ON THERMOCAPILLARY HYSTERESIS

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M. M. KUSAKOV, J. V. VEPAGUNTA (J. V. VEPAGUNTA)

ON THERMOCAPILLARY HYSTERESIS

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In works [1–5] a special case of capillary hysteresis was considered, which may be called capillary hysteresis of shape, since it pertains to capillary tubes of circular cross section varying with height. The question of capillary hysteresis, however, may be considered in a more general form.

We shall call capillary hysteresis the existence, for a single capillary, of several equilibrium heights of capillary rise corresponding to a minimum of the potential energy of the forces of gravity and surface tension acting on the liquid in the capillary. These equilibrium heights can be found from the joint solution of a system of two equations

$$h\rho g = 2\sigma\cos\theta/r,$$

$$\xi = f(h), \tag{1}$$

where h is the height of capillary rise of the liquid; ρ is the density of the liquid; σ is the surface tension of the liquid at its boundary with the saturated vapor; g is the acceleration due to gravity; θ is the contact angle for wetting of the capillary walls by the liquid; r is the radius of the capillary, and ξ is a quantity depending on the height h. For $\xi = r$ we obtain the previously considered capillary hysteresis of shape, and for $\xi = \theta$ or $\xi = \cos\theta$ we obtain capillary hysteresis of wetting; thus, system (1) is valid for liquids completely or partially wetting and nonwetting the walls of capillaries. In all these cases it is assumed that the temperature t is constant, and therefore $\sigma = \text{const}$ and $\rho = \text{const}$. Meanwhile, in most cases of practical interest, isothermal conditions are not fulfilled, in connection with which it is very important to consider the influence of a temperature gradient on the motion of a liquid in single capillaries or porous media.

Let us consider the simplest case of liquid motion in a single cylindrical capillary of circular cross section in the presence of a temperature gradient along the axis. If along the height of the capillary there exists some temperature distribution, i.e., t depends on h, then, obviously, σ and ρ also depend on h. The latter case, however, as a rule is of no interest, since for liquids any appreciable dependence of density on temperature is observed only near the critical temperature. Of greatest interest is the case when $\xi = \sigma$. This case of the existence of several equilibrium heights of capillary rise of a liquid as a consequence of the dependence of surface tension on temperature may be called thermocapillary hysteresis, existing only in that region of values of h in which system (1) has more than one joint solution. The effect of thermocapillary hysteresis should not be confused with the different heights of rise of a liquid at different temperatures, when system (1) has only one joint-

solution, i.e., the curve of the dependence of $2\sigma \cos\theta / r$ on h and the straight line of the dependence $h\rho g$ on h intersect at only one point.

The roots of system (1) correspond to those values of h at which the potential energy U of the liquid column in the capillary has an extremal value, i.e.,

$$\partial U / \partial h = 0. \tag{2}$$

By analogy with the case of capillary hysteresis of form [1], the real and positive roots $h_1, h_2, \dots, h_i, \dots$ of equation (2), for which $(\partial^2 U / \partial h^2)_{h=h_i} > 0$, correspond to heights associated with stable equilibrium. In this case $\partial(2\sigma \cos\theta / r)/\partial h < 0$; when $(\partial^2 U / \partial h^2)_{h=h_i} < 0$, these roots correspond to heights associated with unstable equilibrium, and then $\partial(2\sigma \cos\theta / r)/\partial h > 0$. The rise of the liquid in a cylindrical capillary occurs in the interval of values of h from 0 to h_1 or from h_i to h_{i+1}, if in this interval $\partial U / \partial h < 0$; for values of h corresponding to intervals for which $\partial U / \partial h > 0$, the rise of the liquid in the capillary can be achieved only at the expense of external work. The number of stable and unstable heights of liquid rise in the capillary depends only on the form of the function σ of h (i.e., on the law of temperature distribution along the height of the capillary) and on the radius of the capillary. With a linear and with any monotonic distribution of temperature along the height of the capillary, thermocapillary hysteresis is absent in a cylindrical capillary. If the form of the function σ of h, i.e., $2\sigma \cos\theta / r$ as a function of h, is known in advance (graphically or analytically) (for capillaries of circular cross section varying with height, moreover r depends on h, i.e., capillary hysteresis of form may also exist), then it is always possible (also graphically or analytically) to determine the range of values of h in which capillary hysteresis will be observed.

An experimental verification of these considerations was carried out in cylindrical capillaries with distilled water. The temperature gradient was produced by means of a circular wire ring tightly encircling the capillary tube, through which a current was passed.

For thin capillaries it may be assumed that there is no radial temperature distribution, i.e., that in planes perpendicular to the axis of the capillary the temperature is constant. When the capillary was raised, the heater approached the meniscus from the liquid side, and when it was lowered—from the air side.

Fig. 1. Dependences of $2\sigma/r$, $h\rho g$, and U on h during the rise of water in a cylindrical capillary ($2r = 0.029$ cm)

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The raising or lowering of the capillary was performed very slowly and was recorded with a precision cathetometer. In the first case the meniscus moved in accordance with the temperature distribution established in the capillary. From the height of capillary rise the capillary pressure $2\sigma/r$ was calculated (knowing from tabulated data the dependence of σ on t, one can, evidently, by means of such a "capillary method," construct a graph of the temperature distribution along the height of the capillary), and a graph of the dependence of $2\sigma/r$ on h was constructed. It was assumed in doing so that, with sufficiently slow displacement of the capillary, the liquid near the meniscus has time to assume the temperature of the inner wall of the capillary. In the experiment h corresponded to the displacement of the heater upward from the liquid side.

In Fig. 1, as an example (a cylindrical capillary for which $2r = 0.029$ cm), graphs of $h\rho g$ and $2\sigma/r$ are given. The straight lines a and b delimit the region in which thermocapillary hysteresis can possibly exist and be observed. Thus, if the heater is placed on the capillary in the region from point D to point E, then during the capillary rise of water a stopping of the meniscus is observed near point A (the equilibrium height h_1); and during artificial raising of the liquid in the capillary (by means of a slight reduction of the air pressure in the capillary) to slightly above point B of metastable equilibrium (height h_2), the liquid itself continues to rise–

rise to the point C (the equilibrium height h_3). The points A_1 and C_1 correspond to minima, and the point B_1 to a maximum of the potential energy U.

Figure 1 also shows the curve U, calculated from the relation

$$U = \frac{1}{2}\pi\rho g r^2 h^2 - \pi r^2 \int_0^h \frac{2\sigma}{r}\, dh, \tag{3}$$

where the integral $\int_0^h \frac{2\sigma}{r}\, dh$ was evaluated graphically from the experimental curve $2\sigma/r = f(h)$ (the point C_1 is conventionally assigned the zero value of the potential energy). For the capillary used, the calculated value of the greater height of rise $(h_3)_{\text{calc}} = 9.50$ cm corresponds to the experimentally observed height $(h_3)_{\text{exp}} = 9.66$ cm; similarly, for the smaller height of rise, $(h_1)_{\text{calc}} = 8.85$ cm and $(h_1)_{\text{exp}} = 8.39$ cm. Such agreement should be regarded as satisfactory. The small discrepancy in the second case is explained by the lower accuracy of the "capillary method" for measuring temperature in the region of the capillary filled with water.

Fig. 1. Dependences of $2\sigma/r$, $h\rho g$, and U on h during the rise of water in a cylindrical capillary ($2r = 0.029$ cm)

If the heater is brought closer to the meniscus from the air side, then, for the temperature distribution along the capillary considered above, the meniscus will descend. If the "potential barrier" is overcome by raising the liquid slightly above the point B, then subsequently the meniscus will rise under the action of surface-tension forces up to the point C.

For unit capillaries, the region (or regions) of existence of thermocapillary hysteresis depends on the character of the temperature distribution along the capillary axis, i.e., on the form of the function σ of h.

It is interesting to note that the depth of the "potential wells" in thermocapillary hysteresis is very small and in our experiments amounted to several hundredths of an erg. Thus, in observing thermocapillary hysteresis one is dealing with the measurement of very small energy effects.

In the case of a homogeneous porous medium in which there exists a stationary distribution of temperature along the vertical axis, thermocapillary hysteresis manifests itself in a change in the region of existence of equilibrium capillary-rise heights as compared with the case when the temperature is constant.

Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

Peoples' Friendship University
named after P. Lumumba

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Note: Figure translations are in progress. See original paper for figures.