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Surface Tensions from Detachment of Solid Rods

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Two methods for making surface tension measurements in liquid systems are analyzed theoretically. Both the pin method and the method of Wilhelmy are so-called detachment methods: the force necessary to detach a metal rod (circular or rectangular) from the liquid surface is obtained experimentally. The theoretical analysis involves a calculation of the maximum volume of liquid that is held up by the rod being equal to the detachment force. The surface tension of the liquid is determined by the detachment force, the dimensions of the rod, and, in case of the pin method, the density of the liquid.

Surface tension is given as energy per unit area of surface, or equivalently force per unit length. If the force necessary to detach a metal rod from the liquid surface is measured together with the circumference of the rod, one might try to compute the surface tension of the liquid from the following relation:

$$\gamma = \Delta W_{max}/A \tag{1}$$

Here
γ surface tension in dyne cm^{-1}
A circumference of the rod in cm
ΔW_{max} detachment force in dyne

The pin method [1] (rod with circular endface) and the Wilhelmy method [2,3] (rod with rectangular endface) have both been used for measuring surface tensions of liquid systems at room temperature and up to about 1000°C. ΔW_{max} has been measured by slowly lowering the liquid surface and simultaneously recording the weight of the rod. This weight exhibits a definite maximum just before the contact between the surface and the rod is broken, and ΔW_{max} is given as the difference between this maximum weight and the weight of the rod after the contact is broken.

More than thirty years ago Freud and Freud [4] showed theoretically that relations like eqn. (1), containing only the detachment force and the circumference, do not apply when a ring is detached from the surface of a liquid. It is the purpose of this paper to analyze, theoretically, the detachment of a rod (circular or rectangular) from a liquid surface. Previous investigators[1-3] have calculated surface tension values from eqn. (1), taking A to be the actual circumference of the rod, or alternatively a calibration constant.

For pins we will show that the surface tension is not given by eqn. (1), but that it can be calculated from knowledge of the detachment force, pin radius, and density of the liquid. For rectangular rods eqn. (1) gives a correct result, if edge effects are neglected.

THE PIN METHOD

Using the method of Freud and Freud,[4] the fundamental Laplace equation will be used to calculate the maximum volume of liquid that is held up above the surface by a circular rod. This volume is then connected to the experimental quantity, ΔW_{max}, through the relation

$$\Delta W_{max} = Vg\varrho \tag{2}$$

Here

V volume of liquid above undisturbed surface
ϱ density of the liquid
g constant of gravity

The Laplace equation for the shape of a liquid surface is

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{P}{\gamma} \tag{3}$$

where R_1 and R_2 are the principal radii of curvature at a point on the surface, and P is the pressure at this point relative to the pressure on the undisturbed plane surface (which in this case is the surface at infinite distance from the rod).

For surfaces of revolution [5]

$$\frac{1}{R_1} = \frac{u}{x} \text{ and } \frac{1}{R_2} = \frac{\mathrm{d}u}{\mathrm{d}x}$$

where $u = \sin\alpha$, α being the angle of the surface tangent with the x-axis. The level of the undisturbed surface coincides with the x-axis at an infinite distance from the rod, while the y-axis passes through the center of the rod.

The Laplace equation becomes:

$$\frac{u}{x} + \frac{\mathrm{d}u}{\mathrm{d}x} = -\frac{yg\varrho}{\gamma} \tag{4}$$

To obtain a general equation, the reduced variables y_r and x_r are introduced:

$$y_r = y/(2\gamma/g\varrho)^{\frac{1}{2}},\ x_r = x/(2\gamma/g\varrho)^{\frac{1}{2}} \tag{5}$$

Substitution into eqn. (4) gives:

$$\frac{u}{x_r} + \frac{\mathrm{d}u}{\mathrm{d}x_r} = -2y_r \tag{6}$$

The largest reduced volume of liquid that can be held up above the surface by the pin is

$$V_r = \frac{V}{(2\gamma/g\varrho)^{3/2}} = \pi \int_0^{y_r'} x_r^2 \, dy_r \qquad (7)$$

If the liquid wets the pin, the contact angle between the pin and the liquid surface will be zero. The integration, therefore, is performed from $y_r = 0$ to $y_r = y_r'$, where $u = 1$ and $x_r' = r_r$ (reduced pin-radius $r_r = r/(2\gamma/g\varrho)^{\frac{1}{2}}$). See Fig. 1.

Integration by parts of eqn. (7), and combination with eqn. (6) yields:

$$V_r = \pi r_r^2 \, y_r' + \pi r_r \qquad (8)$$

In order to find y_r', eqn. (6) must be solved. Since it is impossible to integrate this equation by means of known functions,[4] a Taylor expansion has been carried out. As initial values $y_r = u = 10^{-5}$ were selected,[4] while the initial

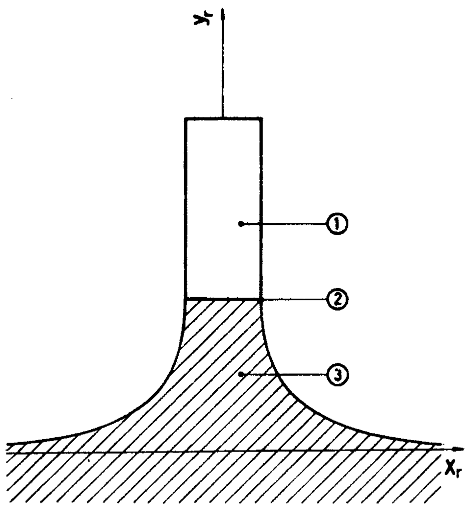

Fig. 1. The pin method. 1, surface tension rod; 2, the point (y_r', x_r'); 3, liquid.

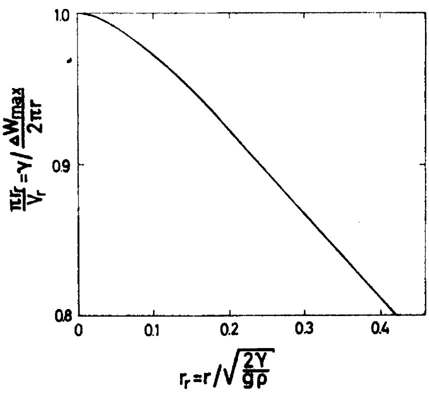

Fig. 2. The quantity $\pi r_r / V_r$ as function of the reduced pin radius r_r.

values for x_r were in the region between 5.4 and 7.5. Lower initial values for y_r and u did not produce significant changes in the results.

These numerical solutions of eqn. (6) made possible the determination of y_r' as a function of r_r from a least squares treatment:

$$y_r' = -1.282 \, r_r + 4.878 \, r_r^{1/2} - 4.770 \, r_r^{1/3} + 1.914 \, r_r^{1/4} \qquad (9)$$

Standard deviation < 0.5 % when

$$8 \times 10^{-3} < r_r < 7 \times 10^{-1}$$

According to eqns. (8) and (9), V_r is now a function of r_r only.

The relationship between the experimental quantity, ΔW_{max}, and the maximum volume of liquid that is held up above the surface by the pin, is:

$$\Delta W_{max} = Vg\varrho = (2\gamma/g\varrho)^{3/2}\, V_r\, g\, \varrho \tag{10}$$

Introducing $r_r = r/(2\gamma/g\varrho)^{\frac{1}{2}}$ in eqn. (10), and rearranging yields:

$$\frac{\gamma}{(\Delta W_{max}/2\pi r)} = \frac{\pi r_r}{V_r} \tag{11}$$

The quantity $\pi r_r/V_r$ is, insofar as its deviation from unity is concerned, a measure of the deviation from the simple, intuitive relation

$$\gamma = \Delta W_{max}/2\pi r \tag{12}$$

This is illustrated in Fig. 2.

It is seen that eqn. (11) may be applied to compute the surface tension value if ΔW_{max}, ϱ and r are known. Since r_r contains γ, an iteration procedure is necessary. The calculations are, however, greatly simplified if the dimensionless quantity r_r^3/V_r is considered:

$$\frac{r_r^3}{V_r} = \frac{(r/(2\gamma/g\varrho)^{\frac{1}{2}})^3}{\dfrac{V}{(2\gamma/g\varrho)^{3/2}}} = \frac{r^3}{V} = \frac{r^3}{\dfrac{\Delta W_{max}}{g\varrho}} \tag{13}$$

Therefore, $\pi r_r/V_r$ has been calculated as a function of r_r^3/V_r by a least squares treatment, and is given as:

$$\pi r_r/V_r = 0.992 + 2.564 \times 10^{-6}/(r_r^3/V_r) - 6.605\ (r_r^3/V_r) + 73.25\ (r_r^3/V_r)^2 - 454.0\ (r_r^3/V_r)^3 \tag{14}$$

Standard deviation $< 0.1\ \%$ when

$$4 \times 10^{-4} < r_r^3/V_r < 6 \times 10^{-2}$$

Thus, the surface tension can be calculated directly from r, ϱ, and ΔW_{max}, by means of eqns. (14), (13), and (11).

THE WILHELMY METHOD

When a rod with a rectangularly shaped endface is withdrawn from a liquid surface, the surface around the rod will no longer be a surface of revolution. Eqn. (6) is therefore not valid in this case.

If the assumption is made that the length L of the rectangle is much greater than the width B, we may write the following expression for the maximum reduced volume that is held up by the rod:

$$V_r' = 2 \int_0^\infty \int_0^{L_r} y_r\, dx_r\, dL_r \tag{15}$$

The x_r-axis coincides with the level of the undisturbed surface at an infinite distance from the rod. The y_r-axis passes through one of the short sides of the rectangle, and is normal to the rectangle (see Fig. 3). As before $1/R_1 =$

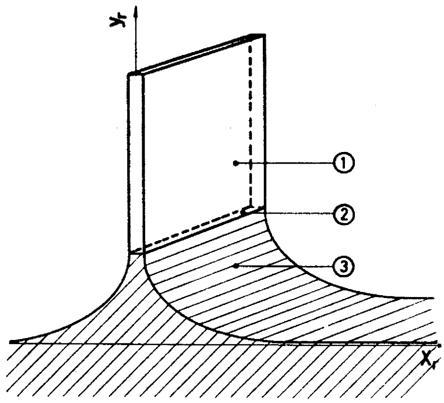

Fig. 3. The Wilhelmy method. 1, surface tension rod; 2, rectangular endface; 3, liquid.

$\mathrm{d}u/\mathrm{d}x_r$, but now $1/R_2 = 0$ because the sides of the rectangle are without curvature ($R_2 \rightarrow \infty$). The transformed and reduced Laplace equation in this case is:

$$\mathrm{d}u/\mathrm{d}x_r = 2y_r \tag{16}$$

(Strictly, the right side of eqn. (16) should be $-2y_r$, but the sign is not important in the following calculations.)

Combination of eqns. (16) and (15) gives:

$$V_r' = \int_0^1 \mathrm{d}u \int_0^{L_r} \mathrm{d}L_r = L_r \tag{17}$$

The total reduced volume that can be held up by the rod is therefore:

$$V_r = L_r + B_r \tag{18}$$

The only approximation implicit in eqn. (18) is that the edge effects have been neglected. Further:

$$\begin{aligned} \frac{\gamma}{\Delta W_{\max}/2(L+B)} &= \frac{2\gamma(L+B)}{V\varrho g} = \frac{2\gamma(L+B)}{(L_r+B_r)(2\gamma/g\varrho)^{3/2}g\varrho} \\ &= \frac{2\gamma(L+B)}{[(L+B)/(2\gamma/g\varrho)^{\frac{1}{2}}](2\gamma/g\varrho)^{3/2}\,g\varrho} = 1 \end{aligned} \tag{19}$$

Thus:

$$\gamma = \Delta W_{\max}/2(L+B) \tag{20}$$

The surface tension can consequently be calculated from $\Delta W_{\max}$, L, and B, by means of eqn. (20). The density of the liquid does not need to be known.

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