force under dry conditions shown by the dotted line is obtained from eq 3. In (b-d), the theoretical bulk meniscus forces predicted by eq 1 are also shown; note that the experimental data are the same as those in (a).

surface force, *F*, and the theoretical meniscus force given by eq 1 becomes less than 5%. This criterion reflects the accuracy of the force measurement. The relative vapor pressure which satisfies eq 4 is obtained by a linear interpolation of the experimental data shown in Figure 2, and the authors define the relative vapor pressure as the 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, that is, $p/p_s > (p/p_s)_c$.

Figure 3 shows the critical relative vapor pressure, $(p/p_s)_c$, for each sample liquid. The tendency is for $(p/p_s)_c$ of the cycloalkanes to be smaller and for that of the polar liquids to be larger than that of the linear alkanes; that

is,

$$(p/p_s)_c^{\text{cycloalkanes}} < (p/p_s)_c^{\text{linear alkanes}} < (p/p_s)_c^{\text{polar liquids}}$$
(5)

When liquid molecules adsorbed on the mica surfaces migrate and gather or liquid molecules condense from the vapor phase at the periphery of the solid contact and they form a liquid nanomeniscus, linear chain molecules may be considered to be entangled in the nanomeniscus bridge. Consequently, linear alkane molecules in the nanomeniscus cannot flow as easily as cycloalkane molecules, and so linear alkanes require a higher critical relative vapor pressure to show characteristics of the bulk liquid than do cycloalkanes which are simple, quasi-spherical molecules. On the other hand, the polar liquids, ethanol and water, used in this study require much higher critical relative vapor pressures than do the others despite their small molecular size. This is because polar molecules interact more strongly with solid surfaces or associate with each other, and consequently, they find it more difficult to move like bulk liquid when confined to a nanomeniscus. The thicknesses of the adsorbed films of

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Figure 3. Critical relative vapor pressure, $(p/p_s)_c$, for each sample liquid. Above the critical relative vapor pressure, the nanomeniscus shows macroscopic characteristics, i.e., $p/p_s > (p/p_s)_c$.

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.²⁷ This means that 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, $(p/p_s)_c$.

Critical Kelvin Radius, $r_{\rm Kc}$, and Dimensionless **Critical Kelvin Diameter**, $2r_{\rm Kc}/\sigma_{\rm e}$. The radius of curvature of the nanomeniscus at which the nanomeniscus begins to show macroscopic characteristics can be estimated from eq 2 by substituting the critical relative vapor pressure, $(p/p_{\rm s})_{\rm c}$, for the relative vapor pressure, $(p/p_{\rm s})$. This Kelvin radius is defined as the critical Kelvin radius, $r_{\rm Kc}$. The critical Kelvin radius for each sample liquid is shown in Figure 4. The critical Kelvin radii of linear alkanes vary linearly with respect to the carbon number, n, of a molecule. The relation between $r_{\rm Kc}$ and n obtained by least-squares fitting to the experimental data is given by

$$r_{\rm Kc} = 0.26n - 0.31 \tag{6}$$

in which the $r_{\rm Kc}$ 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, $r_{\rm Kc}$ for water and ethanol is large compared to their σ_e values. This trend has been observed in previous studies^{1,12} using cyclohexane and water. A comparison of the critical Kelvin diameter, $2r_{\rm Kc}$, and the effective molecular diameter, σ_e , that is, the dimensionless critical Kelvin diameter, $2r_{\rm Kc}/\sigma_e$, is shown in Figure 5. 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,

$$2r_{\rm Kc}/\sigma_{\rm e} \approx 2.1$$
 (7)

although the molecular structure of methylcyclohexane



Figure 4. Critical Kelvin radius, r_{Kc} , for each sample liquid. The critical Kelvin radii are obtained from the critical relative vapor pressure, $(p/p_{\text{s}})_{\text{c}}$, shown in Figure 3 using eq 2. The critical Kelvin radii vary linearly with respect to the carbon number of the linear alkanes as depicted in the figure.



Figure 5. Dimensionless critical Kelvin diameter, $2r_{Kc}/\sigma_e$, for each sample liquid. The critical Kelvin diameters are almost constant for the cycloalkanes.

is slightly different from those of the other two cycloalkanes. This value suggests that the nanomeniscus shows macroscopic characteristics when a single molecular layer of a cycloalkane is arranged on each mica surface. In previous studies,^{5,15,16,28–30} it has been reported that the drainage of liquid molecules and properties of ultrathin

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liquid films under shear confined between solid surfaces begin to deviate from the macroscopic characteristics or macroscopic predictions when the liquid film thickness becomes thinner than 5-10 times the effective molecular diameter of the intervening liquid in the case of the nonpolar and quasi-spherical liquids such as the cycloalkanes, while the results presented here suggest macroscopic behavior for films thicker than 2 layers. For liquids which have long molecules such as the linear or branched alkanes, the liquid properties can be explained by macroscopic theory for film thickness much thinner than 5–10 layers whereas this study suggests films are bulklike around 4-6 layers. Thus, the results shown in Figure 5 (see linear alkanes and cycloalkanes in Figure 5) clearly display a different behavior compared to those of the previous studies. The authors consider that this difference can be attributed to whether the liquid is perfectly confined between two solid surfaces, that is, whether the experimental system involves a free liquid surface. Consequently, the effects of discrete molecules are considered different in each experimental system.

On the other hand, it is found that polar liquids require a nanomeniscus with a radius of curvature much larger than their effective molecular diameter to show macroscopic characteristics. This is also because polar molecules interact more strongly with solid surfaces or associate with each other, and consequently, they find it more difficult to move like bulk liquid when confined to a nanomeniscus as described in the critical relative vapor pressure $(p/p_s)_c$ subsection.

The data shown in Figures 3–5, that is, the critical relative vapor pressure, the critical Kelvin radius, and the dimensionless critical Kelvin diameter, are rewritten in numerical form in Table 3. It is considered that the applicability of macroscopic theories is limited by these critical values.

Summary

An apparatus which can accurately measure the surface forces between solid surfaces in an atmosphere-controlled chamber has been developed. The surface forces between crossed-cylindrical mica surfaces were measured in undersaturated vapors of 10 liquids using this apparatus.

The surface forces change gradually from those measured under dry conditions to be a constant asymptotic

Table 3.	Critical Data in Num	erical Form
	(see Figures 3-5)	

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liquid	critical relative vapor pressure $(p/p_s)_c$	critical Kelvin radius r _{Kc} , nm	nondimensional critical Kelvin diameter 2 <i>r</i> _{Kc} / <i>o</i> _e
<i>n</i> -hexane	0.65	1.2	3.9
<i>n</i> -heptane	0.47	1.5	4.6
<i>n</i> -octane	0.47	1.8	5.1
<i>n</i> -nonane	0.46	2.0	5.4
<i>n</i> -decane	0.47	2.3	5.9
cyclopentane	0.21	0.52	2.1
cyclohexane	0.19	0.62	2.1
methylcyclohexane	0.23	0.80	2.2
ethanol	0.74	1.6	7.3
water	0.74	1.7	12

value with increasing relative vapor pressure. In the case of water, the surface forces gradually increase, while for the other liquids they decrease. The constant values of the surface forces in the region of high relative vapor pressure correspond to the macroscopic meniscus force given by eq 1. The surface forces approach the macroscopic meniscus force more rapidly for the cycloalkanes than for the linear alkanes, and for the polar liquids the change is more gradual than for the other liquids.

We define the critical relative vapor pressure, $(p/p_s)_c$, as the relative vapor pressure above which the nanomeniscus shows macroscopic characteristics. From an analysis of the experimental data, the relation in eq 5 was obtained.

Furthermore, the critical Kelvin radius, $r_{\rm Kc}$, and the dimensionless critical Kelvin diameter, $2r_{\rm Kc}/\sigma_{\rm e}$, are defined. The critical Kelvin radii of linear alkanes varied linearly with respect to the carbon number, *n*, of a molecule, and the relation given by eq 6 was obtained. In the case of cycloalkanes, the dimensionless critical Kelvin diameter was found to be almost constant and eq 7 was obtained. The dimensionless critical Kelvin diameter data suggest that there is a difference between cases in which the experimental system includes a free liquid surface such as those investigated in this study and the case in which a liquid is perfectly confined between solid surfaces.

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