Thickness of the Helium Film as a Function of Height

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The thickness of a film adsorbed on a vertical wall is derived from adsorption thermodynamics as a function of height. The thickness of the helium film calculated from adsorption data is, within the error of the experiments, consistent with those obtained by direct observation.

BOWERS[1,2] has shown that the adsorption of A, N_2, O_2, and of He even in the He II region obeys near saturation, i.e., for P/P_0 between 0.7 and 0.99 (P being the vapor pressure of the adsorbed layer, P_0 that of the bulk liquid), the adsorption isotherm proposed by Frenkel,[3] Halsey,[4] and Hill:[5]

$$-\ln(P/P_0)=k/\nu^3, \tag{1}$$

where ν is the number of adsorbed layers and k a constant. This relation, specifically the third power of ν therein, is a consequence of the fact that the van der Waal's potential of the wall decreases with the third power of the distance.

From the same premise Schiff[6] and Frenkel[7] found that the thickness t of the saturated helium film should vary inversely with the 1/3 power of the height:

$$t_h=t_1/h^{1/3}, \tag{2}$$

where t_1 is the thickness at the height 1. Experimental evidence has never confirmed relation (2); the exponent of h found to describe the experimental results varies from 1/7 to 1. Atkins,[8] Jackson,[9] Bowers,[10] and Picus[11] have recently found values between 0.4 and 0.5 rather than 1/3. Bijl, de Boer, and Michels[12] predict an exponent 1/2 for h in Eq. (2), by considering the zero-point energy of the more or less two-dimensional layer of film and by neglecting the van der Waals' forces. However, their argument would require in Eq. (1) an exponent 2 instead of 3.

It seems important, therefore, to find the reason for the apparent inconsistency and the great variety of the experimental evidence.

As both Schiff[6] and Frenkel[7] derive only the general form of the dependency of t on h by Eq. (2), an alternative derivation of $t=t(h)$ shall be given here by using the thermodynamics of adsorption as given by Guggenheim[13] and by Hill[14] in order to evaluate the different constants numerically.

The differential of the Gibbs free energy F_f of an adsorbed layer is

$$dF_f=-S_f dT+V_f dP-Ad\gamma+\mu_f dn=\mu_f dn+nd\mu_f, \tag{3}$$

or, written in analogy to the Gibbs-Duhem equations:[15]

$$-S_f dT+V_f dP-Ad\gamma-nd\mu_f=0, \tag{4}$$

or, per mole,

$$-s_f dT+v_f dP-(A/n)d\gamma-d\mu_f=0. \tag{4a}$$

S_f is the differential entropy of the film, V_f its volume, μ_f the chemical potential, A the surface area, and n the number of moles. T denotes the temperature, P the pressure, and γ the surface tension. The adsorbed layer is in equilibrium with the vapor:

$$d\mu_f=d\mu_g=-s_g dT+v_g dP, \tag{5}$$

s_g being the molal entropy and v_g the molal volume of the gas. Combining (4a) with (5) at constant T, using the ideal gas law and neglecting v_f compared with v_g, yields:

$$RT\partial \ln P/\partial\gamma=-(A/n), \tag{6}$$

often called the Gibbs adsorption isotherm. Equation (6) is derived without taking the gravitational field into account; it is, therefore, strictly valid only for an adsorbed phase and a vapor at the same height.

TABLE I. Surface tension γ in dynes/cm as a function of the thickness of the film in number of adsorbed layers.

ν	γ_ν
∞	0.3
100	0.33
10	2.8
5	10.3
3	31.2

[1] R. Bowers, Phil. Mag. **44**, 467 (1953).
[2] R. Bowers, Phil. Mag. **44**, 485 (1953).
[3] J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, London, 1946), p. 332.
[4] G. D. Halsey, J. Chem. Phys. **16**, 931 (1948).
[5] T. L. Hill, review in *Advances in Catalysis* (Academic Press, Inc., New York, 1952), Vol. 4, p. 225.
[6] L. I. Schiff, Phys. Rev. **59**, 839 (1941).
[7] J. Frenkel, J. Phys. (U.S.S.R.) **2**, 365 (1940).
[8] K. R. Atkins, "Advances in Physics," Phil. Mag. Supplement **1**, 169 (1952); Proc. Roy. Soc. (London) **A203**, 119 (1950).
[9] D. G. Henshaw and L. C. Jackson, *Proceedings of the National Bureau of Standards Symposium on Low Temperature Physics, 1951*, National Bureau of Standards Circular 519 (U. S. Government Printing Office, Washington, D. C., 1952), p. 183.
[10] R. Bowers, Phil. Mag. **44**, 1309 (1953).
[11] G. S. Picus, Phys. Rev. **94**, 1459 (1954).
[12] Bijl, de Boer, and Michels, Physica **8**, 655 (1941).
[13] E. A. Guggenheim, *Thermodynamics* (Interscience Publications, New York, 1949), p. 36.
[14] T. L. Hill, J. Chem. Phys. **17**, 520 (1949).
[15] Compare reference 13, p. 59, or, reference 14, Eq. (10).

Let us now assume an infinitely long and high wall dipping into a liquid as shown schematically in Fig. 1(a). The height above the liquid level is h. We want to calculate $t=t(h)$. In Eq. (4) two terms have to be added: the weight per mole: $(A/n)\rho_f g t dh$ (ρ_f being the density of the film) hangs essentially on the surface tension, and furthermore the pressure exerted on the film is not P, but

$$P'=P+(1/r_h+1/r_0)\gamma, \tag{7}$$

where r_h is the radius of curvature of the free surface of the film in vertical direction, and r_0 an eventual radius of curvature of the wall itself in horizontal direction. From the fact that $(\partial\mu_f/\partial h)_T=0$, and noting that $(A/n)t=v_f$ and $M=\rho_f v_f$, we get:

$$Mgdh+v_f d[\gamma(1/r_h+1/r_0)]-(v_f/t)d\gamma=0. \tag{8}$$

In order to get a relationship between t and h only, we have to eliminate γ. Making the plausible assumption that γ is a unique function of the thickness t (at constant temperature), we can eliminate γ in the range of validity of Eq. (1) by combining it with Eq. (6) and $t=a\nu$, where a is the spacing of the layers

TABLE II. Thickness of the helium film in number of layers as a function of height in cm and the corresponding change in equilibrium pressure.

h(cm)	ν	$\Delta P/P_0$
0	∞	0
1	126	$2.5\cdot10^{-5}$
5	74	$1.3\cdot10^{-4}$
10	59	$2.5\cdot10^{-4}$
20	47	$5.0\cdot10^{-4}$
50	34	$1.3\cdot10^{-3}$
100	27	$2.5\cdot10^{-3}$

assumed to be 3.6A for the numerical evaluation:

$$d\gamma=-(3RTka/\nu^3 v_f)d\nu \tag{9}$$

and

$$\gamma=\tfrac{3}{2}(RTka/v_f\nu^2)+\gamma_\infty, \tag{10}$$

where γ_∞ is the surface tension of the bulk liquid for $\nu=\infty$. Using the value $k=50$ as found by Bowers[2] for helium in the neighborhood of the λ temperature, and $\gamma_\infty=0.3$ dyne/cm (compare Keesom[16]), we get for P/P_0 between 1 and 0.6, i.e., for ν between ∞ and 3 layers, the values for γ_ν listed in Table I. This table shows the rapid increase of γ with decreasing ν for thin films. Inserting Eq. (9) into Eq. (8) leads to

$$Mgdh+V_f d[\gamma(1/r_h+1/r_0)]+(3RTk/\nu^4)d\nu=0, \tag{11}$$

with

$$1/r_h=(d^2h/dl^2)\frac{1}{(1+dh/dl)^{\frac{3}{2}}}. \tag{12}$$

[16] W. H. Keesom, *Helium* (Elsevier, Amsterdam-New York, 1942), p. 263.

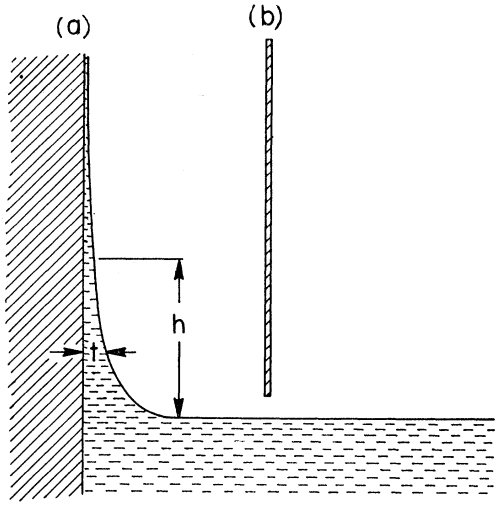

FIG. 1. (a) Schematic profile of the surface of a liquid on an infinitely long plane wall dipping into the liquid. (b) Thin wall not touching the liquid.

Equation (11) can be integrated in principle, at least numerically. However, in the case of helium and an infinitely long straight wall dipping into the liquid, the middle term of Eq. (11) can be neglected as $r_0=\infty$ and the minimum of r_h is greater than 10 cm in a region where $\nu>10$ and $\gamma<2$. We then get:[17]

$$\nu=[RTk/Mg]^{\frac{1}{3}}\cdot(1/h^{\frac{1}{3}}) \quad \text{or} \quad t=t_1/h^{\frac{1}{3}}, \tag{13}$$

and the numerical values of Table II.

The absolute values of the film thickness derived in this way from adsorption data of the *unsaturated* film are in surprisingly good agreement with the experimental results for the saturated film (compare the review given by Bowers[10]). This result is a confirmation of a view expressed in a previous paper[18] that the relation between film thickness, pressure, and temperature is essentially "classical" even in the He II region.

Column 3 in Table II gives the relative changes in gas pressure due to the gravitational field which are also the changes in equilibrium pressure of the film as a function of height h. As pointed out in the earlier paper,[18] experimental determinations of the film thickness are extremely sensitive to minute changes in P due to the asymptotic infinity of Eq. (1) near $P/P_0\sim1$. This is again reflected by the third column of Table II. The whole change in film thickness from infinity at $h=0$ to 34 layers at a height of 50 cm corresponds to a relative change of equilibrium pressure of 10^{-3}. A temperature difference of only 10^{-4} degree can produce the same change in pressure due to the steepness of the vapor pressure curve. Even in extremely carefully con-

[17] Combining Eq. (1) with $\ln(P/P_0)=-Mgh/RT$ for the change of gas pressure with height or considering the balance of forces: The surface tension has to increase by decreasing the thickness of the film in order to carry the weight of the film: $d\gamma=gt\rho_f dh$, and using Eq. (9) leads again to Eq. (13).

[18] L. Meyer, Phys. Rev. **93**, 655 (1954).

ducted experiments it is beyond the experimental accuracy to determine whether or not the inevitable heat influx from the top of the cryostat did not produce temperature differences of this order of magnitude over a length of 50 cm, i.e., gradients of 2.10^{-6} °K/cm. This consideration is confirmed by Bowers'[10] observation that the film thickness is extremely sensitive to radiation.

Any heat influx from the top of the cryostat producing temperature differences of only 10^{-5} degree would, therefore, cause the film thickness to decrease with height faster than given by Eq. (12) or Table II, so that the exponent of h must become greater than 0.33. Jackson's[9] value of 0.4 and Bowers'[10] and Picus'[11] value of 0.5 must therefore be considered as being consistent, within the errors of the experiments, with Eq. (13) or (2).

A small heat influx from the top has the additional effect that in the He II range the film starts flowing to the source of heat. Picus[11] found that the thickness of the film as a function of height is appreciably different for a flowing film than for a stationary film. This result is plausible because the kinetic energy of the motion should be included in a free energy consideration as used above to derive the film thickness.

Such a minute and practically undetectable heat influx can also cause great differences in film thickness when passing the λ point. The same heat influx produces in the He I region much greater temperature differences due to the poor heat conductivity of the film compared with the He II range and therefore reduces the film thickness in a much greater degree above than below the λ point.

Equation (13) gives not only the approximately right value for the thickness of the film, but also its temperature dependence. Bowers[10] and Jackson[9] report that the film thickness and its dependence on height is essentially independent of the temperature in the He II region.

Inserting Eq. (1) into the Clausius Clapeyron equation yields

$$d\ln(P/P_0)/d(1/T)=(\Delta H_f-\Delta H_0)/R=dk/d(1/T), \quad (14)$$

where ΔH_f is the differential heat of vaporization of the film (heat of adsorption) and ΔH_0 the heat of vaporization of the bulk liquid. The middle term of Eq. (14) represents the increase in heat of vaporization due to the van der Waals' forces of the wall and is essentially independent of temperature. As a consequence k has to be inversely proportional to T as borne out by the Teller-McMillan[19] approximation.[20] The factor $(RTk/Mg)^{\frac{1}{3}}$ in Eq. (13) and the equivalent factor in Eq. (10) are therefore independent of the temperature just as the experimental results require. The physical reason is that the balance between the attractive forces of the wall and the gravitational field which produces the film profile is more or less unaffected by the temperature.

There are many cases where the middle term in Eq. (12) arising from the curvature of the film surface does become important. Two of them shall be discussed:

1. Film transfer rates and film oscillations usually have been measured by using beakers of a diameter of ~0.1 cm. Such a small r_0 in Eq. (8) or (11) must influence the film thickness, and the asymmetry often found in filling or emptying the beaker might be caused by this fact as r_0 has the opposite sign at the outer wall compared with the inner wall.

2. It has been claimed that the so-called thick helium film is only formed on surfaces in contact with bulk liquid, and is absent on a specimen not touching the surface of the liquid as shown in Fig. 1(b).

If the specimen touches the liquid, we have the case discussed above and the thickness of the film should correspond to the values of Table II. If the specimen—which is usually a thin foil—does not touch the liquid, a rather sharp convex curvature of the order of 10^{-2} cm is created at the bottom which produces a relative increase in vapor pressure of the film—just as for small drops—of 10^{-4}. Column 3 of Table II shows that such a change in pressure reduces the film thickness at $h=0$ to about 75 layers where it would approach infinity if the specimens touched the liquid. Furthermore, a minute heat influx would also cause a radical change in film thickness when the specimen was pulled out of the liquid, as the heat reaching the specimen cannot be delivered to the bulk liquid as a sink and consequently one gets appreciably greater overheating.

Thanks are again due to Morrel H. Cohen for valuable discussions.

[19] W. G. McMillan and E. Teller, J. Chem. Phys. **19**, 25 (1951).

[20] The curve as drawn by Bowers (see reference 2) for $k=k(T)$ is near the λ point inconsistent with Eq. (14); however, a line obeying (14) can be drawn through his experimental points within the error of experiments.