The calculation of surface tension for simple liquids

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Abstract. We calculate surface tension using the Kirkwood–Buff theory, assuming a smooth variation of density between liquid and vapour (in contrast to the Fowler theory, where the density changes abruptly), and approximating the radial distribution function by its liquid value throughout the transition zone. Comparison with experiment enables us to estimate the thickness of the interface, for which we obtain values in fair agreement with those given by other theories.

1. Introduction

The theory of Kirkwood and Buff (1948, see also Buff 1955), provides a rigorous formalism which enables the surface tension γ of simple liquids to be calculated, provided the interatomic potential $\phi(r)$, and the two-particle distribution function $n_2(r_1, r_2)$ in the liquid–vapour region are known. However, the latter quantity is not well understood, so that approximations must be made if the theory is to be used. The simplest assumption is that the fluid properties change abruptly from their liquid to their vapour values; if, in addition, the vapour density is set equal to zero, then the Kirkwood–Buff formula reduces to an earlier expression due to Fowler (1937), which has recently been calculated for a number of fluids using modern data by Shoemaker *et al* (1970), who obtain agreement with experiment to within 25% for all cases except neon.

In this paper we approximate to $n_2(r_1, r_2)$ in a rather more realistic way, by writing

$$n_2(r_1, r_2) \simeq n(r_1)n(r_2)g(|r_2 - r_1|) \tag{1}$$

where $n(r)$ is the density of the fluid at r and $g(r)$ is the radial distribution function of the bulk liquid. The formula (1) was first suggested by Green (1960), and has recently been discussed and applied by Berry and Reznek (1971). The exact Kirkwood–Buff formula takes on a simple form when (1) is used, if we take the density as $n(z)$ where z is a coordinate perpendicular to the interface, $z \gg 0$ being in the vapour, $z \ll 0$ in the liquid, and $z = 0$ somewhere in the interface.

By further assuming the simple exponential form

$$n(z) = n_0\left(1 - \frac{\exp(+z/L)}{2}\right) \qquad z < 0$$

$$= \frac{n_0}{2}\exp\left(-\frac{z}{L}\right) \qquad z > 0 \tag{2}$$

for the density, we obtain a formula for γ containing the single adjustable parameter L,

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which is a measure of the thickness of the density transition zone. We estimate L by comparing the experimental values of γ with our formula, and obtain results in fair agreement with those of Eyring *et al* (1964), and Egelstaff and Widom (1970), who estimate the same quantity by completely different methods.

2. Theory

In the theory of Kirkwood and Buff (1948), the surface tension γ is calculated directly, as the tangential force acting across a vertical strip of unit width. If we define

$$\mathbf{R} = \mathbf{r}_2 - \mathbf{r}_1 = (X, Y, Z)$$

then their result can be expressed as an integration over the two positions $\mathbf{r}_1$ and $\mathbf{r}_2$ at which the two-particle distribution function is evaluated, namely (Buff 1955)

$$\gamma = \frac{1}{2} \int_{-\infty}^{\infty} dz_1 \int \int \int d\mathbf{R} n_2(z_1, \mathbf{R}) \frac{d\phi(R)}{dR} \frac{X^2 - Z^2}{R}. \tag{3}$$

The idea underlying this formula is that the stress tensor is anisotropic in the liquid–vapour transition region; this approach to surface tension theory has pedagogical advantages over formally equivalent arguments involving surface energy, as has been emphasized by one of us (Berry 1971).

In order to use the approximation (1) in the basic formula (3), we realise that equivalence of X and Y enables us to write

$$X^2 - Z^2 = \tfrac{1}{2}(R^2 - 3Z^2)$$

and that the $\mathbf{R}$ integration can be written in cylindrical–spherical coordinates as

$$\int \int \int d\mathbf{R} = \int_0^{2\pi} d\Phi \int_0^{\infty} dR R \int_{-R}^{R} dZ.$$

Substitution of the approximation (1) into (3), and use of these relations, followed by an integration by parts, then gives

$$\gamma = \frac{\pi}{2} \int_0^{\infty} dR \frac{d\phi(R)}{dR} g(R) \left(- \int_{-R}^{R} dz (R^2 z - z^2) \int_{-\infty}^{\infty} dz_1 \frac{dn(z_1)}{dz_1} n(z_1 + z) \right). \tag{4}$$

Any reasonable density profile may be employed to calculate γ, and we choose the simple exponential form given by equation (2). After some lengthy algebra, this yields

$$\gamma = \frac{\pi n_0^2 L^4}{8} \int_0^{\infty} dR g(R) \frac{d\phi(R)}{dR} \left\{ \frac{R^4}{L^4} - \frac{8R^2}{L^2} + 72 \right.$$
$$\left. - \exp\left(-\frac{R}{L} \right) \left(\frac{4R^3}{L^3} + \frac{28R^2}{L^2} + \frac{72R}{L} + 72 \right) \right\}. \tag{5}$$

This expression reduces for $L = 0$ to the result of Fowler (1937)

$$\gamma = \frac{\pi n_0^2}{8} \int_0^{\infty} dR g(R) \frac{d\phi(R)}{dR} R^4. \tag{6}$$

3. Calculations

In order to apply equations (5) or (6), it is necessary to know the intermolecular potential $\phi(R)$. We assume this to be of the Lennard–Jones form

$$\phi(R) = 4\epsilon\left\{\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right\}.$$

We calculate γ for nitrogen, oxygen, methane, neon and argon in their own vapours, at temperatures for which $g(R)$ data are available. The formulae (5) and (6) are very sensitive to the precise values of ϵ and σ, so we follow Shoemaker *et al* (1970) and calculate these parameters from measurements of the saturated vapour pressure p and the configurational energy U at the temperatures with which we are dealing. Then ϵ and σ are given exactly by

$$\epsilon = \frac{S_{10}(p - n_0 kT + 4n_0 U/N_0)^2}{(4n_0 S_4)^2 \pi (p - n_0 kT + 2n_0 U/N_0)}$$

$$\sigma = \left(\frac{S_4(p - n_0 kT + 2n_0 U/N_0)}{S_{10}(p - n_0 kT + 4n_0 U/N_0)}\right)^{1/6}$$

where

$$S_n = \int_0^\infty \frac{g(R)}{R^n}\,\mathrm{d}R$$

and N_0 is Avogadro's number.

As our source of data we used the compilations in 'simple dense fluids' (Frisch and Salsburg 1968) for all cases except argon, whose values of $g(R)$ were provided by Clayton (unpublished).

Using these data, the surface tensions γ were calculated from equation (5) as a function of L, and the results plotted as figure 1; it is seen that all the curves exhibit a maximum when L is somewhat less than unity. The points where the experimental values of γ intersect the curves are marked by circles (where there are two possible points, the one with the larger, more physically realistic, value of L is taken). These values of L are listed in table 1, together with the experimental value (γ_{exp}) of surface tension, and the value ($\gamma(0)$) given by the Fowler approximation, which corresponds to the case $L = 0$. The differences between our values of $\gamma(0)$ and the values calculated by Shoemaker *et al* (1970) are insignificant except for the case of argon, where we use different data.

The experimental measurements of γ are subject to uncertainties of at most $1\cdot6\%$ for all cases (Frisch and Salsburg 1968, chap 2) except neon where we certainly expect the error to be less than 3% (1 significant figure in table 1). In terms of the deduced value of L, these experimental errors imply an uncertainty about $0\cdot2$ Å for neon, and $0\cdot1$ Å for the other fluids.

We take $3L$ as the thickness of the transition zone, and obtain an estimate m_1 (table 1) for the number of molecular layers by dividing by the intermolecular distance D, given by

$$D = \left(\frac{\text{molecular weight}}{\text{density} \times N_0}\right)^{1/3}.$$

This expression for D, which implies a simple cubic structure, was chosen, rather than the slightly larger values corresponding to the first peak in the radial distribution function,

because we want to compare our values m_1, with the number of layers m_2 (table 1) which we estimated from the density curves calculated by the 'method of significant structures' (Eyring *et al* 1964), which is a lattice theory. We have also included in table 1 the values m_3 for the number of layers derived by Egelstaff and Widom (1970), on the basis of an interpretation of the constancy of the product of γ and the isothermal compressibility for a wide range of substances near their triple points.
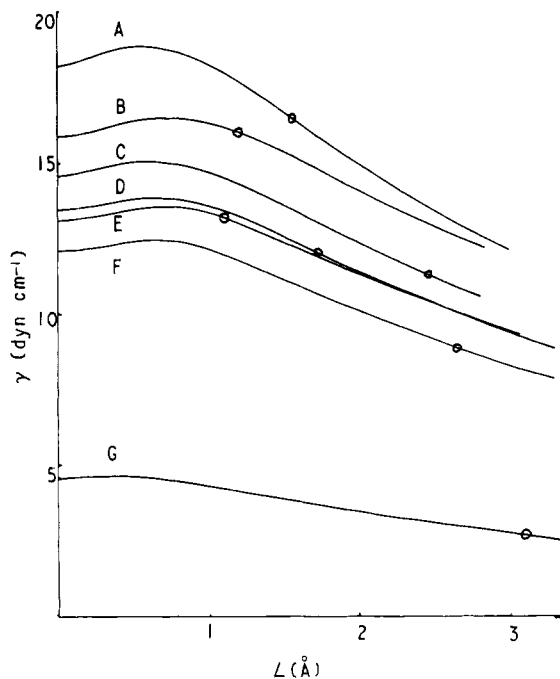

Figure 1. Calculated surface tension (γ) against interfacial thickness (L). A Oxygen at 77 K; B methane at 96 K; C methane at 121 K; D nitrogen at 64 K; E nitrogen at 77 K; F argon at 84·3 K; G neon at 33·1 K. Open circles are the experimental values of γ.

Table 1

Substance	Temperature (K)	γ_{exp} (dyn cm^{-1})	$\gamma(0)$	L(Å)	D(Å)	$m_1 = 3L/D$	m_2	m_3
Nitrogen	64	12·0	13·42	1·73	3·8	1·36	0·8	1·3
Nitrogen	77	8·9	12·08	2·65	3·9	2·03	1·3	
Oxygen	77	16·5	18·33	1·56	3·5	1·34		0·9
Methane	96	16·0	15·90	1·2	3·9	0·92	0·8	
Methane	121	11·3	14·60	2·45	4·0	1·83	1·3	
Neon	33·1	2·7	4·49	3·1	3·1	3·0		
Argon	84·3	13·2	13·10	1·1	3·6	0·92	0·9	1·6

4. Discussion

The curves in figure 1 suggest that those cases (methane at 96 K and argon at 84·3 K) where the Fowler approximation is in very close agreement with experiment are fortuitous.

From table 1 it is clear that there is a fair order of magnitude agreement between the number of molecular layers in the interface as estimated by us (m_1), Eyring *et al* (1964) (m_2), and Egelstaff and Widom (1970) (m_3); however, our interfacial thicknesses are generally rather larger than those predicted by the other theories. In the cases of nitrogen and methane, L and m_1 (and m_2) increase with temperature, as they surely must in order to account for the considerable decrease in γ.

The case of neon, where γ is very small, provides an interesting test of our approach to surface tension theory. The Fowler approximation grossly overestimates γ (table 1) and it is, therefore, necessary (figure 1) to take a rather large value for the interfacial thickness. This is exactly what one would expect, in view of the relative weakness of the intermolecular potential in neon ($\epsilon_{neon}/\epsilon_{argon} \simeq 0.25$). The small value of γ can thus be explained within a purely classical framework provided the Fowler approximation is not made, and it is not necessary to invoke quantum effects, as suggested by Shoemaker *et al* (1970). (Such effects, while perhaps just appreciable in neon (Egelstaff 1967), would certainly not be expected to grossly alter the value of γ.)

Finally we must emphasize that our method, and also the Fowler approximation, would yield nonsensical answers if the Lennard–Jones parameters were not estimated in a selfconsistent way, from measurements on the liquid at the temperature under consideration, as indicated by Shoemaker *et al* (1970).

Acknowledgments

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