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On the location of surface of tension in the planar interface between liquid and vapour[†]

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The structure of the interface of an argon-like fluid in equilibrium with its own vapour at 110 K is studied using the Monte Carlo method. The two components $P_N(z)$ and $P_T(z)$ (normal and tangential) of the pressure tensor $\mathbf{P}(\mathbf{r})$ for the planar interface are determined in the simulation. The normal component is a constant along the direction perpendicular to the surface (the z-direction) and is equal to the hydrostatic pressure. The tangential component varies across the surface. The surface tension γ , and the surface of tension z_s are determined. The location of the surface of tension is compared with the location of the Gibbs equimolar dividing surface, and the results are used to determine the curvature dependence of the surface tension for spherical droplets. The results are compared with theory.

1. INTRODUCTION

Recent computer simulations of liquids in equilibrium with their own vapour have contributed much to our understanding of the structure of the interface. Both planar [1-8] and spherical interfaces [9, 10] have been studied. The surface tension of a droplet differs from that of a planar interface. It is difficult if not impossible to determine experimentally how the surface tension $\gamma(r)$ of a droplet depends on its radius of curvature [11], yet this dependence plays an important role in the theories of nucleation. Computer simulations can provide important information on this otherwise experimentally inaccessible behaviour. It is possible to simulate droplets in equilibrium with vapour and thereby to determine the surface tension as a function of droplet size. This requires the simulation of many systems of different sizes. Rather than follow this elaborate path, we present here a study of the planar interface and deduce from this an estimate of the dependence of γ on the radius of curvature for droplets. First we determine the explicit dependence of the pressure tensor on position and from this determine the positions of the surface of tension and the Gibbs equimolar dividing surface. The relative position, δ , of the former with respect to the latter together with the surface tension of the planar surface can be used to estimate $\gamma(r)$ [12–14]. Here we present the results for an argon-like fluid in equilibrium with its own vapour at a temperature of 110 K. This study shows that the dependence of $\gamma(r)$ on r is likely to be too small to be determined by the direct simulation of a droplet.

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2. SIMULATION

We have simulated a plane sheet of liquid in equilibrium with its own vapour on both sides at 110 K, using 2048 atoms interacting via a truncated Lennard-Jones potential

$$\phi(r) = V(r) - V(r_0), \quad r < r_0,$$

= 0, $r \ge r_0$, with $r_0 = 2 \cdot 5\sigma$.

where

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \tag{1}$$

The Monte Carlo method is used with a step size of 0.2σ for the Metropolis random walk. The details of preparing and ageing the system have been described elsewhere [7]. The size of the periodic box is $14.66\sigma \times 14.66\sigma \times 25.1\sigma$. At equilibrium the vapour density $n_g^* = 0.05$ and the liquid density $n_1^* = 0.65$, where the star denotes reduced units. The usual density profile $n^*(z^*)$ is shown in figure 2. The origin is chosen to be the Gibbs equimolar dividing surface [14] given by

$$z_{\rm G}^{*} = \frac{L_z^{*}}{2} \frac{(\bar{n}^{*} - n_{\rm g}^{*})}{(n_{\rm l}^{*} - n_{\rm g}^{*})},\tag{2}$$

where $\bar{n}^* = N/V^*$ is the average density. The surface tension, γ , is defined as the free energy per unit area of the surface. Since there is no external field acting on the plane sheet the pressure is isotropic everywhere except at the surface. In the interface, the change in density along the direction normal to the surface



Figure 1. Variation of the normal $[P_N^*(z^*)]$ and tangential $[P_T^*(z^*)]$ components of the pressure tensor as a function of height, z^* , in a liquid-vapour interface. $z^*=0$ denotes the Gibbs equimolar dividing surface with the liquid phase at $z^* < 0$ and the vapour phase at $z^* > 0$.

(the z-direction) produces an asymmetry in the pressure tensor $\mathbf{P}(\mathbf{r})$. It is easy to see from symmetry of the system that the pressure tensor has only two components, $P_{\rm N}(z)$ and $P_{\rm T}(z)$, which are respectively the normal and the tangential components. Hydrostatic equilibrium imposes the condition that $P_{\rm N}(z)$ is everywhere a constant (even in the interface) and is equal to the hydrostatic pressure. The tangential component differs from the normal component in the surface zone and it is this component against which work must be done when the surface area of the liquid is changed.

In the computer simulation the two components of the pressure tensor are determined as functions of z. The pressure tensor P(r) can be written as

$$\mathbf{P}(\mathbf{r}) = P_{\mathrm{T}}(z)(\mathbf{e}_{x}\mathbf{e}_{x} + \mathbf{e}_{y}\mathbf{e}_{y}) + P_{\mathrm{N}}(z)\mathbf{e}_{z}\mathbf{e}_{z}, \qquad (3)$$

where \mathbf{e}_x , \mathbf{e}_y , \mathbf{e}_z are the three unit vectors along the three mutually perpendicular directions. The usual statistical mechanical expression for the pressure [12–14] tensor, depending only on the one- and two-particle densities $n_1(\mathbf{r})$ and $n_2(\mathbf{r}_1, \mathbf{r}_2)$, can be written after considerable algebraic manipulations in terms suitable for a numerical evaluation of $P_{\rm T}(z)$ and $P_{\rm N}(z)$.

Following reference [14], the pressure tensor can be written as

$$\mathbf{P}(\mathbf{r}) = n(\mathbf{r})kT - \frac{1}{2} \left\langle \sum_{\substack{i,j \\ i \neq j}}^{N} \int_{\infty}^{\infty} d\eta \theta(\eta) \theta(1-\eta) \times \frac{\mathbf{r}_{ij}\mathbf{r}_{ij}}{|\mathbf{r}_{ij}|} \phi'(|\mathbf{r}_{ij}|) \delta[\mathbf{r} - (\mathbf{r}_{i} + \eta \mathbf{r}_{ij})] \right\rangle, \quad (4)$$

where $\theta(\eta)$ is the unit step function, $|r_{ij}|$ is the distance between two particles, *i* and *j*, $(r_{ij} = r_j - r_i)$ and $\phi'(r)$ is the first derivative of the pair potential with respect to *r*. Equation (4) applies to a surface of any shape. For a planar surface this specializes to,

$$P_{\mathrm{T}}(z) = n(z)kT - \frac{1}{4A} \left\langle \sum_{i \neq j} \frac{[x_{ij}^2 + y_{ij}^2]}{|r_{ij}|} \frac{1}{|z_{ij}|} \phi'(|r_{ij}|) \times \theta\left(\frac{z - z_i}{z_{ij}}\right) \theta\left(\frac{z_j - z}{z_{ij}}\right) \right\rangle$$
(5)

and

$$P_{\mathrm{N}}(z) = n(z) \ kT - \frac{1}{2A} \left\langle \sum_{i \neq j} \frac{|z_{ij}| \phi'(r_{ij})}{|r_{ij}|} \ \theta\left(\frac{z - z_i}{z_{ij}}\right) \ \theta\left(\frac{z_j - z}{z_{ij}}\right) \right\rangle, \tag{6}$$

where A is the cross sectional area of the surface.

In figure 1 we show $P_N^*(z^*)$ and $P_T^*(z^*)$ as functions of z^* obtained from the simulation with 3.07 million moves. $P_N^*(z^*)$ is observed to be constant within 7 per cent. This picture clearly shows the 'relatively larger fluctuations associated with the determination of the pressure tensor. In figure 2, $[P_N^*(z^*) - P_T^*(z^*)]$ is given by the solid line. The surface tension, γ , is given by the area under this curve [12]

$$\gamma = \int_{-L/2}^{L/2} [P_{\rm N}(z) - P_{\rm T}(z)] z \, dz.$$
(7)

Evaluation of the integral gives a value of 0.42 reduced units (=6.0 dynes/cm in argon units).

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Figure 2. Dots indicate density profile $n^*(z^*)$ as a function of z^* . The solid line shows the difference between the normal and tangential components of the pressure tensor. The area under the solid line gives the surface tension.

Figure 2 shows that the transverse pressure is asymmetric around the Gibbs dividing surface. An important measure of this asymmetry is given by the first moment [13–16]

$$z_{\rm s} = \frac{1}{\gamma} \int_{-L/2}^{L/2} [P_{\rm N}(z) - P_{\rm T}(z)] z \, dz.$$
(8)

This defines the position of the surface of tension. This surface can also be used to divide the liquid phase from the vapour phase instead of the usual Gibbs equimolar surface. In a planar interface the surface tension does not depend on any particular choice of the dividing surface, but in spherical droplets the use of the dividing surface is essential since precise meaning is given to the concepts of area and curvature. The surface of tension defined by equation (8) plays an important role in spherical droplets. The location of z_s measured from the Gibbs dividing surface ($\delta_{\infty} = z_G - z_s$) is called the curvature dependence of surface tension in spherical droplets [13–15]

$$\gamma(r) = \gamma_{\infty} \left(1 - \frac{2\delta_{\infty}}{r} \right), \tag{9}$$

where γ_{∞} is the surface tension of the planar interface and r is the radius curvature of the droplet. From our simulation δ_{∞}^* is found to be positive and is 0.96 ± 0.12 .

3. Discussion of the results

Both the surface tension and the location of the surface of tension depend only on the one-particle and the two-particle distribution functions of the fluid, $n_1(z)$ and $n_2(z_1, z_2, u_{12})$ where $u_{12} = \sqrt{(x_{12}^2 + y_{12}^2)}$. Most theories of the interface attempt to relate these quantities to the bulk fluid correlation functions n_1 and $n_2(r, n_1)$; that is to the properties of the homogeneous liquid in which no surfaces are

<i>r</i> *	g(r*)	r*	g(r*)	r*	g(r *)
0.71	0.0	1.31	1.2035	1.91	0.9769
0.73	0.0	1.33	1.1260	1.93	1.0054
0.75	0.0	1.35	1.0608	1.95	1.0266
0.77	0.0	1.37	1.0049	1.97	1.0513
0.79	0.0	1.39	0.9536	1.99	1.0726
0.81	0.0	1.41	0.9129	2.01	1.0955
0.83	0.0	1.43	0.8751	2.03	1.1134
0.85	0.0	1.45	0.8415	2.05	1.1305
0.87	0.0	1.47	0.8171	2.07	1.1404
0.89	0.0005	1.49	0.7947	2.09	1.1506
0.91	0.0070	1.51	0.7798	2.11	1.1565
0.93	0.0450	1.53	0.7657	2.13	1.1564
0.95	0.1702	1.55	0.7572	2.15	1.1559
0.97	0.4345	1.57	0.7439	2.17	1.1480
0.99	0.8453	1.59	0.7402	2.19	1.1422
1.01	1.3091	1.61	0.7422	2.21	1.1304
1.03	1.7508	1.63	0.7472	2.23	1.1200
1.05	2.0815	1.65	0.7498	2.25	1.1044
1.07	2.2956	1.67	0.7568	2.27	1.0925
1.09	2.3696	1.69	0.7633	2.29	1.0750
1.11	2.3616	1.71	0.7716	2.31	1.0612
1.13	2.2875	1.73	0.7929	2.33	1.0435
1.15	2.1652	1.75	0.8037	2.35	1.0286
1.17	2.0308	1.77	0.8199	2.37	1.0125
1.19	1.8862	1.79	0.8372	2.39	1.0000
1.21	1.7439	1.81	0.8591	2.41	0.9863
1.23	1.6189	1.83	0.8843	2.43	0.9759
1.25	1.4985	1.85	0.9103	2.45	0.9667
1.27	1.3949	1.87	0.9328	2.47	0-9583
1.29	1.2943	1.89	0.9556	2.49	0.9463

Table 1. Pair correlation function of the uniform fluid at $T^*=0.922$ and $n_1^*=0.65$ averaged over six runs of 100 passes† each.

 $\uparrow 1$ pass $\equiv N$ attempted moves where N is the number of particles in the system (= 216)

present. Kirkwood and Buff have derived a set of formulae relating the surface tension and the location of the surface of tension to these bulk liquid distribution functions [12, 14, 16]

$$\gamma = \frac{\pi (n_1)^2}{8} \int_{-\infty}^{\infty} \phi'(r) g_2^{1}(r) r^4 dr$$
 (10)

and

$$\delta_{\infty} = -z_{\rm s} = \frac{4}{15} \frac{\int g_2^{\rm l}(r)\phi'(r)r^5 dr}{\int g_2^{\rm l}(r)\phi'(r)r^4 dr}.$$
 (11)

where $g_2^{1}(r) = g(r)$ is the radial distribution function for the bulk fluid.

To test the accuracy of these expressions we have also simulated a bulk fluid (N=216) with the same density as the interior of the film $(n_1^*=0.65)$ interacting

with the potential given in equation (1). The radial distribution function is presented in table 1. Using these data in equations (10) and (11) we obtain $\gamma^* = 0.39$ and $\delta_{\infty}^* = 0.65$. This should be compared with the values of $\gamma^* = 0.42$, $\delta_{\infty}^* = 0.96 \pm 0.12$ determined from the simulation of the surface using the correct equations (7) and (8). The close agreement of γ^* might just be due to its insensitivity to the structure of the two-particle distribution. The difference in δ_{∞}^* is noteworthy. The pressure tensor presented in this paper gives a more stringent test of the theory.

It was shown recently that both Monte Carlo and molecular dynamics simulations can be used to study spherical droplets in equilibrium with vapour [11]. It is possible to measure the pressure tensor in such a droplet and obtain both surface tension and the surface of tension satisfying the Kelvin relation

$$P_{\rm liq} - P_{\rm gas} = \frac{2\gamma(r)}{r}.$$

However, the surface tension can also be estimated from the measurement of the location of the surface of tension in the plane interface using equation (9). In table 2, these values of $\gamma(r^*)$ are presented as a function of r^* . The smallness of the correction in the case of liquid argon makes the determination of the surface tension directly from a simulation of droplets not worthwhile. In other systems where the Gibbs dividing surface is far away from the surface of tension, it would be straightforward to measure the surface tension as a function of the radius of the droplet.

$\frac{4}{3}\pi r^3 n_1$ Number of particles)	r*	γ*(r*)†
	8	0.42
21781	20	0.38
2722	10	0.34
341	5	0.26
74	3	0.15

Table 2. Variation of surface tension with droplet radius.

† In units of ϵ/σ^2 .

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