PHYSICAL REVIEW A VOLUME 17, NUMBER 1 JANUARY 1978

Surface energy and surface tension of liquid Ar near the triple point

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(Received 22 August 1977)

The effect of the transition zone on the surface energy and the surface tension near the triple point is reported. Both quantities are calculated from the extended Kirkwood-Buff formulas for the cases of a linear, a cubic, and a Fermi density profile. The realistic Barker-Fisher-Watts (BFW) potential and the Parson, Siska, and Lee (MSVIII) potential are used. The experimental radial distribution function of Yarnell *et al.* is used for the bulk liquid and as an approximation for the transition zone. As a function of the zone width both realistic potentials lead to the same rapid monotonic increase for the surface energy, but a different mild monotonic decrease for the surface tension. The transition zone width can be determined approximately from the surface energy. If the three-body nonadditivity effects on both quantities are ignored, the experimental value 34.9 erg/cm^2 of the surface energy suggests a zone width of 6.2 to 8.5 Å, thus predicting a value of the tension of 12.1 dyn/cm for the BFW potential and 12.8 dyn/cm for the MSVIII potential as compared to the experimental value of 13.1 dyn/cm. Including the three-body nonadditivity effects estimated from the Axilrod-Teller triple-dipole potential, the zone width needed for a correct value of the surface energy is slightly larger (7.2 to 9.5 Å). However, the surface tension thus predicted is too small for all potentials.

I. INTRODUCTION

Recently the Kirkwood-Buff (KB) molecular theory of surface tension and surface energy[1] has been extended to include nonadditivity and transition zone effects for liquid Ar at 85 °K (near the triple point.[2-5] At this temperature the radial distribution function $g(r)$ of the liquid is accurately given by the neutron diffraction data of Yarnell *et al.*[6] The surface properties of Ar were estimated from the realistic two-body intermolecular potential of Barker, Fisher, and Watts (BFW)[7] or of Parson, Siska, and Lee (MSVIII),[8] and the Axilrod-Teller three-body interaction potential[9] and the superposition approximation were used for the nonadditivity effects. Results of the extended KB calculations were then compared with the experimental data[10] as well as the values obtained from other models such as Monte Carlo or molecular-dynamics calculations.

Using a linear and a cubic density profile and several reasonable radial distribution functions in the transition zone, the two-body contribution to the surface tension γ_2 was evaluated as a function of the width of the transition zone. As was reported in Ref. 4, γ_2 turns out to be a slowly varying function of the width of the transition zone. Starting from a zero-width value of 13.7 dyn/cm for the BFW potential, and 15.0 dyn/cm for the MSVIII potential, the value of the tension decreases monotonically as a function of zone width. Both potentials lead to values of γ_2 quite compatible with the experimental value of 13.1 dyn/cm. A unique determination of the zone width is nevertheless impossible because of the mild dependency of γ_2 on the width and uncertainty about the nonadditivity effects.

In Refs. 2 and 3, the three-body nonadditivity contribution to the surface tension γ_3 is also evaluated. Using Fowler's step-function density profile, Kirkwood's superposition triplet-correlation function,[11] and Axilrod and Teller's triple-dipole interaction, the value of γ_3 is estimated to be -4.5 dyn/cm. The combined value of γ_2 and γ_3 is therefore always smaller than the experimental value. Presently it is not clear whether the value of γ_2 or γ_3 is less accurately estimated. A recent Monte Carlo calculation of Myazaki, Barker, and Pound based on the Lennard-Jones (L-J) 12-6 potential leads to a value of 18.3 dyn/cm for γ_2.[12] The perturbational calculation of Lee, Barker, and Pound based on the BFW potential and the Axilrod-Teller triple-dipole interaction leads to a value of 16.87 dyn/cm for γ_2 and -3.99 dyn/cm for γ_3.[13] On the other hand, the molecular-dynamics calculation of Raó and Levesque based on a truncated L-J 12-6 potential leads to the value of 12.2 dyn/cm for γ_2.[14]

In a recent calculation we have also estimated $U_3^{(s)}$, the nonadditivity contribution to surface energy of Ar (excess internal energy per unit area of the surface).[5] Using the same assumption of those in the calculation of the tension γ_3, the $U_3^{(s)}$ is estimated to be -2.4 erg/cm^2 for Ar at 85 °K. This is to be considered with the two-body contribution $U_2^{(s)}$ of 26.3 erg/cm^2 obtained from Fowler's formula[15] using the same radial distribution function and using either the BFW or MSVIII potential.[16] Since the experimental value is close to 34.9 erg/cm^2, the above $U_3^{(s)}$ is opposite in sign to the correction needed to improve the two-body contribution $U_3^{(s)}$ obtained from Fowler's formula. Using the L-J 12-6 potential, the Monte Carlo calculation of Miyazaki, Barker, and Pound however leads to a value of $U_2^{(s)}+U_3^{(s)}$ of 34.7 erg/cm^2.[12]

It is desirable to consider the effect of the transition zone on the two-body contribution to the surface energy $U_2^{(s)}$. At 85 °K the density of the vapor is very small. As the width of the transition zone increases, the number of particles in the transition zone increases, and the surface energy is expected to increase. Surface energy can therefore be a very sensitive function of the width of the transition zone. A simultaneous consideration of both the surface tension and surface energy can provide a more comprehensive understanding of the nature of the transition zone.

In the following, we shall first extend the KB formulation to surface energy using an approach different from those using superficial densities.[17] Starting from the definition of the surface energy, $U_2^{(s)}$ is obtained by subtracting the internal energies of the two individual bulk phases from the actual internal energy of the inhomogeneous system. A construction of the conventional superficial densities is therefore avoided. The previously reported formulation on surface tension[4] shall also be extended to a more realistic Fermi profile. Only simple numerical integrations are involved in evaluating these formulas, and the computing time is much less than those in typical Monte Carlo[12,18] or molecular-dynamics calculations.[14]

II. FORMULATION

Starting from the definition of the surface energy and surface tension

$$U_2^{(s)}=\tfrac{1}{2}\int dz_1\int d\tau_2 u(r_{12})\,[\rho(z_1)\rho(z_2)g(z_1,z_2,r_{12}) - \rho_l^2\theta(z_1)g_l(r_{12})]\,, \tag{1}$$

$$\gamma_2=\tfrac{1}{2}\int dz_1\int d\tau_2 u'(r_{12}) \times\rho(z_1)\rho(z_2)g(z_1,z_2,r_{12})\frac{x_{12}^2-z_{12}^2}{r_{12}}\,, \tag{2}$$

with

$$\theta(z)=\begin{cases}1, & z\geq 0\\ 0, & z<0\,,\end{cases}$$

where

$$\int dz\,[\rho(z)-\rho_l\theta(z)]=0\,, \tag{3}$$

and vapor density ρ_v is taken to be zero.

In the above formula, the Gibbs dividing surface is positioned at $z=0$, with the liquid above ($z>0$) and the vapor below ($z<0$). As the $\rho(z)$ and the radial distribution function $g(z_1,z_2,r_{12})$ are unknown in the transition zone, three alternative representations of $\rho(z)$ are used for the following calculations.

The simplest form other than Fowler's step-function profile is the linear profile for a transition zone of width d:

$$\rho(z)=\rho_l(z/d+\tfrac{1}{2}),\quad |z|\leq\tfrac{1}{2}d. \tag{4}$$

A slightly more complicated form is a cubic profile:

$$\rho(z)=\rho_l[-2(z/d)^3+\tfrac{3}{2}(z/d)+\tfrac{1}{2}],\quad |z|\leq\tfrac{1}{2}d\,. \tag{5}$$

A somewhat more realistic profile is a Fermi profile:

$$\rho(z)=\rho_l/(1+e^{-wz})\,,\quad \text{all } z\,. \tag{6}$$

with $d=2\ln 19/w$. The width d of the Fermi profile is arbitrarily taken to be between the positions where the value of $\rho(z)$ is 95% and 5% of the value ρ_l of the bulk liquid.

In addition to the assumed profiles, we also need the specific values of $g(z_1,z_2,r_{12})$. It is clear that the $g(z_1,z_2,r_{12})$ tends to $g_l(r_{12})$ as z_1 and z_2 approach the bulk liquid, and tends to $g_v(r_{12})$ as z_1 and z_2 approach the vapor. Since $g_v(r_{12})$ is very close to $g_b(r_{12})$, the Boltzmann factor $\exp[-u(r_{12})kT]$ for a small ρ_v, it is tempting to represent the $g(z_1,z_2,r_{12})$ as an interpolation between $g_l(r_{12})$ and $g_b(r_{12})$ (see Ref. 4). A closer examination however indicates that this kind of interpolation is not accurate for most of the regions in the transition zone, where $\rho(z)$ is substantially larger than ρ_v. The $g_b(r_{12})$, which has a high peak for $T=85$ °K, implies more neighbors relative to $g_l(r_{12})$, which has a much lower first peak. To get a quantitative comparison, we shall arbitrarily define the number of near neighbors by

$$\mathfrak{N}\equiv\int_{d_0\leq r_{12}\leq 2d_0}\rho(z_2)g(z_1,z_2,r_{12})\,d\tau_2\,, \tag{7}$$

where d_0 is the distance of closest approach of the molecules in the liquid. Replacing $g_l(r_{12})$ by $g_b(r_{12})$ in the *bulk* liquid amounts to changing this number from 20 to 39. At the middle point of the transition zone, the number of near neighbors is still too large if an interpolation is used. Thus an interpolation between $g_l(r_{12})$ and $g_b(r_{12})$ should only be valid for the region where $\rho(z)$ is comparable to ρ_v. An alternative method of approximating $\rho^{(2)}(\vec{r}_1,\vec{r}_2)=\rho(z_1)\rho(z_2)g(z_1,z_2,r_{12})$ is to use $g_l(r_{12})$ throughout the whole transition zone. In the following we shall, therefore, use $g_l(r_{12})$ only for $g(z_1, z_2, r_{12})$ without any consideration of mixing between $g_l(r_{12})$ and $g_b(r_{12})$.[19]

Using the above density profiles and the empirical values of $g_l(r_{12})$, the surface energy and the surface tension can be calculated. From Eqs. (1) and (2), corresponding to Fowler's model, $\rho(z) = \rho_l \theta(z)$, and $g(z_1, z_2, r_{12}) = g_l(r_{12})$, we get the standard formulas

$$U_F^{(s)} = -\frac{\pi}{2}\rho_l^2 \int_0^\infty dr\, r^3 u(r) g_l(r) , \tag{8}$$

$$\gamma_F = \frac{\pi}{8}\rho_l^2 \int_0^\infty dr\, r^4 u'(r) g_l(r) . \tag{9}$$

For convenience, we estimate $U_2^{(s)} - U_F^{(s)}$ and $\gamma_2 - \gamma_F$ instead. A careful exchange of the variables leads to

$$\Delta U^{(s)} \equiv U_2^{(s)} - U_F^{(s)} = 2\pi \int_0^\infty dr\, r u(r) \int_{-d/2}^{d/2} dz_1 \int_{z_1}^{z_1+r} dz_2 [\rho(z_1)\rho(z_2) g(z_1, z_2, r_{12}) - \rho_l^2 \theta(z_1)\theta(z_2) g_l(r_{12})] , \tag{10}$$

$$\Delta\gamma \equiv \gamma_2 - \gamma_F = \pi \int_0^\infty dr\, u'(r) \int_{-d/2}^{d/2} dz_1 \int_{z_1}^{z_1+r} \rho(z_1)\rho(z_2)\, g(z_1, z_2, r_{12})[r^2 - 3(z_1 - z_2)^2] . \tag{11}$$

The z_1, z_2 dependence of the formulas can be explicitly calculated. With some straightforward algebra, we can obtain

$$\Delta U^{(s)} = -\frac{\pi}{2}\rho_l^2 \int_{d_0}^\infty dr\, r^3 u(r) g_l(r) E\left(\frac{r}{d}\right) , \tag{12}$$

$$\Delta\gamma = \frac{\pi}{8}\rho_l^2 \int_{d_0}^\infty dr\, r^4 u'(r) g_l(r) T\left(\frac{r}{d}\right) . \tag{13}$$

Corresponding to the linear profile, the surface energy and the surface tension are obtained from

$$E(x) = (2/3x - 1 + \tfrac{2}{3}x - \tfrac{1}{6}x^2)\theta(1-x) + (1/6x^2)\theta(x-1) , \tag{14}$$

$$T(x) = (-1 + \tfrac{16}{15}x - \tfrac{1}{3}x^2)\theta(1-x) + (\tfrac{1}{15} - \tfrac{1}{3}x^2)x^{-4}\theta(x-1) . \tag{15}$$

Corresponding to the cubic profile:

$$E(x) = (18/35x - 1 + \tfrac{4}{5}x - \tfrac{2}{5}x^2 + \tfrac{1}{5}x^4 - \tfrac{1}{70}x^6)\theta(1-x) + (1/10x^2)\theta(x-1) , \tag{16}$$

$$T(x) = (-1 + \tfrac{32}{25}x - \tfrac{32}{35}x^3 + \tfrac{1}{2}x^4 - \tfrac{1}{25}x^6)\theta(1-x) + (\tfrac{9}{350} - \tfrac{1}{5}x^2)x^{-4}\theta(x-1) . \tag{17}$$

Corresponding to the Fermi profile:

$$E(x) = \frac{4\ln 2}{\omega dz} - \frac{4}{\omega^2 d^2 x^2} \int_0^1 \frac{dy}{1+y} \left(\ln \frac{y + e^{-\omega d x}}{y+1} + \frac{1}{y} \ln \frac{y + e^{\omega d x}}{y+1} \right) , \tag{18}$$

$$T(x) = 8 \int_0^1 dy\, \frac{y(1-3y^2)}{1 - e^{\omega d xy}} . \tag{19}$$

The expressions for the surface tension for the linear and cubic profile have been reported previously.[4] Using the method of superficial densities, the corresponding expressions for the surface energy also lead to the same results reported here.[19] Notice that the surface energy diverges linearly with the width of the transition zone. This is partially due to the fact that ρ_v is almost zero. As the width increases, more particles are involved. Since the number of near neighbors of a particle in the transition zone is less than that in the bulk liquid, the contribution to the binding energy is smaller. The total contribution to the surface energy of all the particles, therefore, increases as the number of particles in the transition zone increases. Values of the surface energy and the surface tension using both the BFW potential and the MSVIII potential are discussed in Sec. III.

III. RESULTS AND DISCUSSION

In Tables I and II we have listed the values of the surface energy and tension for both the BFW and the MSVIII potential. Although these two potentials are slightly different, they lead to almost identical results for all the values of $U_2^{(s)}$. The other most striking feature of $U_2^{(s)}$ is its sensitivity with respect to the width of the transition zone for all three types of density profiles. In each case the surface energy $U_2^{(s)}$ increases very rapidly as the zone width increases. However, if mixing between $g_l(r_{12})$ and $g_b(r_{12})$ is allowed throughout the transition zone, the $U_2^{(s)}$ values decrease instead of increasing as a function of the zone width. This is due to the fact that the inclusion of $g_b(r_{12})$ packs the particles too closely in the neighboring region as was discussed before and causes an artifical increase in binding energy, thus decreasing the surface energy. The resultant values of $U_2^{(s)}$ under the condition of mixing between $g_l(r_{12})$ and $g_b(r_{12})$ are not reported here.[19]

If these values of the surface energy are compared with the experimental value, the Fermi profile leads to a value of the transition zone width

TABLE I. Dependence of surface energy of Ar $U_2^{(s)}$ (erg/cm^2) at 85 °K on the zone width for different potentials ($\rho_l = 0.021\,25/\text{Å}^3$).

Width	Linear profile		Cubic profile		Fermi profile	
d(Å)	MSVIII	BFW	MSVIII	BFW	MSVIII	BFW
0.0	26.31	26.31	26.31	26.31	26.31	26.31
0.5	26.36	26.37	26.34	26.34	26.40	26.45
1.0	26.52	26.52	26.43	26.44	26.57	26.58
1.5	26.78	26.79	26.59	26.60	26.86	26.87
2.0	27.14	27.15	26.81	26.82	27.27	27.28
2.5	27.61	27.63	27.09	27.10	27.81	28.83
3.0	28.19	28.21	27.44	27.45	28.46	28.47
3.5	28.87	28.89	27.84	27.86	29.22	29.23
4.0	29.65	29.68	28.31	28.33	30.08	30.10
4.5	30.53	30.57	28.85	28.87	31.04	31.07
5.0	31.51	31.56	29.44	29.47	32.09	32.12
5.5	32.58	32.63	30.09	30.13	33.21	33.26
6.0	33.72	33.79	30.80	30.84	34.40	34.46
6.5	34.93	35.00	31.57	31.61	35.65	35.72
7.0	36.19	36.28	32.38	32.43	36.95	37.03
7.5	37.53	37.61	33.25	33.30	38.30	38.39
8.0	38.90	38.99	34.16	34.21	39.69	39.80
8.5	40.31	40.40	35.09	35.15	41.13	41.24
9.0	41.75	41.85	36.07	36.13	42.59	42.72
9.5	43.23	43.33	37.08	37.14	44.08	44.23
10.0	44.71	44.83	38.11	38.18	45.60	45.76

TABLE II. Dependence of surface tension of Ar γ_2 (dyn/cm) at 85 °K on the zone width for different potentials ($\rho_l = 0.021\,25/\text{Å}^3$).

Width	Linear profile		Cubic profile		Fermi profile	
d(Å)	MSVIII	BFW	MSVIII	BFW	MSVIII	BFW
0.0	14.99	13.70	14.99	13.70	14.99	13.70
0.5	14.99	13.71	14.99	13.71	14.99	13.72
1.0	14.99	13.74	14.99	13.72	14.99	13.76
1.5	14.99	13.77	14.99	13.75	14.99	13.79
2.0	14.97	13.81	14.98	13.78	14.95	13.80
2.5	14.92	13.83	14.97	13.80	14.87	13.78
3.0	14.84	13.82	14.94	13.82	14.73	13.71
3.5	14.69	13.74	14.88	13.82	14.53	13.57
4.0	14.47	13.58	14.80	13.79	14.28	13.38
4.5	14.17	13.34	14.68	13.72	14.00	13.15
5.0	13.82	13.05	14.51	13.60	13.68	12.88
5.5	13.45	12.71	14.31	13.44	13.35	12.59
6.0	13.05	12.35	14.07	13.25	13.00	12.28
6.5	12.66	11.99	13.81	13.03	12.66	11.97
7.0	12.27	11.63	13.54	12.79	12.31	11.65
7.5	11.89	11.28	13.26	12.54	11.97	11.33
8.0	11.52	10.93	12.96	12.27	11.63	11.03
8.5	11.17	10.60	12.67	12.00	11.31	10.72
9.0	10.83	10.28	12.38	11.74	11.00	10.43
9.5	10.51	9.98	12.09	11.47	10.69	10.15
10.0	10.21	9.68	11.81	11.20	10.40	9.87

6.3 Å. The corresponding width for the linear and cubic profiles are 6.5 and 8.5 Å, respectively. If the surface energy $U_2^{(s)}$ and $U_3^{(s)}$ are considered together and compared to the experimental value, the corresponding width would be 7.2 Å for the Fermi profile, 7.5 Å for the linear profile, and 9.5 Å for the cubic profile. All the estimated widths are less than three times the distance of closest approach in the bulk liquid.

It is interesting to use the width determined by the surface energy to estimate the surface tension. The values of γ_2 thus obtained are different for the BFW and the MSVIII potential. Using the width determined by the $U_2^{(s)}$ alone, the BFW potential gives 12.1 dyn/cm (Fermi), 12.0 dyn/cm (linear), and 12.0 dyn/cm (cubic), as compared to those given by the alternative MSVIII potential: 12.8 dyn/cm (Fermi), 12.7 dyn/cm (linear), and 12.7 dyn/cm (cubic). The above values of the surface tension should be compared with the experimental value of 13.1 dyn/cm.

On the other hand it may be more meaningful to include the nonadditivity effects on $U^{(s)}$ and γ.[2,3,5] Using the combined value of $U_2^{(s)}$ and the three-body contribution $U_3^{(s)}$ (−2.4 erg/cm^2), the BFW potential and $U_3^{(s)}$ leads to the values $\gamma_2 + \gamma_3$ of 6.9 dyn/cm (Fermi), 6.7 dyn/cm (linear), and 7.0 dyn/cm (cubic), respectively. The MSVIII potential leads to 7.6 dyn/cm (Fermi), 7.4 dyn/cm (linear), and 7.6 dyn/cm (cubic) instead. If the three-body nonadditivity contribution γ_3 is as large as what was estimated in Refs. 2 and 3, none of the above values of the surface tension is satisfactory.

The differences between the predictions of the BFW potential and the MSVIII potential can be traced to the sensitivity of the surface tension γ_2 with respect to the region of small r_{12}, where the $u'(r_{12})$ is large and negative. The contributions to the surface tension due to the region of larger r_{12} are actually identical.[4] Also a small deviation of $g(z_1, z_2, r_{12})$ away from the $g_l(r_{12})$ in the transition region with a small r_{12} would not alter the value of the surface energy $U_2^{(s)}$ very much. At the same time the surface tension γ_2 can be changed considerably. Considerations of this nature also arise in the self-consistency equations of the density profile $\rho(z)$ and the $\rho^{(2)}(z_1, z_2, r_{12})$. The Born-Bogolyubov-Green-Kirkwood-Yvon (BBGKY)[20] first-hierarchy relation involves the $u'(r_{12})$, and is therefore sensitive to the repulsive region of r_{12}. In order to improve the Kirkwood-Buff type of calculation of the surface tension, we need also to look into the BBGKY type of relationships for the transition zone. The calculations on γ_2 favor the MSVIII potential over the BFW potential, when the nonadditivity effects are not included.

IV. CONCLUSIONS

Using the extended Kirkwood-Buff formula, the effects of the transition zone width on the surface energy $U_2^{(s)}$ of Ar near the triple point can be formulated. To evaluate these formulas, we employed two realistic potentials, several approximate single-density profiles, and an experimental radial distribution function of the bulk liquid for the transition zone (instead of an interpolation between the liquid and the vapor distribution functions in the transition zone). Both the BFW and the MSVIII potentials lead to the same rapid monotonic increase for the surface energy as a function of the transition zone width. If the nonadditivity effects on surface energy are ignored, the experimental value of $U_2^{(s)}$ suggests a zone width of 6.2 to 8.5 Å, which is quite reasonable. These zone widths in turn predict a value of the tension γ_2 of 12.1 dyn/cm for the BFW potential and 12.8 dyn/cm for the MSVIII potential. Comparing to the experimental value of 13.1 dyn/cm, the MSVIII potential is favored over the BFW potential. Including the three-body nonadditivity effects estimated from the Axilrod-Teller triple-dipole potential, the zone width needed for the correct value of the surface energy is slightly larger (7.2 to 9.5 Å). But the surface tension thus predicted from both potentials is much too small.

ACKNOWLEDGMENT

We are grateful to Professor R. D. Present for many suggestions and criticisms throughout the course of this work.

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