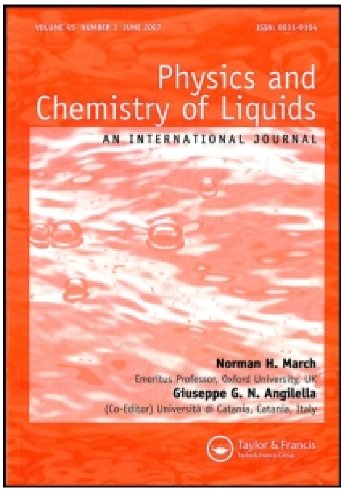

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Letter

The Width of the Liquid-Vapour Interface in a Van der Waals Fluid

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It is shown that the simplest Van der Waals description of a fluid leads to realistic liquid-vapour interfacial widths for argon and mercury.

If σ is the surface tension and κ_T is the isothermal compressibility of a liquid, then it is an experimental fact[1,2] that $\sigma\kappa_T$ is fairly constant (within a factor of about 3) for a wide variety of cases near their triple points, despite the wide variability of the individual factors. Such a simple and general result should be capable of a similar theoretical explanation and the work, for example, of Widom,[3] Bhatia and March[4] and Mon and Stroud[5] has been thus motivated and with considerable success. In such work $\sigma\kappa_T$ emerges as a measure of the liquid-vapour interfacial width l which leads one then to focus upon $l/\sigma\kappa_T$.

The framework within which recent theoretical work has been performed was proposed by Van der Waals,[6] rediscovered by Cahn and Hilliard[7] and recently reviewed by Evans.[8] In its simplest form it expresses the surface tension through the variational functional

$$\sigma = \int [f(n) - \mu n + P]\,\mathrm{d}z + \tfrac{1}{2}A \int \left(\frac{\mathrm{d}n}{\mathrm{d}z}\right)^2 \mathrm{d}z \tag{1}$$

where z is measured perpendicular to the flat surface, $n(z)$ is the local number density, f is the Helmholtz free energy density, μ is the chemical potential and P is the pressure. In reality, the coefficient A should be written as $A(n)$ inside the integral sign, when it can be defined in terms of the direct correlation function,[9] and there should also be higher-order gradient terms.[6,8] But motivated as we are by the universality of the experimental result, we neglect the higher terms and take A to be density-independent but unknown (*a priori*). Some general theoretical justification for doing this is provided by Mon and Stroud and by Henderson.[10]

Focussing, therefore, on Eq. (1), the corresponding Euler equation is $A\,\mathrm{d}^2n/\mathrm{d}z^2 = (\mathrm{d}f/\mathrm{d}n) - \mu$ and this may be integrated to give

$$\frac{A}{2}\left(\frac{\mathrm{d}n}{\mathrm{d}z}\right)^2 = f(n) - \mu n + P \equiv \xi^2(n). \tag{2}$$

For a specified $f(n)$, one can readily evaluate $\xi(n)$ and then

$$\sigma/\sqrt{2A} = \int_{n_v}^{n_l} \mathrm{d}n\ \xi(n);\ \sqrt{2/A}\,l = \int_{n'}^{n''} \mathrm{d}n/\xi(n) \tag{3}$$

where n_v and n_l are the bulk vapour and liquid densities and $n' = 0.1n_l + 0.9n_v$ and $n'' = 0.9n_l + 0.1n_v$ for a 10–90 width. At this stage one sees that though σ and l both depend on A, which will vary from system to system and with temperature, their ratio does not.

Once again, for reasons already discussed, we opt for universality and choose the Van der Waals description of a fluid so that, in the usual notation and with $x = bn$,

$$\frac{bf}{kT} = \left[\ln\left(\frac{\lambda^3}{b}\right) - 1\right]x - x\ln\left[\frac{(1-x)}{x}\right] - \left(\frac{a}{bkT}\right)x^2 \tag{4}$$

(The thermal wavelength λ is included in (4) for completeness but drops out of $\xi(n)$). Numerical results thus found are shown in Figure 1.

Over the range $0.35 \lesssim T/T_c \lesssim 0.9$, which covers virtually all relevant cases, we find each of l/σ and κ_T to vary by more than two orders of magnitude and yet their ratio $l/\sigma\kappa_T$, by comparison, varies very little. Mon and Stroud also obtain a slowly varying result

$$\left(\frac{l}{\sigma\kappa_T}\right)_{MS} = 26.4\left(1 - \frac{n_v}{n_l}\right)^{-2} \tag{5}$$

but, in contrast with ours, this is a monotonically rising function of T. An equivalent alternative method of making this comparison is shown in Figure 2 where $(l/\sigma\kappa_T)(1 - n_v/n_l)^2$, calculated entirely from the Van der Waals approach, is displayed.

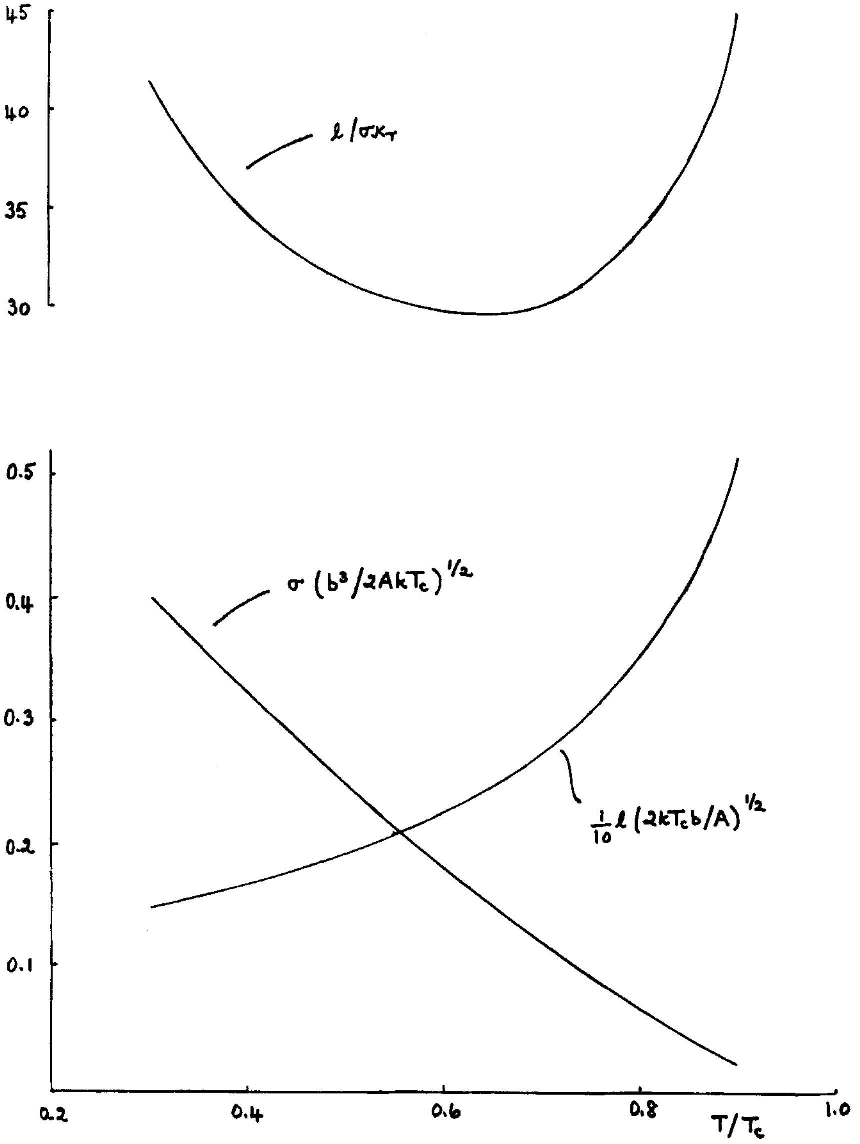

FIGURE 1 Surface tension (σ), 10–90 vapour-liquid surface width (l) and $l/\sigma\kappa_T$ (where κ_T is the isothermal compressibility) for a Van der Waals fluid. The parameters a, b and T_c are connected by the usual relationship $kT_c = 8a/27b$.

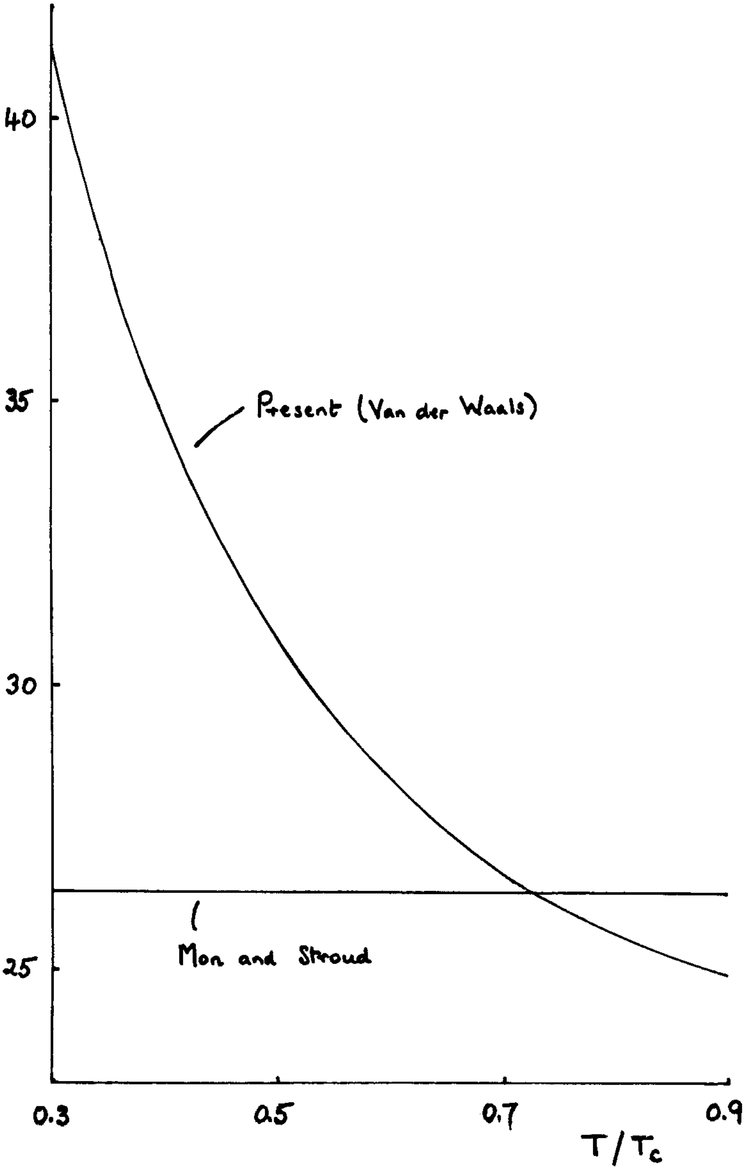

FIGURE 2 $(1/\sigma\kappa_T)(1 - n_v/n_l)^2$ calculated from the Van der Waals theory of this paper compared with the constant (26.4) Mon–Stroud result.

To test these results, we turn first to argon ($T_c = 150.9$ K) where measured widths have been reported[11] at 90 and 120 K. With the aid of Figure 1 and the observed surface tensions[12] and compressibilities[13] we obtain the results shown in Table 1. (Incidentally, from the basic theory of Yang *et al.*[9] and the reasonable supposition that n at maximum dn/dz is insensitive to temperature, we might expect $A \propto T$. On this assumption, Figure 1 gives $\sigma_{90}/\sigma_{120} = 2.4$ compared with the observed 2.3).

The only other measurement of l of which we are aware is by Lu and Rice[14] on mercury at 298 K. Mercury is not a Van der Waals fluid (see, for example, Neale, Cusack and Johnson)[15] so that the above description is not obviously applicable. Nevertheless, in the spirit of Mon and Stroud's approach, we might regard the Van der Waals a and b merely as parameters to be chosen so as to provide, at the constant temperature of interest, a reasonably accurate extrapolation of the free energy from the normal bulk material (for which measured data are usually available) to the centre of the profile. We may determine the parameters by fitting the observed pressure P and compressibility κ_T to the observed density n_l and thereby obtain

$$\frac{T_{c\,\mathrm{eff}}}{T} = \frac{8}{27}\left\{\frac{(\sqrt{c}+\sqrt{1+c})^2}{\sqrt{c(1+c)}} - \frac{P}{n_l kT}\left[1+\sqrt{\frac{c}{1+c}}\right]\right\}$$

where $c = n_l kT/(\kappa_T^{-1} - 2P)$. Thus, in the present case, we find $T_{c\,\mathrm{eff}} = 551$ K and then Figure 1, together with the observed $\kappa_T = 4.0 \times 10^{-12}$ cm^2/dyne (quoted by Weast)[16] and the observed $\sigma = 485$ dyne/cm (quoted by Allen)[17] yield the further entry in Table 1. The above extrapolation, though in keeping with the philosophy of much current work, nevertheless has its hazards and so the argon results (both of ourselves and of Mon and Stroud) should carry more weight.

Table I suggests that the present approach is of comparable accuracy with that of Mon and Stroud. Theoretically, their weakest link is their ansatz

TABLE I

	l (Mon & Stroud)	l (Present)	l (Observed)
Ar (90 K)	7.45	8.3	7.9 ± 0.5
Ar (120 K)	11.85	12.9	15.2 ± 1.0
Hg (298 K)	5.15	6.0	6.2 ± 0.5

Interfacial widths l in Å Beaglehole states that his Ar results are conceivably low by 10% at 90 K and 3% at 120 K. Lu and Rice report a width based on the maximum slope of a density profile which they conclude is consistent with a tanh shape; we have therefore, multiplied their result by ln 3 = 1.1 to obtain a 10–90 width for consistent presentation.

for the thermodynamic potential which forces a simple but over-symmetric tanh profile solution of Eq. (2). Ours is the use of the Van der Waals equation of state. In this respect such calculations as those of Ebner, Saam and Stroud[18] and of Telo da Gama and Evans,[19] which involve interatomic potentials, direct correlation functions, etc., are in principle better, although in practice they are not so amenable to the above general type of analysis.

It is unfortunate that all three comparisons shown in Table 1 are for effectively high temperatures ($T/T_c = 0.60, 0.80$ for Ar, 0.54 for Hg) and here our results and those of Mon and Stroud are quite similar. At lower temperatures, by contrast, their $l/\alpha\kappa_T$ (recall Eq. (5)) falls to 26.4 whereas ours (Figures 1, 2) is rising to much higher than this. For example, for oxygen at its triple point, $T/T_c = 0.35$ so that we predict $l/\sigma\kappa_T = 38$ for this case. An experimental test would be very desirable.

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