

The effect of the variation of surface tension with temperature on the motion of bubbles and drops

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The boundary conditions at the surface of a small bubble rising in a liquid are examined theoretically, and it is shown by order-of-magnitude arguments, which are confirmed by detailed calculation in a special case, that although surface-tension gradients must always exist around the bubble, they are too small to affect the motion appreciably unless surface-active substances are present. This is because gradients of surface tension imply gradients of temperature in a *pure* liquid, and these turn out to be always small near the bubble if they tend to zero at large distances from it. The same is true for drops of one fluid in another.

1. Introduction

Bubbles of gas rising in liquids are well known to behave like rigid spheres and obey Stokes's law if they are sufficiently small. As the size increases, there is a gradual transition until ultimately the interface between gas and liquid seems to become free of tangential stress. If the Reynolds number is still very small at this stage, the velocity of rise is $1\frac{1}{2}$ times that predicted by Stokes's law. The theory for this case is due to Hadamard and Rybczynski (independently); see Lamb (1932, Art. 337), or Levich (1962, §§ 70 and 81).

Bond (1927) suggested that the apparent rigidity of small bubbles was caused by surface-active impurities, dissolved in the liquid, being swept around to the rear of the bubble (i.e. from top to bottom), until the surface-tension gradient set up by the accumulation of impurity balanced the viscous traction around the bubble. With enough surface-active material, the surface would be brought to rest relative to the bubble. We shall refer to this as the 'surface contaminant' theory.

Afterwards, Bond & Newton (1928) put forward a 'surface energy' theory, stating that if the bubble were small enough and the surface tension high enough, insufficient energy would be available to stretch or compress elements of interfacial area, even in a pure liquid, and the surface would have to be at

(relative) rest. This explanation is also offered by Lane & Green (1956). However, Frumkin & Levich (1947; see also Levich 1962, § 71) believed that the 'surface energy' mechanism was theoretically impossible, but that the 'surface contaminant' one was satisfactory. Further consideration of the 'surface contaminant' mechanism is given in Farley & Schechter (1963).

In this paper it will be shown that the 'surface energy' argument is valid, and can indeed be reduced to the same form as that of Frumkin & Levich. The reason is that heat energy can be thought of as a surface-active solute in the liquid, whose solubility is proportional to the specific heat and whose surface activity is determined by the variation of surface tension with temperature. However, the 'bulk solubility' of heat in all liquids happens to be very high, and its surface activity relatively weak. As a result, the 'surface energy' mechanism is quite inadequate to explain the observed immobility of the surfaces of small bubbles. Frumkin & Levich were thus right to reject the theory, but for unconvincing reasons.

Similar arguments lead to the same conclusions for drops of one liquid moving in another or in a gas. The theory also applies to the case of a bubble held at rest by an externally imposed temperature gradient (Young, Goldstein & Block 1959). Here, too, it produces a non-vanishing, but very small, effect.

2. The surface energy mechanism

Consider an approximately spherical bubble of radius a , rising steadily at speed U in a liquid of density ρ , kinematic viscosity ν and surface tension γ , at absolute temperature T . Let $Ua/\nu = R$, the Reynolds number. We shall assume that the density ρ_g of the gas in the bubble is very small in comparison with ρ . For the bubble to be nearly spherical, both R and variations of γ must be sufficiently small, but we do not require that $R \ll 1$ unless the liquid is such that the sphericity condition implies it.†

Suppose the bubble's surface is free to move. Then the tangential component of velocity, in a frame of reference in which the centre of the bubble is at rest, is of order U downwards at the equator and tends to zero at the upper and lower poles. Elements of area on the upper half of the bubble will thus be growing, and on the lower half shrinking, at equal rates of total order of magnitude Ua .

To see what effect this stretching and shrinking of surface elements has on the temperature of the interfacial layer we must apply the first law of thermodynamics. If we assume that the transfer of heat between the interfacial layer (which is only a few molecular diameters in thickness) and the adjacent fluid is reversible we find that the heat δQ which must be added to an element of surface when its area increases from A to $A + dA$ is given by

$$\delta Q = d(EA) - \gamma dA,$$

where E is the internal energy of the interfacial layer per unit area. E is to close approximation a function of T alone so, on rearrangement, we have

$$(E - \gamma) dA = \delta Q - A(dE/dT) dT. \quad (1)$$

† Moore (1965) suggests that bubbles will be very nearly spherical if $R \ll (g\mu^4/\rho\gamma^3)^{\frac{1}{2}}$, and for many liquids the right-hand side can be $O(10^2)$.

Now from Zemansky (1957, Art. 14.5)

$$E - \gamma = -T(d\gamma/dT) > 0,$$

(for liquids other than liquid metals) so that we can deduce from (1) that the change in area of surface elements has two effects.

Because of the first term on the right in (1) heat will flow into the upper half of the interfacial layer and flow out of the lower half of the interfacial layer. This will tend to make the upper half of the interfacial layer colder than the surrounding fluid and the lower half warmer.

Because of the second term on the right, and because

$$dE/dT < 0,$$

there will be a tendency for the element to rise in temperature while it is stretching and fall in temperature while it is shrinking. This would make the interfacial layer hottest at the equator and coldest at the poles.

We shall show later that the second term on the right is negligible so that the first effect dominates. Thus the rate \dot{Q} at which heat must be supplied to an element of area A , changing at a rate \dot{A} , is

$$\dot{Q} = -T(d\gamma/dT) \dot{A}. \quad (2)$$

Moreover, in the absence of the second effect the temperature of the interfacial layer is such that the surface tension will be higher towards the top of the bubble. Thus a tangential stress is established which opposes the motion.

An upper bound for this stress can be found by placing an upper bound on the temperature differences which exist around the bubble. This can easily be done by ignoring heat transfer in the air and vapour inside it. If K denotes the thermal conductivity of the liquid, δ the thermal boundary-layer thickness, and if temperature variations around the bubble are of order ΔT , then

$$-T(d\gamma/dT) Ua \sim Ka^2 \Delta T / \delta,$$

or

$$\Delta T \sim -T(d\gamma/dT)(U\delta/Ka). \quad (3)$$

The tangential stress e_S due to variations of surface tension is then given by

$$e_S \sim \left| \frac{1}{a} \frac{d\gamma}{dT} \Delta T \right| \sim \left| \frac{TU\delta}{Ka^2} \left(\frac{d\gamma}{dT} \right)^2 \right|. \quad (4)$$

This is to be compared with the tangential stress e_V due to viscosity, for which

$$e_V \sim \mu U/a, \quad (5)$$

where μ is the dynamic viscosity of the liquid. Equation (5) is obvious if $R \lesssim 1$, and has been shown by Moore (1959) to be true also if $R \gg 1$ and the surface is effectively stress-free. We assume merely that (5) remains true for intermediate values of R .

The dimensionless ratio

$$\frac{e_S}{e_V} \sim \frac{\delta}{a} \frac{T}{\mu K} \left(\frac{d\gamma}{dT} \right)^2 = O\left(\frac{T}{\mu K} \left(\frac{d\gamma}{dT} \right)^2 \right), \quad (6)$$

because the thermal boundary-layer thickness δ is of order a or smaller. This ratio happens to be small for all liquids for which data are available (Hodgman

1960), its greatest value at 20 °C being 0.074, for acetone. For water the value is 0.011. Therefore the actual motion of the bubble should be only slightly different from that predicted for a bubble with uniform surface tension, and the large difference observed for small bubbles must be due to the effects of surface contaminants. This is our principal result.

The same dimensionless ratio as in (6) is reached if one starts from Levich's (1962) equations (74.13) and (75.7), which give his parameter γ_2 in the form

$$\gamma_2 = -\frac{2}{3} \frac{\delta}{a} \frac{\Gamma_0}{D} \frac{\partial \gamma}{\partial c_0}, \quad (7)$$

when the obvious error of sign is corrected. Here D is the diffusivity of the surface-active material in the liquid, Γ_0 is its surface concentration, and $\partial \gamma / \partial c_0$ the rate of change of surface tension with respect to concentration (c_0) of the material in the liquid. Putting in the values for heat, i.e.

$$D = K / \rho c_p, \quad \Gamma_0 = -T d\gamma / dT, \quad dc_0 = \rho c_p dT, \quad (8)$$

where c_p is the specific heat of the liquid, and the second equation is derived from the formula for entropy per unit area, we transform (7) to

$$\gamma_2 = \frac{2}{3} \frac{\delta T}{a K} \left(\frac{d\gamma}{dT} \right)^2. \quad (9)$$

Now Levich shows (his equations (74.10) and (74.11)) that if $\gamma_2 \ll \mu$ (which is the same as the condition that $e_s \ll e_v$ in our equation (6)) the motion of the bubble is practically the same as if $\gamma_2 = 0$, in agreement with our conclusion above.

For the case where R and $\rho c_p U a / K$ (the Péclet number) are very small we may obtain a precise result by using linearized equations. If ψ is the dimensionless Stokes (axisymmetric) stream function given by

$$\frac{u_r}{U} = \frac{1}{r^2 \sin \theta} \frac{\partial \psi}{\partial \theta}, \quad \frac{u_\theta}{U} = -\frac{1}{r \sin \theta} \frac{\partial \psi}{\partial r},$$

where (r, θ) are dimensionless spherical polar co-ordinates based on the centre of the bubble and (u_r, u_θ) the corresponding velocity components, then

$$D^4 \psi = 0, \quad \text{where} \quad D^2 = \frac{\partial^2}{\partial r^2} + \frac{\sin \theta}{r^2} \frac{\partial}{\partial \theta} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \right),$$

is the equation governing the fluid motion. Similarly, if τ is the dimensionless temperature perturbation given by

$$T_0 \tau = T - T_0,$$

T_0 being the fluid temperature far from the bubble, then, since convection is negligible,

$$\nabla^2 \tau = 0$$

is the equation governing the fluid temperature. The relevant boundary conditions as $r \rightarrow \infty$ are

$$\tau \rightarrow 0, \quad \psi \rightarrow \frac{1}{2} r^2 \sin^2 \theta,$$

corresponding to uniform temperature and uniform flow at infinity. At $r = 1$, the surface of the bubble, there are three boundary conditions, on normal velocity, normal heat flux and tangential stress. The first is obviously

$$u_r = 0 \quad \text{or} \quad \partial\psi/\partial\theta = 0.$$

For the second, since equation (2) gives

$$\dot{A} = A \operatorname{div}^* \mathbf{u},$$

$$K(\partial T/\partial n) = -T_0(d\gamma/dT)_0 \operatorname{div}^* \mathbf{u},$$

where n is the unit outward normal at the bubble and div^* represents a two-dimensional divergence taken over the bubble surface, or in terms of ψ

$$\frac{\partial\tau}{\partial r} = \frac{U}{K} \left(\frac{d\gamma}{dT} \right)_0 \frac{1}{\sin\theta} \left(\frac{\partial^2\psi}{\partial r \partial\theta} \right)_{r=1}.$$

Finally, the tangential stresses due to viscosity and variations in surface tension must balance, so that

$$(d\gamma/dT)_0 \operatorname{grad}^* T + \mathbf{p}_s = 0,$$

where grad^* is taken over the surface only and \mathbf{p}_s is the surface component of the viscous stress. Thus

$$\frac{\partial\tau}{\partial\theta} = \frac{\mu U}{T_0(d\gamma/dT)_0} \frac{1}{\sin\theta} \left[\frac{\partial}{\partial r} \left(\frac{1}{r^2} \frac{\partial\psi}{\partial r} \right) \right]_{r=1}.$$

The relevant solution can be obtained directly by elementary means as

$$\psi = (\frac{1}{2}r^2 + Ar + B/r) \sin^2\theta, \quad \tau = C \cos(\theta/r^2),$$

where $A = -\frac{3}{4} + \frac{1}{4}F, \quad B = \frac{1}{4} - \frac{1}{4}F, \quad C = -\frac{U}{2K} \left(\frac{d\gamma}{dT} \right)_0 F$

and $F = \left\{ 1 + \frac{T_0}{3\mu K} \left(\frac{d\gamma}{dT} \right)_0^2 \right\}^{-1}.$

It is worth noting that $F = 1$ corresponds to the case of zero boundary shear-stress (Hadamard's solution) while $F = 0$ to the case of zero boundary velocity (Stokes's solution). This shows that the absolute value of $(T_0/3\mu K)(d\gamma/dT)_0^2$ is a very good estimate of the proportional change in surface shear stress (and thus of rising velocity of the bubble) caused by surface-tension variations.

The drag on the bubble D , is given by

$$D = 6\pi a U \mu (1 - \frac{1}{3}F).$$

So far, we have considered only a liquid in which the temperature far from the bubble is uniform. If it is not, the bubble will tend to move towards warmer fluid, because the surface energy will then be decreased. This was shown by Young *et al.* (1959), who considered the case of a bubble held at rest against gravity by an appropriate temperature gradient. They ignored heat transfer into the surface layers of their bubbles, however, and their heat flux equation (8e) should thus have contained an extra term corresponding to our \dot{Q} . But it is readily shown that the error caused by neglecting it is of the same order as e_s/e_r above, which is small, and this accounts for the agreement between their theory and experiments.

3. Accuracy of the approximations

We now return to (1) to investigate the validity of the assumption that the second term on its right-hand side is negligible. Its ratio to the first term is

$$\begin{aligned} \frac{A(d^2\gamma/dT^2)\dot{T}}{A d\gamma/dT} &\sim \frac{a^2(d^2\gamma/dT^2)U\Delta T/a}{Ua d\gamma/dT} \\ &= O\left(\frac{TU}{K} \frac{d^2\gamma}{dT^2}\right), \end{aligned} \quad (10)$$

where (2) has been used to estimate ΔT . As $K/(Td^2\gamma/dT^2)$ is a velocity of order 10^5 cm/sec or more for most ordinary liquids, and U is of order 40 cm/sec or less (Haberman & Morton 1953) for bubbles in which surface tension is relevant at all in determining the motion, the right-hand side of (9) can be taken to be very small, as required. The approximation is, in effect, that the behaviour of the surface is so nearly isothermal that the variation of internal energy of the interfacial layer with temperature is negligible.

The above estimate requires some knowledge of $d^2\gamma/dT^2$; we used the power-law variation of γ given by Zemansky (1957). This is only approximately true for real liquids, but the inaccuracy can hardly be great enough to upset the result.

4. Conclusions

In a pure liquid with no dissolved surface-active substances, the variations in surface tension around small bubbles, while not vanishing (as Levich appears to claim) are too small to slow down internal circulation by the observed amounts. Levich's own analysis can be used to support this result.

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