Flow of polymolecular films

N.V. Churaev

Institute of Physical Chemistry, Moscow, 117915, USSR

Abstract – Experimental investigation of film flow over the molecularly smooth surfaces of quartz capillaries has shown that the films of nonpolar liquids having the thickness $h \gg 1$ nm flow as viscous bulk liquids. This is also the case for thin water films, but the corresponding calculations are complicated due to the nonuniformity in the film thickness on the partially wetted quartz surface.

Introduction The flow of polymolecular films, depending on their thickness, may be considered as viscous flow, or as two-dimensional surface diffusion. In the first case, equations of hydrodynamics must be used for describing the flow of films; and in the second case, the equations of diffusion. It is important to establish the scope of application of those approaches.

In this connection, here will be considered the experimental results relating to the flow of polymolecular liquid films over the molecular-smooth surface of fine cylindrical capillaries (having the radius on the order of 0.1 to 1 μm) drawn from pure quartz (the content of $SiO_2 > 99.99\%$).

Film flow under the effect of pressure gradient The first technique consisted in measuring the evaporation rates of liquids from the capillaries. For this purpose the rate of the meniscus retreat was measured with means of a microscope. In the case of low volatile liquids a considerable contribution to the evaporation rate is given by the film flow over the wall of the capillary.

In Fig. 1 are represented the results of such experiments on decane during its evaporation at low Knudson numbers λ/r (λ is the free path) into an evacuated chamber, where a definite relative pressure of vapour p_0/p_s was maintained [1]. Measurements were carried out for the capillaries having the radii r from 0.18 to 1.5 μm. Here K is the permeability coefficient, included in the mass flow equation $q = K (p_m - p_0)/l$, g/cm^2 sec, where $p_m \simeq p_s$ is the pressure of vapour over the meniscus, and l is the distance from the mouth to the meniscus in a capillary. The values of K are related to the coefficient of Knudsen diffusion of vapour $K_1 = (8r/3)(\mu/2\pi RT)^{1/2}$ at $r/\lambda \rightarrow 0$, where μ is the mass of a mole,
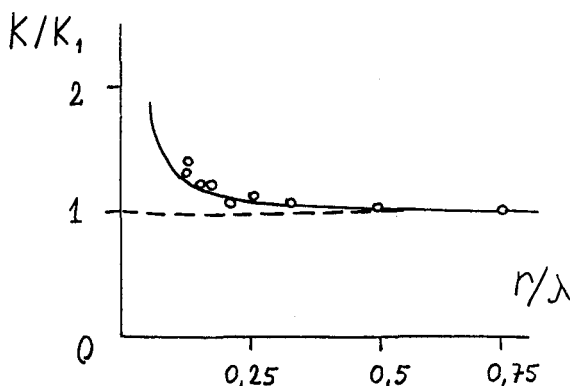

Fig. 1. The influence of the flow of polymolecular films on evaporation of decane from fine capillaries.

R is the gas constant, and T is temperature. The dashed line indicates the theoretical dependence of $K_1(r/\lambda)$ for vapour flow. The experimental points for fine capillaries are located above this curve, and this is associated with an additional mass transfer in a polymolecular film of decane.

The experimental data relating to the film thicknesses of about 5 to 1 nm, can be described on the basis of the equation of hydrodynamics of liquid films, $q = (\rho h^2/3\eta)\nabla\Pi$, where $\Pi(h)$ is the disjoining pressure [2] , ρ is the density, and μ is the viscosity of liquid in the film. Using the conditinn of the local equilibrium of the curved film with vapour

$$\Pi(h) + (\gamma/r) = -(\rho RT/\mu)\ln(p/p_s),\qquad(1)$$

one can obtain the following expression for K/K_1 [3] :

$$\frac{K}{K_1} = 1 - \frac{\rho^2 RT(2\pi RT/\mu)^{1/2}}{4\eta\mu r^2(p_m - p_o)}\; p_o\int_{p_m}\frac{h^3(p)}{p}\,dp\qquad(2)$$

The second term in Eq. (1) characterize the capillary pressure in the film, where γ is the surface tension of the liquid.
The wetting films of nonpolar decane are stable due to the action of long-range dispersion forces. The $\Pi(h)$ isotherm correlating the thickness of a film with the disjoining pressure acting in it, has the form $\Pi = A/6\pi h^3$, where $A = 1.6 \times 10^{-20}$ J, the Hamaker constant. Its value was calculated on the basis of the spectral data of quartz and decane [4] in accordance with the macroscopic theory of dispersion forces [5] . Using Eq. (1), we shall find the isotherm of polymolecular adsorption h(p) . Than after integrating Eq. (2) we obtain:

$$\frac{K}{K_1} = 1 + \frac{A(2RT/\pi\mu)^{1/2}}{24\eta r^2(p_m - p_o)}\;\ln\left[\frac{\ln(p_o/p_s) - (\mu\gamma/\rho\, rRT)}{\ln(p_m/p_s) - (\mu\gamma/\rho\, rRT)}\right]\quad(3)$$

The theoretical dependence $K/K_1(r/\lambda)$, represented in Fig. 1 by a continuous curve, was plotted with Eq. (3), using the bulk values of γ , ρ , and η . The experimental points are located close to that curve. This enables one to consider that wetting films of decane (h $\gg$ 1 nm) preserve the properties of the bulk liquid, and that the equations of viscous flow apply to these.
In Fig. 2 are presented the results of similar experiments carried out on water [3] . As is known, not only dispersion forces, but also electrostatic and structural forces act in the films of polar water [2] . This complicate the theoretical determination of h(p) isotherm. In this case the known experimental isotherm h(p) [4] was used to make calculations with Eq. (2). The thickness of the films is small, and the experimental data tally with the theoretical curve 1 for the Knudsen flow of vapour, when a low relative pressure of vapuur is maintained in the chamber (points 1). Now, at higher values of $p_o/p_s = 0.97 - 0.98$ the experimental points are

located close to the curve 2, which was plotted by using Eq. (2). However, the theory can be in agreement with the experimental data (points 2 and 3) only when 4 times higher values of film viscosity η as compared with bulk viscosity η_o are adopted. Yet the viscosity of water can hardly be increased so much. In accordance with the measurements done in fine pores (r = 2-3 nm) of silica gels and porous glasses [2] the largest changes in the viscosity of water amount to 1.5 η_o. The detected increase in the viscous resistance is probably associated with the formation of water film of nonuniform thickness on the surface of quartz. This may be attributed to the microheterogeneity of the quartz surface, containing not only hydrophilic silanol areas, but also siloxane ones that are less hydrophilic. As a result, the thicker films that are formed over the hydrophilic areas prove to be separated by thinner ones that give rise to a higher viscous resistance. The isotherms h(p) of polymolecular water film on flat quartz surface, which are experimentally obtained by the ellipsometric method, are characteristic of only the mean thickness of the film.

As appears from Fig. 2, for water films the equations of viscous flow may be also formally used, but in this case including some effective values of either viscosity or thickness of the film. However, it is difficult to predict theoretically these effective values. To obtain more reliable
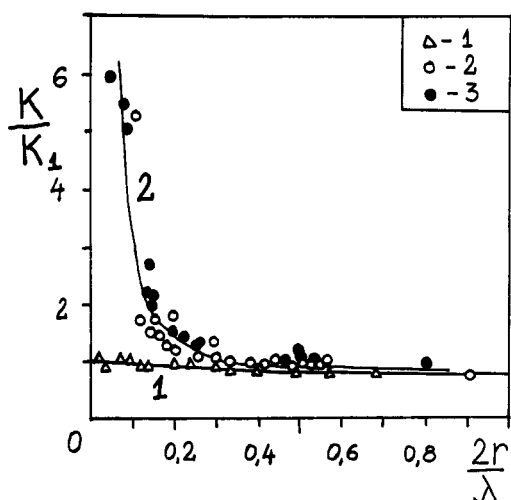
Fig. 2. The increase in the evapora-
tion rate of water from fine capill-
aries owing to the flow of polymole-
cular adsorption films of water.
The relative pressure of vapour in
the chamber: $p_0/p_s = 0.75$ (1);
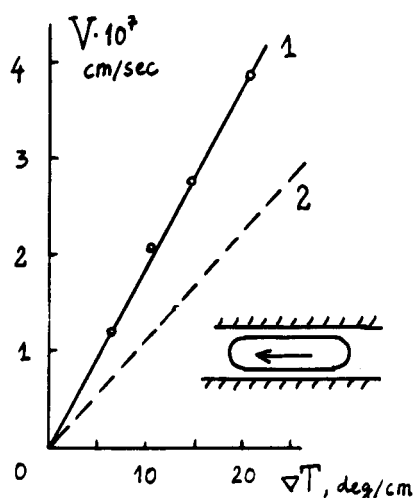0.97 (2); and 0.98 (3)

Fig. 3. The influence of the thermo-
capillary flow of dodecane films
(h = 2.5 nm) on the rate of menisci
displacement V in a glass capillary
at mean temperature of +31°C.

quantitative data on the polymolecular films of water requires carrying
out the experiments on more uniform surfaces.

In the general case of heterogeneous surfaces such a transport mechanism
may be realized, when the viscous flow over the areas of thicker films is
combined with the surface diffusion of water molecules on the "dry" areas
separating the films from one another.

Thermocapillary film flow   The second applied technique consisted in ob-
serving the film flow over the portion of the capillary located between the
menisci (Fig. 3) [6] . The flow of the films occurred under the effect of
the temperature gradient ∇T which gave rise to the gradient of the surface
tension of the film. The velocity of the gas bubble shift V is determin-
ed by the thermocapillary flow of the film V_f, and the diffusion of vapour
V_d :

$$V = V_f + V_d = \left[(h^2/r\eta)(\partial\gamma/\partial T) + (\mu D/\rho RT)(\partial p/\partial T)\right]\nabla T , \qquad (4)$$

where D is the coefficient of diffusion of vapour through gas.

The film flow rate was calculated from Eq. (4) as the difference between
the directly measured velocity of bubble shift V , and the calculated
value of V_d . In Fig. 3 are shown the results for low volatile dodecane
in a glass capillary r = 0.73 µm. The experimental dependence $V(\nabla T)$
(curve 1) is linear in agreement with Eq. (4). The dashed line 2 indicate
the V_d values calculated according to Eq. (4) using the known values of D
and dp/dT for dodecane. The difference between the curves 1 and 2 gives
the rate of the film flow, amounting up to about 40% of the total flow
rate.

The obtained values of V_f tally well with those calculated by the aid of

Eq. (4), using the bulk values of γ (T) and η for dodecane. The
thickness of films was determined from the isotherms $\Pi = A/6\pi h^3 = \gamma/r$,
with the Hamaker constant A = 1.35×10^{-20}J [4] . The applicability of
the equations of viscous flow was corroborated by the series of experiments
done on the capillaries having the radii from 0.4 to 17 µm, which corres-
ponds to the film thicknesses from 2 to 10 nm.
The thermocapillary flow of water films is complicated by the hysteresis
of the contact angle. In distinction to dodecane, water is able to wet
quartz but partially. Between the retreating and advancing menisci arise
a difference in the pressure $\Delta P = (2\gamma/r)(\cos\Theta_R - \cos\Theta_A)$ that caused

the counter flow in the film. However, in the case of relatively thick water films (h = 5-10 nm) the flow may also be described by the viscous flow equations.

Thermocrystallization film flow   We have eliminated the influence of hysteresis, when examining the thermal flow of nonfreezing, polymolecular adsorbed water films between two ice menisci in a capillary. The flow of a liquid films is accompanied by the phase transitions taking place on the menisci. In this case the thermocrystallization film flow occurs, that is described by the following equation [7] :

$$V_f = (2 \rho L h^3 / 3 \eta r \rho_i T) \nabla T, \qquad (5)$$

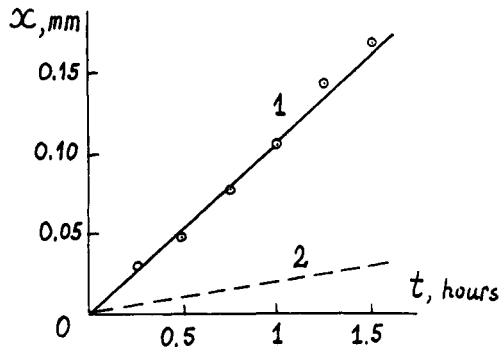where L is heat of fusion, and ρ_i is the density of ice.

Fig. 4. Microscopilally measured ice menisci displacement x versus time t in quartz capillary (r = 2.5 μm) at - 0.56°C, and ∇T = 12.4 degrees/cm.

In Fig. 4 is shown one of the experimentally obtained dependences x(t).

As in Fig. 3, the dashed line 2 indicates the calculated contribution of the diffusion of vapour. A low pressure of vapour over ice, and the excess gas pressure in a bubble (increased up to 1.7 atm by sealing up the capillary in the nitrogen medium), enabled one to suppress the diffusion of vapour [6] . On the basis of x(t) dependences one can calculate the rate of displacement $V = V_f + V_d$ = dx/dt and compare the results with theory.

Measurements done in capillaries having the radii from 1 to 10 μm within the temperature range of minus 6°C to minus 0.5°C have shown that the flow of nonfreezing films from 1 to 8 nm thick obeys the Eq. (5).

Conclusion   The films of nonpolar liquids having the thickness h ≳ 1 nm flow as viscous bulk liquids. This approach may also be applied to polymolecular water films; yet a possible nonuniformity in the thickness of thin polymolecular water films on microheterogeneous, only partially wettable surfaces interferes with the quantitative comparison with theory.

REFERENCES

1. Z.M. Zorin, A.V. Novikova and N.V. Churaev, In: Problems on the Physics of Formation and Phase Transformations, p.42, Tula Polytech, Inst. USSR (1973).
2. B.V. Derjaguin, N.V. Churaev and V.M. Muller, Surface Forces, Plenum Press, New York (1987).
3. Z.M. Zorin, A.V. Novikova, A.K. Petrov and N.V. Churaev, In: Surface Forces in Thin Films, and Stability of Colloids, p. 94, Nauka, Moscow (1974).
4. B.V. Derjaguin and N.V. Churaev, Wetting Films, Nauka, Moscow (1984).
5. I.E. Dzyaloshinsky, E.M. Lifshitz and L.P. Pitaevsky, Adv. Phys., 10, 165-187 (1961).
6. B.V. Derjaguin, N.V. Churaev, O.A. Kiseleva and V.D. Sobolev, Langmuir, 3, 631-634 (1987).
7. B.V. Derjaguin, N.V. Churaev, V.D. Sobolev and S.S. Barer, J. Colloid and Interface Sci., 84, 182-190 (1981).