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Physics. — *"On the measurement of the capillary pressure in a soap-bubble."* By Prof. J. P. KUENEN. (Communication N°. 145*a* from the Physical Laboratory at Leiden).

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In the measurement of the pressure in a soap-bubble by means of an open liquid gauge the peculiar case may present itself, that the measurement becomes impossible owing to the condition becoming unstable. This fact accidentally came under my notice, when an attempt was being made to increase the accuracy of the measurement of the comparatively small pressure by the use of a micromanometer; in this instrument the construction of which is otherwise of no importance for the present purpose the pressure to be measured acts on a large liquid surface (about 4π cm^2) which on a change of pressure is displaced over the same distance, as if the instrument were a simple open water-gauge with two tubes of the same width. When this manometer was used, it appeared impossible to work with soap-bubbles of less than about 1 cm. diameter, as smaller bubbles always contracted of their own accord, though no leakage could be discovered in the apparatus, whereas with a gauge with narrow tubes a similar difficulty had never presented itself.

A consideration of the equilibrium-relations had to lead to the explanation of the phenomenon and it soon appeared, that it was connected with the change of volume in the gauge which accompanies the displacement of the liquid surface on a change of pressure. Starting from a condition of equilibrium between the surface-tension σ and the excess of pressure $p - p_0$ ($p_0 =$ atmospheric pressure), in which therefore $p - p_0 = \frac{4\sigma}{r}$ ($r =$ radius of bubble), and applying to the bubble a virtual change, say a diminution of the radius, the capillary pressure will increase and this will cause the liquid-surface in the gauge to descend, which in its turn involves an increase of the volume. Now the condition will certainly be unstable, if this increase of volume exceeds the diminution of volume given to the soap-bubble; because in the enlarged volume the pressure of the gas will be smaller and this decrease will cause a further contraction of the soap-bubble. It now also becomes clear, why the phenomenon was observed for the first time in using the wide gauge: the increase of volume which goes with an increase of pressure is much more prominent in this case.

One might be inclined to draw the conclusion, that the limit between stable and unstable must be found in that condition, where the two changes of volume referred to are equal to each other. This conclusion appears to be incorrect, however, when the condition for stability or non-stability is accurately established. The nature of the equilibrium depends upon, whether in a virtual contraction of the soap-bubble the pressure caused by the surface-tension increases less or more than the pressure of the gas, and the latter is given by BOYLE's law, if the temperature is supposed to remain constant. In the former case the gas-pressure prevails, when the bubble contracts, and the condition is stable, in the latter case the condition is unstable.

Calling the volume of the space from the orifice of the tube, on which the bubble is blown, to the liquid surface, when the pressures inside and outside are equal, v_0, the displacement of the liquid h and the cross-section of the manometer-tube O, and treating the bubble as a complete sphere, the total volume is

$$v = v_0 + \frac{4}{3}\pi r^3 + hO,$$

whereas, d being the density of the liquid in the gauge,

$$2hdg = p - p_0 = \frac{4\sigma}{r},$$

so that

$$v = v_0 + \frac{4}{3}\pi r^3 + \frac{2\sigma O}{rdg}.$$

The change of the capillary pressure is given by the relation

$$-\frac{d(p-p_0)}{dr} = \frac{4\sigma}{r^2},$$

whereas for the gas-pressure $pv = c$, so that

$$-\frac{dp}{dr} = -\frac{dp}{dv}\frac{dv}{dr} = \frac{c}{v^2}\left(4\pi r^2 - \frac{2\sigma O}{r^2 dg}\right) = \frac{p}{v}\left(4\pi r^2 - \frac{2\sigma O}{r^2 dg}\right)$$

and the condition will be stable or unstable, according to whether:

$$\frac{4\sigma}{r^2} \lessgtr \frac{p}{v}\left(4\pi r^2 - \frac{2\sigma O}{r^2 dg}\right).$$

The same result is obtained from the condition, that in stable, respectively unstable equilibrium the free energy ψ of a closed system at constant temperature is a minimum, respectively a maximum. In our case ψ may be written in the form:

$$\psi = 8\pi r^2 \sigma - c \log v + O h^2 dg + p_0 v,$$

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whence:

$$\frac{d\psi}{dr} = 16\,\pi\, r\, \sigma - \frac{c}{v}\frac{dv}{dr} + 2O\, h\, dg \frac{dh}{dr} + p_0 \frac{dv}{dr},$$

or after reduction

$$\frac{d\psi}{dr} = 16\,\pi\, r\, \sigma - (p - p_0)\, 4\,\pi\, r^2.$$

The condition of equilibrium $\frac{d\psi}{dr} = 0$ gives the relation $p - p_0 = \frac{4\sigma}{r}$, made use of above.

We have further:

$$\frac{d^2\psi}{dr^2} = 16\,\pi\,\sigma - (p - p_0)\, 8\,\pi\, r - \frac{dp}{dv}\frac{dv}{dr}\, 4\,\pi\, r^2 =$$

$$= -\,16\,\pi\,\sigma + \frac{p}{v}\left(4\,\pi\, r^2 - \frac{2\sigma O}{r^2 dg}\right) 4\,\pi r^2 \gtrless 0,$$

which leads to the same unequality as arrived at above.

This relation reveals the remarkable fact, that even without the *manometer the condition may be unstable, viz. when*

$$\frac{4\sigma}{r^2} > \frac{p}{v}\, 4\,\pi\, r^2 \quad \text{or} \quad r^4 < \frac{\sigma}{\pi}\frac{v}{p}.$$

The value of r is limited by the circumstance, that it cannot be smaller than the radius of the tube to which the soap-bubble is blown, and, as p is of the order 10^6, σ for a soap-solution being about 25, the unstable condition cannot be realized unless with a large volume v. In order to test the above result a carboy of 30 liters ($v = 30000$) was attached to the apparatus without gauge: in this case the condition becomes $r < 0.7$ cm. That the condition was unstable, was manifested in blowing the bulb in the fact, that, as soon as the bubble exceeded the half-sphere, it blew itself up quickly to a considerable size. In diminishing the bulb below the given limit by letting out air the unstable nature of the equilibrium showed itself less clearly. The bubble sometimes remained for a considerable time without appreciable change in size; this must be due to a retardation the nature of which was not fully explained: as a rule by tapping the tube the bubble could be made to contract in accordance with expectation.

As shown by the above complete relation, the addition of the gauge on which the second term on the right-hand side depends will make it possible to realize the unstable condition with a much smaller volume, the more easily the larger the section O of the manometer is. Calculation shows, that even with $v = 1000$ cc. the left hand side of the relation is much too small to have an effect, and the condition thus becomes with near approximation

$$4\pi r^2 \gtrless \frac{2\sigma O}{r^2 dg} \quad \text{or} \quad r^4 \gtrless \frac{\sigma O}{2\pi dg}.$$

In this case the condition for the transition to the unstable condition agrees, as is at once seen, with that mentioned in the beginning, that the change of volume of the bubble becomes smaller than that of the gauge.

In order to make the phenomenon even more prominent than with the open gauge, the latter was replaced by a large funnel which was connected to the apparatus and placed upside down in a large trough of water with its rim just below the water level. The area O' was now 64π cm^2 and moreover the displacement h was almost completely confined to the water-surface inside the funnel (as the level in the large trough does not change appreciably) and thus twice as large as with the open gauge with tubes of the same width. In this case $hdg = p - p_0$ and the condition becomes

$$r^4 \gtrless \frac{\sigma O}{\pi dg},$$

which with the numerical values given above leads to $r < 1.1$ cm. as the transition to the unstable condition. In agreement with this result the experiment showed, that the bubble could not be made smaller than 2 cm. in diameter without the bubble gradually beginning to contract.

The contraction continues, as long as the bubble is larger than a half-sphere; beyond this state r begins to increase; the capillary pressure thus begins to diminish and the contraction will cease, when the capillary pressure has become equal to the pressure exerted by the gas present. The condition can now but be stable, as a further contraction involves a diminution of the capillary pressure and therefore a diminution of the volume in the gauge and an increase of the gas-pressure.

By means of the above relations the further question may be solved whether an increase of c in the formula $pv = c$, i.e. an increase of temperature or of the quantity of gas, will make the bubble larger or smaller. The relation:

$$\frac{dc}{dr} = p\frac{dv}{dr} + v\frac{dp}{dr} = p\frac{dv}{dr} - v\frac{4\sigma}{r^2}$$

shows, that in the stable condition the bubble will increase and conversely in the unstable condition.