LIQUID FILM CREEPING UPWARD ON SOME SOLID SURFACES AT A ROOM TEMPERATURE

SHOSUKE SASAKI
Department of Physics, College of General Education,
Osaka University, Toyonaka Osaka 560, Japan

ABSTRACT

It has been observed that some liquids, methanol, perfluorokerosine and water, creep upward on some solid surfaces (pyrex glass or film of X-ray) against the gravity at a room temperature. These phenomena are the same as in superfluid helium. Since the present liquids have viscosity, the flow velocities are extremely slower than the one of superfluid helium. The amounts of the upward flows have been measured in several cases. In our observations, the smaller amount has been about 10 droplets per month for perfluorokerosine and the larger amount has been about one droplet per hour for methanol. These upward flows are caused by intermolecular forces between molecules in the solid surface and the ones in the liquid. If the attractive intermolecular forces between the liquid and the solid surface are stronger than the intermolecular forces between the liquid and itself, then the liquid spreads on the solid surface, and creeps upward against the gravity.

INTRODUCTION

One of the most characteristic phenomena of superfluidity is the fact that superfluid helium creeps upward on a vertical solid surface. Superfluid helium containing in a beaker spreads on the inner surface, and after then on the outer surface as a thin liquid film, and drops down from the outer surface of the bottom of the beaker. These phenomena have been investigated by many authors [1]-[3]. The dropping rate of superfluid helium is about one droplet for a few seconds, though the rate depends on the diameter of the beaker, the height difference (between the top of the beaker and the level of liquid helium), and the substance from which the beaker is made [4].

At a room temperature, similar phenomena have occurred even in a normal viscous liquid [5]. The upward surface flow is produced by the intermolecular forces between the beaker and the liquid. In order to explain the mechanism, we illustrate the thin liquid film in Fig.1.

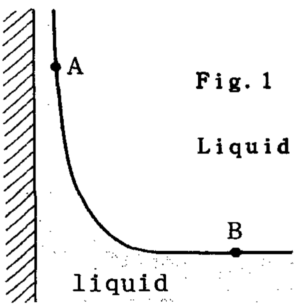

Fig. 1

Liquid Surface near Solid Wall

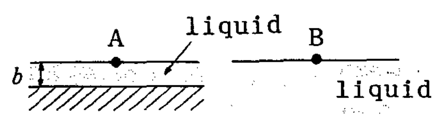

Fig. 2 (a)
Potential
near point A

Fig. 2 (b)
Potential
near point B

Let us compare the force acting to the molecule at point A in Fig.1 with one at point B. This comparison can be more easily seen in Fig.2(a) and 2(b) which are shown near the points A and B, respectively. Fig.2(a) has been drawn by turning Fig.1 anticlockwise through an angle of 90°. The liquid molecules A and B feel the same intermolecular potential from liquid molecules inside the thickness b. However, the molecule A feels the intermolecular potentials between solid and liquid at a more distance than the thickness b, which are different from the intermolecular potentials acting to the molecule B. If the intermolecular potential between the solid and the liquid molecules is more attractive than the one between the liquid and the liquid molecules (namely solid-liquid potential is lower than liquid-liquid potential), then the molecule at point A feels a lower intermolecular potential than the one at point B. In this case, the solid surface completely wets with the liquid (namely the contact angle is equal to zero).

The static liquid surface is determined as the sum of the intermolecular potential and the gravitational potential at point A is equal to the sum at point B. When the thickness, b, at point A becomes smaller than that of static case, the total potential at point A (including the gravitational potential) is lower than that at point B. Consequently, the thin liquid film flows upward on the solid surface, because the liquid molecule moves towards the place with a lower total potential. Thus, this kind of phenomena always occur on the perfectly wetting solid surface with the liquid. In a viscous liquid, the flow velocity is extremely small due to its viscosity, and, however, these phenomena certainly occur even at a room temperature.

We have succeeded in solving the Navier-Stokes equation of this thin liquid-flow on a solid surface for viscous liquids. The calculation of the solution and one preliminary experiment have been shown in the previous paper [5]. In this paper, we will discuss researches in chemistry relating to these phenomena and will show more clear experiments.

ZISMAN PLOT

A quarter century ago, W.A. Zisman investigated contact angle, θ , between solid surface and liquid surface. He plotted cosθ (θ : contact angle) versus surface tensions, γ_L , of liquids for a common solid surface. Then he found that the graph of cosθ versus γ_L is a straight line for any low-energy surface as in Fig.3. The intercept between the straight line and cosθ =1 has been named the critical surface tension, γ_c , of the solid.

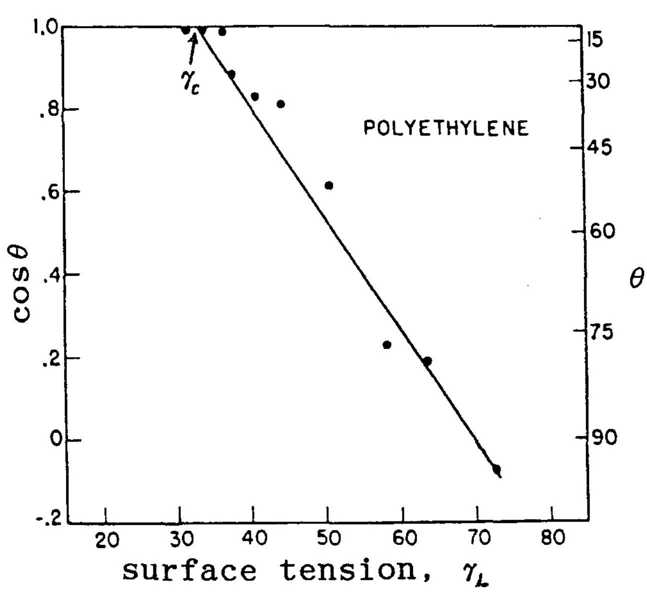

Fig. 3

Plot of contact angles of various kind of liquid with different surface tention, γ_L, against polyethylene surface

When we select such a pair of liquid and solid as $\gamma_L < \gamma_c$, what happens? In the case, the liquid creeps upward on the vertical surface of the solid. In the previous paper [5], we have selected perfluorokerosine which has one of the smallest surface tension at a room temperature. Then, we have succeeded in finding the thin liquid-flow creeping upward. In the next section, we show another examples where the attractive intermolecular forces between liquid and solid are stronger than the previous case.

THIN LIQUID-FLOW ON X-RAY FILM

A thin liquid-flow rate has been determined by our previous calculation in ref.[5]. The results show that the flow rate becomes larger as the intermolecular force between liquid and solid becomes stronger and longer-range force. In this paper, we try to measure the flow rates on such a surface of which solid material has large electric dipole moments.

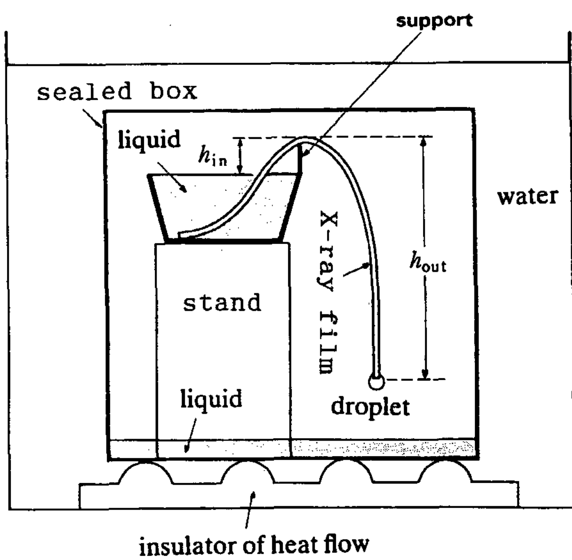

Fig. 4

Experimental instrument by which we measure flow-rates of various kinds of liquid

Our experimental instrument is illustrated in Fig.4. The outer box shown in Fig.4 has the size of 60 cm x 30 cm x 35 cm, and is filled with water which plays a role of keeping the temperature constant. We put a tightly sealed box into this outer box. In the sealed box, we set a small vessel on a stand, and fill the vessel with the liquid of our experimental object. As can be seen in Fig.4, one end of the film sheet is steeped in the liquid and the other end is held in the gas of the saturated vapor pressure. Of course, the height of the latter end is sufficiently lower than the level of the liquid.

We have used several materials as the film sheet, but have failed in setting them except X-ray film. We report the results for X-ray film.

Procedure in the Experiment

We have placed the instrument in a dark room in order to avoid vaporization caused by an external light. We have waited all detections during longer time than 12 hours after the finish of setting all our instruments. Our instruments become a constant temperature and the gas inside the sealed box becomes the saturated vapor pressure during this waiting time. After then, we put on a fluorescent lamp in order to record the fall of the liquid droplet on videotape. But the lamp is separated from our instruments at a sufficiently far distance in order to avoid vaporization of the liquid on the film. The results of the falling rate of the droplet are shown in Table I for water and Table II for methanol.

Table I : water (h_{out}=91 mm)

h_{in}	falling time	interval	water temperature in outer box
5.8 mm	10hour13min.52sec.		18.9℃
		48min.33sec.	
〃	11 : 02 : 25		
		48 : 25	
〃	11 : 50 : 50		
		48 : 47	
〃	12 : 39 : 37		
		48 : 50	
〃	13 : 28 : 27		
		48 : 40	
〃	14 : 17 : 07		
		48 : 40	
〃	15 : 05 : 47		19.0℃

Table II : methanol (h_{out}=100 mm)

h_{in}	falling time	interval	water temperature in outer box
10mm	9hour39min.43sec.		17.9℃
		57min.27sec.	
	10 : 37 : 10		
		56 : 58	
	11 : 34 : 08		
		57 : 39	
	12 : 31 : 47		
		58 : 31	
	13 : 30 : 18		
		59 : 05	
	14 : 29 : 23		
		59 : 25	↓
	15 : 28 : 48		17.9℃
20mm	10 : 17 : 53		18.9℃
		2hour3min.45sec.	
	12 : 21 : 38		
		2 : 8 : 05	
	14 : 29 : 43		
		2 : 13 : 24	↓
	16 : 43 : 07		19.0℃

mass of one droplet of methanol : 43.6± 0.6 mg

The X-ray film is Type N producted by Sakura Co.LTD.in Japan, and its width is 5 cm.

The heights of h_{in} and h_{out} are shown in each Table. In the case of water, we have steeped the X-ray film during 30 seconds into solution of NaOH whose concentration is 1 N, and have immediately steeped it into water. In the case of methanol, we have not done this procedure (namely we have used original X-ray film for methanol).

EXPERIMENT IN A SCHALE

One might ask the following questions concerning our experiment described in the previous section:

(1) May the droplet have resulted from the vapor condensation?
(2) May the liquid-flow have passed through the gel inside the film?

We have carried out another experiment in order to answer these questions.

Experiment with schale

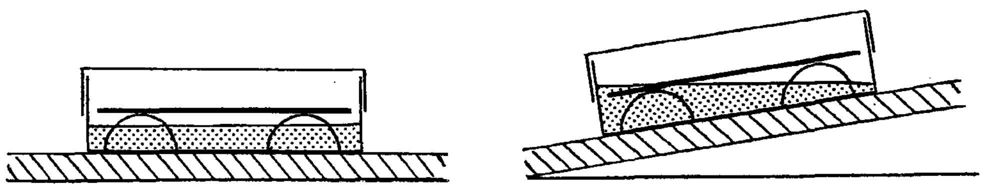

Fig. 5
Schale is held horizontally

Fig. 6
Schale is titled

We set X-ray film in a schale as shown in Fig.5. The film is not still steeped in methanol. We close the cover of the schale and wait for one minute. After then, we tilt the schale as shown in Fig.6. At that time, the one end of the film is steeped into methanol. As seen in Fig.6, we can set the slope of the film to be very small, and therefore we can make the effect of the gravity to become small. Then, the thin liquid spreads upward on the X-ray film considerably fast. Also, we can easily see that the wetting part with methanol creeps upward on the X-ray film.

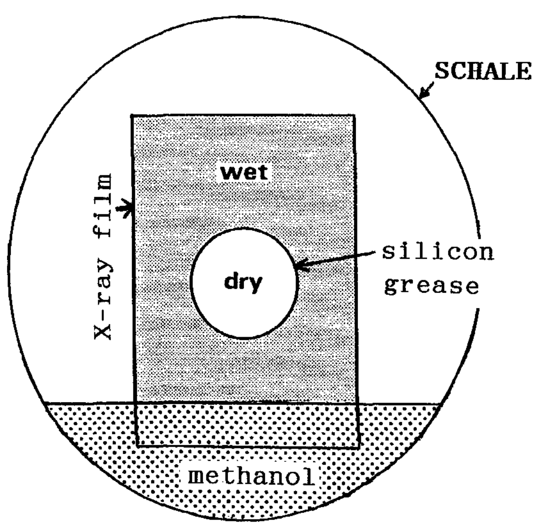

Fig. 7
Experimental set-up used to confirm that the liquid-flow creeps on the solid surface but neither through the film-inside nor via vaporization-condensation

Now, we paint silicon grease in a shape of circumference on the X-ray film as shown in Fig.7. When we carry out the same procedure for this film, we find out the fact that the outside of the circumference gets wet with methanol, but the inside never does. If the opinion (1) or (2) is correct, both the inside and the outside of the circumference should be wetting. Consequently, our detected liquid-flow is on a solid surface. Thus, it has been clarified in this paper that there certainly exists the thin liquid-flow creeping upward on a solid surface at a room temperature, though the phenomena were theoretically derived in our previous work and were detected by the preliminary experiment before this work.

Acknowledgments

The experiment of the section "THIN LIQUID-FLOW ON X-RAY FILM" has been carried out by cooperation of Dr. A. Yoshimura (in Department of Chemistry, College of General Education, Osaka University) and me. I would like to express my hearty thanks to Dr. A. Yoshimura. I wish also to acknowledge Dr. M. Fukuhara in Toshiba Tungaloy for publication of this article.

References

1) Frenkel J., J. Phys. (Moscow), 1940, 2, 365.
2) Nagamiya, T., Liquid Helium: Series of Physics vol.7, Kawade Shobou, pp92 (in Japanese).
3) Richmond P. and Ninham B.W., J. Low Temp. Phys., 1971, 5, 177.
4) Kitano Y., and Sasaki. S., Jpn. J. Appl. Phys. Proc. LT 18, 1987, 26-3, 81.
5) Sasaki S., J. Phys. C 1988, 21, 871.
6) Zisman W.A., Advan. Chem. Ser. 1964, 43, 1.
Newman S., J. Colloid and Interface Sci. 1967, 25, 341.
Dann J.R., J. Colloid and Interface Sci. 1970, 32, 302.