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Determination of surface thickness assuming a linear-density profile

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Assuming a one-parameter model for the two-particle distribution function of a surface, one can choose a value of the "width parameter" to yield a correct surface tension. In order to then identify the width of the surface layer with the value of the width parameter, as is often done, one can check the validity of the model by verifying that other properties (e.g., surface energy) are correctly calculated, or, as proposed herein, by demonstrating that different formulas for the surface tension give identical results. A new formula is derived, and the relation between the different formulas discussed. Calculations are performed for the Ar system. For the model used, no choice of the parameter can yield identical results for both ways of calculating surface tension. This points to problems in the interpretation of the width parameter. Misleading results may be obtained if one- and two-particle distributions not related by the Born-Green-Yvon equation are used together.

I. INTRODUCTION

For most systems studied, it now appears¹ that the variation of density through the region of a vapor-liquid interface is monotonic. A suggestion of Fitts² for determining the width of the interfacial region is thus applicable: Assume a monotonic form for the density variation, including a parameter representing the width, and find the value of the parameter required to give agreement of the calculated surface tension with the experimental value. Fitts applied this method to ³He and ⁴He. For identification of this parameter with the width of the interfacial region, however, one should at least check that, with the same value for the parameter, the model used can give some other property correctly. Shih and Uang³ used surface energy as a second property for Ar, and showed that, with a single value of the width parameter, both surface energy and surface tension could be calculated in agreement with experiment.

In the present paper, I point out that the second property could be surface tension itself, as calculated by a different formula. The formula is derived and calculations are carried out for Ar with a "linear density profile." It is found that it is impossible to obtain identical surface tension with both formulas. This throws doubt on any conclusions based on interpretations of the model used.

The surface energy is given⁴⁻⁶ by the expression (for a multicomponent system)

$$U = \frac{1}{2} \sum_{ij} \int \Gamma_{2ij}(\vec{r}_{12}) \phi_{ij}(r_{12}) d\vec{r}_{12}. \quad (1)$$

Here i and j sum over components, the interaction potential ϕ_{ij} between a particle of species i and a particle of species j is assumed to depend only on the interparticle distance, and the surface excess

two-particle density is

$$\Gamma_{2ij}(\vec{r}_{12}) = \int_{-\infty}^{\infty} dz_1 [\rho_{ij}^{(2)}(z_1, \vec{r}_{12}) - \rho_{ij}^{\text{bulk}}(z_1, \vec{r}_{12})]. \quad (2)$$

We consider the interface between a liquid and its vapor with the equimolar dividing surface^{4,6} at $z = 0$; $\rho_{ij}^{(2)}$ is the two-particle distribution function for species i and j , and

$$\rho_{ij}^{\text{bulk}}(z_1, \vec{r}_{12}) = \rho_{ij}^{(2,l)}(r_{12})[1 - \Theta(z_1)] + \rho_{ij}^{(2,v)}(r_{12})\Theta(z_1), \quad (3)$$

with $\Theta(z)$ the unit step function, and with $\rho_{ij}^{(2,l)}$ the two-particle distribution function for bulk liquid and $\rho_{ij}^{(2,v)}$ that for bulk vapor. We assume

$$\rho_{ij}^{(2)}(z_1, \vec{r}_{12}) = \rho_i^{(2,l)}(r_{12})f(z_1)f(z_2), \quad (4)$$

with $f(z)$ the one-particle density and

$$\rho_{ij}^{(2,l)}(r_{12}) = \rho_i \rho_j g_{ij}(r_{12}),$$

where ρ_i is the density of species i , and g_{ij} is the bulk-liquid correlation function between species i and j [$g_{ij}(r) \rightarrow 1$ for $r \rightarrow \infty$]. The vapor density is neglected.

These assumptions permit all calculations to be made in terms of properties of the bulk liquid, which are assumed known. While more sophisticated models have been used, they require considerably more information.⁷ The choice of $1 - \Theta(z)$ for $f(z)$ in Eq. (4) was suggested by Fowler⁸ and used by Kirkwood and Buff⁶ in their basic calculations for the argon surface. The linear density profile considered below corresponds to

$$f(z) = 1 - \Theta(z) + g(z), \quad (5a)$$

where

$$\begin{aligned}
g(z) &= (-z-d)/2d \quad \text{for } -d < z < 0 \\
&= (-z+d)/2d \quad \text{for } 0 < z < d \\
&= 0 \quad \text{otherwise.}
\end{aligned} \tag{5b}$$

The parameter d is to be identified with the half-width of the interfacial region. Other one-parameter forms for $f(z)$, to be used in Eqs. (1)–(4), have been suggested.⁹

II. SURFACE-TENSION FORMULAS

One definition for the surface tension γ is obtained by replacing ϕ_{ij} by $\phi'_{ij} x_{12}^2/r_{12}$ in Eq. (1). However, the resulting expression for γ is not the expression normally used. Instead, one notes that, because of the properties of ρ_{ij}^{bulk}

$$\frac{1}{2} \sum_{ij} \int d\tilde{\mathbf{r}}_{12} \rho_{ij}^{\text{bulk}}(z_1, \tilde{\mathbf{r}}_{12}) \frac{\phi'_{ij} x_{12}^2}{r_{12}} = P_x = P_z, \tag{6}$$

where P_x and P_z are components of the pressure, and are equal and independent of position in an isotropic bulk fluid. The exact two-particle distributions for the interface make the z component of the pressure (but not the x component) equal at any point in the interface to the pressure of either of the bulk phases,^{4,10,11} as required by mechanical equilibrium (this is guaranteed by the Born-Green-Yvon equation). Therefore one may use P_z for the quantity on the left-hand side of (6) which appears in the expression for the surface tension, obtaining

$$\begin{aligned}
\gamma &= \frac{1}{2} \sum_{ij} \int_{-\infty}^{\infty} dz_1 \int d\tilde{\mathbf{r}}_{12} \rho_{ij}^{(2)} \frac{\phi_{ij} x_{12}^2}{r_{12}} - \int_{-\infty}^{\infty} dz_1 P_z \\
&= \frac{1}{2} \sum_{ij} \int_{-\infty}^{\infty} dz_1 \left(\int d\tilde{\mathbf{r}}_{12} \rho_{ij}^{(2)} \frac{\phi'_{ij} x_{12}^2}{r_{12}} \right. \\
&\quad \left. - \int d\tilde{\mathbf{r}}_{12} \rho_{ij}^{(2)} \frac{\phi_{ij} x_{12}^2}{r_{12}} \right)
\end{aligned} \tag{7}$$

for the surface tension. The second equation fol-

lows because $P_x(z_1) = P_z$ for all z_1 . It is (7) that usually serves as the starting point for calculations of surface tension. With the linear profile model of Eq. (5) it leads to^{3,5,9,10}

$$\begin{aligned}
\gamma &= \pi \sum_{ij} \rho_i \rho_j \left[\int_0^{2d} dr \phi'_{ij} g_{ij} \left(\frac{r^5}{15d} - \frac{r^6}{96d^2} \right) \right. \\
&\quad \left. + \int_{2d}^{\infty} dr \phi'_{ij} g_{ij} \left(\frac{r^4}{8} - \frac{r^2 d^2}{6} + \frac{2d^4}{15} \right) \right].
\end{aligned} \tag{8}$$

The usual formula for surface energy is obtained by inserting Eqs. (5) into (1). This gives

$$\begin{aligned}
U &= \frac{1}{2} \sum_{ij} \rho_i \rho_j \int d\tilde{\mathbf{r}}_{12} \phi_{ij}(r_{12}) g_{ij}(r_{12}) \\
&\quad \times \left(\int_{-\infty}^{\infty} dz_1 [g(z_2) - \Theta(z_2)] \right. \\
&\quad \left. + \int_{-d}^d dz_1 g(z_1) [g(z_2) + 1 - \Theta(z_2)] \right),
\end{aligned} \tag{9}$$

which, after some lengthy algebra (see below), leads^{3,5,10} to

$$\begin{aligned}
U &= \frac{\pi}{2} \sum_{ij} \left[\int_0^{2d} dr \phi_{ij} g_{ij} \left(\frac{r^5}{24d^2} - \frac{r^4}{3d} - \frac{4dr^2}{3} \right) \right. \\
&\quad \left. + \int_{2d}^{\infty} dr \phi_{ij} g_{ij} \left(-r^3 - \frac{2}{3}rd^2 \right) \right].
\end{aligned} \tag{10}$$

A surface-tension formula similarly derived from the equation obtained by replacing ϕ_{ij} by $\phi'_{ij} x_{12}^2/r_{12}$ in (1) will differ from (8). The derivation of (7) does not follow if an approximation is used for the $\rho_{ij}^{(2)}$ —it requires that the Born-Green-Yvon equation be satisfied, and none of the simple forms for $\rho_{ij}^{(2)}$ does this. We now proceed to obtain the surface tension for the linear profile model, starting from the expression analogous to (1). In (9), therefore, we replace ϕ_{ij} by $\phi'_{ij} x_{12}^2/r_{12}$. To carry out the integrations, we use cylindrical coordinates, so that $r^2 = r_{12}^2 = s_{12}^2 + (z_1 - z_2)^2$. The term not involving $g(z)$ is

$$\begin{aligned}
&-\frac{1}{2} \sum_{ij} \rho_i \rho_j \int_{-\infty}^0 dz_1 \int_0^{\infty} dz_2 \int_{-\infty}^{\infty} s_{12} ds_{12} \int_0^{2\pi} d\phi \phi'_{ij}(r_{12}) g_{ij}(r_{12}) [r_{12}^2 - (z_1 - z_2)^2] \cos^2 \phi r_{12}^{-1} \\
&= -\frac{\pi}{2} \sum_{ij} \rho_i \rho_j \int_{-\infty}^0 dz_1 \int_0^{\infty} dz_2 \int_{\kappa_2 - \kappa_1}^{\infty} dr_{12} \phi'_{ij}(r_{12}) g_{ij}(r_{12}) [r_{12}^2 - (z_1 - z_2)^2].
\end{aligned}$$

After interchanging orders of integration twice, we obtain

$$\gamma_F = -\frac{\pi}{8} \sum_{ij} \rho_i \rho_j \int_0^{\infty} dr \phi'_{ij} g_{ij}(r) r^4. \tag{11}$$

Similarly, the terms linear in $g(z)$ are

$$\begin{aligned}
&\pi \sum_{ij} \rho_i \rho_j \int_{-\infty}^0 dz_1 \int_{-d}^d dz_2 g(z_2) \int_{|\kappa_{12}|}^{\infty} dr \phi'_{ij} \pi g_{ij}(r) (r^2 - z_{12}^2) \\
&= \frac{\pi}{4d} \sum_{ij} \rho_i \rho_j \left(\int_0^d dr \phi'_{ij} g_{ij} \left(-\frac{4}{15}r^5 - \frac{4}{3}r^3 d^2 + r^4 d \right) + \int_d^{\infty} dr \phi'_{ij} g_{ij} \left(-\frac{2}{3}r^2 d^3 + \frac{1}{15}d^5 \right) \right),
\end{aligned}$$

and the terms quadratic in $g(z)$ are

$$\begin{aligned} \frac{\pi}{2} \sum_{ij} \rho_i \rho_j \int_{-d}^d dz_1 g(z_1) \int_{-d}^d dz_2 g(z_2) \int_{|z_{12}|}^{\infty} dr \phi'_{ij} g_{ij} (r^2 - z_{12}^2) \\ = \frac{\pi}{16d^2} \sum_{ij} \rho_i \rho_j \left[\int_0^d dr \phi'_{ij} g_{ij} \left(\frac{16d^3 r^3}{g} - 2d^2 r^4 + \frac{8dr^5}{15} + \frac{r^6}{18} \right) \right. \\ \left. + \int_d^{2d} dr \phi'_{ij} g_{ij} \left(\frac{-4d^6}{15} + \frac{8d^4 r^2}{3} - \frac{32d^3 r^4}{9} + 2d^2 r^3 - \frac{8dr^5}{15} + \frac{r^6}{18} \right) + \int_{2d}^{\infty} dr \phi'_{ij} g_{ij} \frac{4d^6}{9g} \right]. \end{aligned}$$

Combining γ_F with the following terms, we have our surface tension

$$\gamma = \frac{\pi}{4} \sum_{ij} \rho_i \rho_j \left[\int_0^{2d} dr \phi'_{ij} g_{ij} \left(\frac{-8dr^3}{g} - \frac{2r^5}{15d} + \frac{r^6}{72d^2} \right) + \int_{2d}^{\infty} dr \phi'_{ij} g_{ij} \left(\frac{-r^4}{2} - \frac{2r^2 d^2}{3} + \frac{8d^4}{45} \right) \right]. \quad (12)$$

Equation (12) is quite different from (8). Since properties of the exact $\rho_{ij}^{(2)}$ are used to obtain (7) from the equation of the form (1) (i.e., that obtained by substituting $\phi'_{ij} x_{12}^2/r_{12}$ for ϕ_{ij}), it is not surprising that, with an approximate model such as (4) for the $\rho_{ij}^{(2)}$, the two expressions lead to different results. Use of the correct $\rho_{ij}^{(2)}$ would give the same results with all formulas. For the Fowler model,⁸ which corresponds to $d=0$, Eqs. (12) and (8) give, respectively, (11) and the negative of (11). This violent disagreement, already remarked by Pastor and myself,¹⁰ points up the extremely crude nature of the Fowler model. [See Eqs. (20) *et seq.* of Ref. 10 for the derivation of the formulas for $d=0$.]

Fitts,² starting from still another expression which would be equivalent to (7) for distributions obeying the Born-Green-Yvon equation, obtained (for a one-component system)

$$\begin{aligned} \gamma = \pi \rho^2 \left[\int_0^{2d} dr \phi' g \left(\frac{1}{15} \frac{r^5}{d} - \frac{1}{96} \frac{r^6}{d^2} \right) \right. \\ \left. + \int_{2d}^{\infty} dr \phi' g \left(\frac{r^4}{8} \right) \right]. \quad (13) \end{aligned}$$

Again, the difference between (12) and (13) is due to the fact that they are obtained by the insertion of the approximate forms of (4) and (5) into expressions which are identical for the exact $\rho^{(2)}$. The equality between (8) and (13) is simply (for one-component systems)

$$\int_{2d}^{\infty} dr \phi' g \left(\frac{2d^2}{5} \right) = \int_{2d}^{\infty} dr \phi' g \left(\frac{r^2}{3} \right).$$

For a large value of d , the contribution of these terms to γ may in any case be small. Comparing (8) and (12), however, we get a more complicated condition, because (8) and (12) are so different. Formulas analogous to (8), (12), and (13) could of course be derived with other^{2,3} one-parameter forms for $f(z)$.

It seems reasonable that if the model represented by (4) and (5) is employed, the choice of d

should be made such that the various expressions for the surface tension give the same results.

This would constitute a route to the calculation of surface tension, surface energy, and other properties, for which knowledge of a second experimental property such as surface energy would be unnecessary. The equality of the expressions is a necessary, but not sufficient, condition for $\rho_{ij}^{(2)}$ and $\rho_i^{(1)} = f(z)$ to obey the Born-Green-Yvon equation, as the exact two- and one-particle distributions for a surface must do. Therefore comparison of (8), (12), and (13) is a check on the model for the distribution functions. If a value of d is chosen on other grounds [for example, that the surface energy is correctly given by (10)], a large discrepancy between (8) and (12) would tend to cast doubt on the interpretation of the model.

III. RESULTS AND CONCLUSIONS

To investigate the consequences of my proposed procedure, we consider the case of argon, for which a surface thickness of 6.2–8.5 Å has been proposed by Shih and Uang,³ on the basis that this value of d gives simultaneously good values of surface tension and surface energy, when used in

TABLE I. Comparison of surface tensions calculated with Eq. (8) and with Eq. (12).

d (Å)	Surface tension (dyn/cm)	
	Eq. (8)	Eq. (12)
0.0	13.60	-13.60
0.25	13.61	-13.58
0.50	13.64	-13.56
0.75	13.68	-13.51
1.0	13.72	-13.45
1.5	13.74	-13.30
2.0	13.52	-13.18
2.5	12.84	-12.88
3.0	12.31	-13.24
3.5	11.59	-13.46
4.0	10.84	-13.84
4.5	10.24	-14.17
5.0	9.65	-14.64

the linear profile and other one-parameter models. (If three-body interactions are taken into account, the proper thickness is increased by about 1 Å.) We employ the same interatomic potential and correlation function as did Shih and Uang: ϕ is the Barker-Fisher-Watts¹² potential, and g is the experimental correlation function tabulated by Yarnell *et al.*¹³

In Table I, surface tensions calculated according to (8) and (12) are given for various values of d . According to (5), $2d$ is the thickness or width of the interfacial region. It is clear from the results shown that no value of d can make (8) and (12) agree. Perhaps this is already evident from the expressions themselves. Clearly, (8) can give reasonable surface tensions with the present model, if d is correctly chosen,³ while (12) cannot.

However, there is no *a priori* reason for preferring one to the other.

Writing $\rho^{(2)}$ as the bulk-liquid correlation function $g(r_{12})$ multiplied by $f(z_1)f(z_2)$ may indeed be a good approximation for certain choices of $f(z)$. However, we contend that f cannot necessarily be interpreted as the one-particle density. If it were, the Born-Green-Yvon equation would be satisfied on insertion of f and $\rho^{(2)}$ for the one- and two-particle densities, and the same surface tension would be obtained from (12) as from (8). The Born-Green-Yvon equation is very far from being satisfied; if it were used to derive the one-particle density corresponding to $\rho^{(2)}$, it would give something very different from f . Interpretation of the shape of f or the value of d in terms of the interfacial density profile is hence suspect.

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