PHYSICAL REVIEW A VOLUME 22, NUMBER 2 AUGUST 1980

Location of surface of tension in argon liquid-vapor interface near the triple point

Yea-Hwang Uang
Department of Chemistry and Department of Physics, The University of Iowa, Iowa City, Iowa 52242
(Received 29 January 1980)

The Kirkwood-Buff molecular theory of surface tension is used to determine the location of the surface of tension for a planar liquid-vapor interface of liquid argon near the triple point. A nonzero interfacial thickness is considered in this phenomenological study for the cases of a linear and a cubic density profile. It is found that the product of the surface tension and the location of the surface of tension is independent of the width of the liquid-vapor transition zone. Both linear and cubic density profiles lead to the same invariance relation. The realistic Barker-Fisher-Watts (BFW) potential and the Parson, Siska, and Lee (MSV-III) potential are used for numerical calculation. The experimental radial-distribution function of Yarnell *et al.* is used for the bulk liquid and as an approximation for the transition zone. Results are compared to those previously reported. Curvature dependence of the surface tension for large-size droplet or cluster is also discussed.

I. INTRODUCTION

Based on the Kirkwood-Buff molecular theory of surface tension,[1] the effect of the transition zone on the surface energy and surface tension for liquid argon near the triple point was thoroughly studied.[2] A simultaneous consideration of both the surface tension and the surface energy has provided a more comprehensive understanding of the nature of the liquid-vapor transition zone. Although it is suggested by Goodisman[3] that misleading results may be obtained if one- and two-particle distribution functions not related by the Born-Bogolivbov-Green-Kirkwood-Yvon[4] equation are used together, the modeling of realistic density profiles and radial-distribution functions has been widely adopted in the study of a liquid-vapor coexisting system.[5-7] Recently, Henderson and Lekner[8] have shown a numerical consistence in the surface-thickness determination from various modeling calculations.

The planar interface between liquid and vapor has been predominately investigated because of its simple nature with well-developed theories.[9,10] However, considerable study of the spherical interface[11-14] is also essential to the understanding of nucleation phenomena.[15] Particularly, the curvature dependence of the surface tension (e.g., droplet, bubble, microcluster) is playing an important role in connection with theories of nucleation.[15] Many theoretical approaches on curvature dependence of the surface tension $\gamma(R)$ have been limited to the cases of large radius of curvature R. The approximate relation of γ to R is expressed in terms of a planar interface quantity δ, which is defined as the relative distance between the so-called Gibbs *surface of tension* z_G and the *equimolecular dividing surface* z_{eq}(i.e., $\delta = z_{eq} - z_G$).[16]

Several estimations have confirmed the sign of δ to be positive, but they differ in magnitude from one another by using different methods with different input information. Using the Lennard-Jones potential and Fowler's step-function (zero-width)[17] profile, the Kirkwood-Buff theory gave 3.63 Å for Ar at 90 K. Hill, however, estimated 2.81 Å in his model which led a smooth density profile in the surface zone.[18] The scale-particle model of Plesner and Platz yielded an estimated δ of 2.01 Å at 84 K for Ar.[19] The temperature dependence of δ was given by Toxvaerd, whose estimation, however, yielded a value three times larger compared with the above average value.[20] The most recent work by Rao and Berne,[21] involving a Monte Carlo simulation of the pressure tensor, also gives a value of about 3.27 Å (0.96 in reduced units) at 110 K.

It is our desire to pursue another calculation for δ. Based on the Kirkwood-Buff theory, we considered a realistic nonzero width of a liquid-vapor system. A linear and a cubic density profile are assumed for the interfacial region.[2] At 85 K, it is justifiable to take argon vapor density to be effectively zero. It is also argued that using a bulk-liquid radial-distribution function $g_l(r)$ in the transition zone is an accurate approximation as long as the liquid density ρ_l is much larger than the vapor density.[2] In the following, we shall first extend the Kirkwood-Buff formulation to evaluate the thickness effect on the location of the surface of tension. In Sec. III, numerical results from the simple integration of formulations in Sec. II will be given as compared to those previously reported. In Sec. IV, we shall briefly discuss the size dependence of the surface tension from Tolman's theory.[11] Finally, conclusions are given in Sec. V.

II. FORMULATION

We start from the Kirkwood-Buff formula to express the location of Gibbs surface of tension z_G in terms of surface tension γ, a two-body interaction potential $u(r_{12})$, and a certain special function $\Gamma_\nu^{(2)}$; i.e.,[14,16]

$$z_G = \frac{1}{2\gamma} \int \frac{1}{r_{12}} \frac{du(r_{12})}{dr_{12}} (z_{12}\Gamma_2^{(2)} + x_{12}^2 \Gamma_1^{(2)}) d\tau_{12}, \tag{1}$$

where

$$\gamma = \int \frac{1}{r_{12}} \frac{du(r_{12})}{dr_{12}} (z_{12}\Gamma_1^{(2)} + \tfrac{1}{2}x_{12}^2 \Gamma_0^{(2)}) d\tau_{12}, \tag{2}$$

and

$$\Gamma_\nu^{(2)}(r_{12}, z_{12}) = \int_{-\infty}^{0} z_1^\nu [\rho(z_1)\rho(z_2) g(z_1, z_2, r_{12}) - \rho_l^2 g_l(r_{12})] dz_1 + \int_0^\infty z_1^\nu [\rho(z_1)\rho(z_2) g(z_1, z_2, r_{12}) - \rho_v^2 g_v(r_{12})] dz_1 . \tag{3}$$

It is conventional to specify $z_{\text{eq}} = 0$ to be the equimolecular dividing surface in the interfacial region. This choice leads to the particle-conservation criterion

$$\int_{-\infty}^{0} [\rho_l - \rho(z)] dz = \int_0^\infty [\rho(z) - \rho_v] dz , \tag{4}$$

and therefore a simple relation

$$\delta = z_{\text{eq}} - z_G = -z_G . \tag{5}$$

Here, z is chosen to be the direction perpendicular to the dividing surface; $g_l(r_{12})$, $g_v(r_{12})$, and $g(z_1, z_2, r_{12})$ stand for the two-body distribution function in the bulk liquid, bulk vapor, and the transition zone, respectively. ρ_l and ρ_v are the bulk-liquid and bulk-vapor density, respectively. Singlet-density function $\rho(z)$ is subject to the boundary conditions

$$\rho(z) = \begin{cases} \rho_l, & z \to -\infty \\ \rho_v, & z \to \infty \end{cases} \tag{6}$$

where $\rho(z)$ changes drastically from ρ_l to ρ_v in the interfacial zone, a width d of several molecules in size. For a nonzero thickness, we assume a smooth profile which is antisymmetric about the equimolecular dividing surface. To satisfy Eq. (4), two simple choices for $\rho(z)$ are used: (i) linear density profile

$$\rho(z) = \rho_l \left[\frac{1}{2}\left(1 - \frac{z}{b}\right) \right] \quad -b \leq z \leq b , \tag{7}$$

and (ii) cubic density profile

$$\rho(z) = \rho_l \left[\frac{1}{2} - \frac{3}{4}\left(\frac{z}{b}\right) + \frac{1}{4}\left(\frac{z}{b}\right)^3 \right] \quad -b \leq z \leq b , \tag{8}$$

where b is the half-width of the transition region ($d = 2b$). Assuming $\rho_v \equiv 0$ and $g(z_1, z_2, r_{12}) \equiv g_l(r_{12})$, one can proceed to evaluate $\Gamma_\nu^{(2)}(r_{12}, z_{12})$ analytically. An explicit expression for $\Gamma_\nu^{(2)}$ in this approximation has been given by Fitts.[22] It is straightforward to obtain the following.

(i) For linear density profile

$$\Gamma_1^{(2)} = \begin{cases} \rho_l^2 g_l b^2 \left(\frac{1}{6} + \frac{z_{12}^2}{2b^2} \right) & (2b < z_{12}) \\ \rho_l^2 g_l b^2 \left(\frac{1}{6} + \frac{z_{12}}{6b} + \frac{z_{12}^2}{4b^2} + \frac{z_{12}^3}{8b^3} - \frac{z_{12}^4}{48b^4} \right) & (0 < z_{12} \leq 2b) \\ \rho_l^2 g_l b^2 \left(\frac{1}{6} + \frac{z_{12}}{6b} + \frac{z_{12}^2}{4b^2} + \frac{z_{12}^3}{8b^3} + \frac{z_{12}^4}{48b^4} \right) & (-2b < z_{12} \leq 0) \\ \rho_l^2 g_l b^2 \left(\frac{1}{6} \right) & (z_{12} \leq -2b) \end{cases} \tag{9a}$$

and

$$\Gamma_2^{(2)}=\begin{cases}\rho_l^2 g_l b^3\left(-\frac{z_{12}}{3b}-\frac{z_{12}^3}{3b^3}\right) & (2b<z_{12})\\ \rho_l^2 g_l b^3\left(-\frac{1}{15}-\frac{z_{12}}{6b}-\frac{z_{12}^2}{4b^2}-\frac{z_{12}^3}{8b^3}-\frac{z_{12}^4}{12b^4}+\frac{z_{12}^5}{80b^5}\right) & (0<z_{12}\leqslant 2b)\\ \rho_l^2 g_l b^3\left(-\frac{1}{15}-\frac{z_{12}}{6b}-\frac{z_{12}^2}{4b^2}-\frac{5z_{12}^3}{24b^3}-\frac{z_{12}^4}{12b^4}-\frac{z_{12}^5}{80b^5}\right) & (-2b<z_{12}\leqslant 0)\\ 0 & (z_{12}\leqslant -2b).\end{cases}\tag{9b}$$

(ii) For cubic density profile

$$\Gamma_1^{(2)}=\begin{cases}\rho_l^2 g_l b^2\left(\frac{1}{10}+\frac{z_{12}^2}{2b^2}\right) & (2b<z_{12})\\ \rho_l^2 g_l b^2\left(\frac{1}{10}+\frac{9z_{12}}{70b}+\frac{z_{12}^2}{4b^2}+\frac{3z_{12}^3}{20b^3}-\frac{z_{12}^5}{32b^5}+\frac{3z_{12}^6}{320b^6}-\frac{z_{12}^8}{4480b^8}\right) & (0<z_{12}\leqslant 2b)\\ \rho_l^2 g_l b^2\left(\frac{1}{10}+\frac{9z_{12}}{70b}+\frac{z_{12}^2}{4b^2}+\frac{3z_{12}^3}{20b^3}-\frac{z_{12}^5}{32b^5}-\frac{3z_{12}^6}{320b^6}+\frac{z_{12}^8}{4480b^8}\right) & (-2b<z_{12}\leqslant 0)\\ \rho_l^2 g_l b^2\left(\frac{1}{10}\right) & (z_{12}\leqslant -2b)\end{cases}\tag{9c}$$

and

$$\Gamma_2^{(2)}=\begin{cases}\rho_l^2 g_l b^3\left(-\frac{z_{12}}{5b}-\frac{z_{12}^3}{3b^3}\right) & (2b<z_{12})\\ \rho_l^2 g_l b^3\left(-\frac{11}{315}-\frac{z_{12}}{10b}-\frac{6z_{12}^2}{35b^2}-\frac{z_{12}^3}{6b^3}-\frac{z_{12}^4}{16b^4}-\frac{3z_{12}^5}{160b^5}+\frac{11z_{12}^6}{480b^6}-\frac{13z_{12}^7}{2240b^7}+\frac{z_{12}^9}{8064b^9}\right) & (0<z_{12}\leqslant 2b)\\ \rho_l^2 g_l b^3\left(-\frac{11}{315}-\frac{z_{12}}{10b}-\frac{6z_{12}^2}{35b^2}-\frac{z_{12}^3}{6b^3}-\frac{z_{12}^4}{16b^4}+\frac{3z_{12}^5}{160b^5}+\frac{11z_{12}^6}{480b^6}+\frac{13z_{12}^7}{2240b^7}-\frac{z_{12}^9}{8064b^9}\right) & (-2b<z_{12}\leqslant 0)\\ 0 & (z_{12}\leqslant -2b).\end{cases}\tag{9d}$$

Next, to evaluate Eq. (1), we shall first use cylindrical coordinates $(\rho_{12}, \theta_{12}, z_{12})$, and then transfer ρ_{12} to r_{12}, $(r_{12}^2=\rho_{12}^2+z_{12}^2)$,

$$\delta(d)=\frac{-1}{2\gamma(d)}\int\frac{1}{r_{12}}\frac{du}{dr_{12}}\left(z_{12}\Gamma_2^{(2)}+x_{12}^2\Gamma_1^{(2)}\right)d\tau_{12}\tag{10a}$$

$$=\frac{-1}{2\gamma(d)}\int_{-\infty}^{\infty}dz_{12}\int_0^{\infty}d\rho_{12}\rho_{12}\int_0^{2\pi}d\theta_{12}\frac{1}{r_{12}}\frac{du}{dr_{12}}\left(z_{12}\Gamma_2^{(2)}+\rho_{12}^2\cos^2\theta_{12}\Gamma_1^{(2)}\right)\tag{10b}$$

$$=\frac{-1}{2\gamma(d)}\int_{-\infty}^{\infty}dz_{12}\int_{|z_{12}|}^{\infty}dr_{12}\frac{du}{dr_{12}}\left[2\pi z_{12}\Gamma_2^{(2)}+\pi(r_{12}^2-z_{12}^2)\Gamma_1^{(2)}\right].\tag{10c}$$

We split the region of integration in Eq. (10c) into four portions according to Eqs. (9a)–(9d) (see also Fig. 1), and change the order of integration of r_{12} and z_{12}. The contribution to $\delta(d)$ in each portion is then as follows[23]:

Region A $(2b<z_{12})$,

$$\delta_A(d)=\frac{-1}{2\gamma(d)}\int_{2b}^{\infty}dz_{12}\int_{|z_{12}|}^{\infty}dr_{12}G=\frac{-1}{2\gamma(d)}\int_{2b}^{\infty}dr_{12}\int_{2b}^{r_{12}}dz_{12}G,\tag{11}$$

Region B $(0<z_{12}\leqslant 2b)$,

$$\delta_B(d) = \frac{-1}{2\gamma(d)} \int_0^{2b} dz_{12} \int_{|z_{12}|}^{\infty} dr_{12} G$$

$$= \frac{-1}{2\gamma(d)} \left(\int_0^{2b} dr_{12} \int_0^{r_{12}} dz_{12} G + \int_{2b}^{\infty} dr_{12} \int_0^{2b} dz_{12} G \right), \tag{12}$$

Region C $(-2b < z_{12} \leq 0)$,

$$\delta_C(d) = \frac{-1}{2\gamma(d)} \int_{-2b}^{0} dz_{12} \int_{|z_{12}|}^{\infty} dr_{12} G$$

$$= \frac{-1}{2\gamma(d)} \left(\int_0^{2b} dr_{12} \int_{-r_{12}}^{0} dz_{12} G + \int_{2b}^{\infty} dr_{12} \int_{-2b}^{0} dz_{12} G \right), \tag{13}$$

Region D $(z_{12} \leq -2b)$,

$$\delta_D(d) = \frac{-1}{2\gamma(d)} \int_{-\infty}^{-2b} dz_{12} \int_{|z_{12}|}^{\infty} dr_{12} G = \frac{-1}{2\gamma(d)} \int_{2b}^{\infty} dr_{12} \int_{-r_{12}}^{-2b} dz_{12} G, \tag{14}$$

where G is defined in terms of the respective $\Gamma_\nu^{(2)}$ in the different regions,

$$G(r_{12}, z_{12}) \equiv \frac{du(r_{12})}{dr_{12}} [2\pi z_{12} \Gamma_2^{(2)}(r_{12}, z_{12}) + \pi (r_{12}^2 - z_{12}^2) \Gamma_1^{(2)}(r_{12}, z_{12})]. \tag{15}$$

Then we have

$$\delta(d) = \delta_A(d) + \delta_B(d) + \delta_C(d) + \delta_D(d). \tag{16}$$

Now we can substitute Eqs. (9a)–(9d) into Eqs. (11)–(15). After a lengthy algebraic manipulation, it is somewhat surprising to see that both linear and cubic profile cases lead to an identical simple relation

$$\delta(d)\gamma(d) = + \frac{\pi \rho_l^2}{30} \int_0^{\infty} dr\, r^5 u'(r) g_l(r). \tag{17}$$

Equation (17) implies that the product of the location of the surface of tension and the surface tension is independent of thickness d.

For Fowler's model, $d=0$, $\gamma(0)$ is

$$\gamma(0) = \frac{\pi \rho_l^2}{8} \int_0^{\infty} dr\, r^4 u'(r) g_l(r). \tag{18}$$

This shows that $\delta(0)$ is in agreement with the expression given by Kirkwood and Buff[1]

$$\delta(0) = \frac{4}{15} \frac{\int_0^{\infty} dr\, r^5 u'(r) g_l(r)}{\int_0^{\infty} dr\, r^4 u'(r) g_l(r)}. \tag{19}$$

It is unclear whether this invariant relation Eq. (17) is also valid for more complicated (or realistic) profiles. However, it provides certain insight where the Gibbs surface of tension is located within the surface region for the above simple models. The width-dependent surface tension $\gamma(d)$ for both linear and cubic density profiles has been reported earlier.[2] They are (i) for linear density profile,

$$\gamma(d) = \pi \rho_l^2 \int_0^{2b} dr\, u'(r) g_l(r) \left(\frac{r}{15b} - \frac{r^2}{96b^2} \right) r^4 + \pi \rho_l^2 \int_{2b}^{\infty} dr\, u'(r) g_l(r) \left(\tfrac{2}{15} b^4 - \tfrac{1}{6} b^2 r^2 + \tfrac{1}{8} r^4 \right); \tag{20}$$

and (ii) for cubic density profile

$$\gamma(d) = \pi \rho_l^2 \int_0^{2b} dr\, u'(r) g_l(r) \left(\frac{2r}{25b} - \frac{r^3}{70b^3} + \frac{r^4}{256b^4} - \frac{r^6}{12800b^6} \right) r^4 + \pi \rho_l^2 \int_{2b}^{\infty} dr\, u'(r) g_l(r) \left(\tfrac{9}{175} b^4 - \tfrac{1}{10} b^2 r^2 + \tfrac{1}{8} r^4 \right). \tag{21}$$

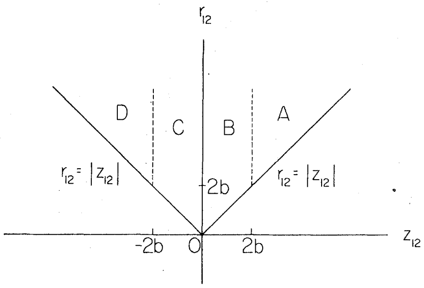

FIG. 1. Regions of integration for Eq. (10), $b \geq 0$.

III. RESULTS AND DISCUSSION

We have listed the values of $\gamma(d)$ and $\delta(d)$ for both the Barker-Fisher-Watts (BFW)[24] and Parson, Siska, and Lee (MSV-III)[25] potential in Tables I and II. Only pairwise additive potentials are considered. The accurate radial-distribution function $g_l(r)$ obtained from the neutron-diffraction data of Yarnell *et al.*[26] is used in the simple numerical integration. For liquid Ar at 85 K, the bulk-liquid density ρ_l is taken to be 0.021 25/Å^3 (Ref. 27). One can see that δ varies slowly for $d < 10$ Å. Although the BFW and MSV-III potentials give slightly different values for the surface tension, they do show almost no difference in δ for $d > 4.5$ Å for their respective density profiles. In fact δ is a quite stable value (2.9 ~ 3.2 Å), corresponding to an acceptable thickness range[8] despite the different density profile or different potential, whichever is used. The Fowler step-function profile seems not to lead to severe differences in the determination of δ values. Since there are no direct or indirect experimental values to test how good those results are, it can only make this study worthwhile by comparing the present calculation with other estimations previously reported in Table III.

TABLE I. Dependence of the location of the surface of tension z_G of Ar at 85 K on the zone width d using BFW potential (Ref. 24) ($\delta = -z_G$).

d	Linear profile		Cubic profile	
(Å)	γ(dyn/cm)	δ(Å)	γ(dyn/cm)	δ(Å)
0.0	13.71	2.90	13.71	2.90
0.5	13.72	2.90	13.71	2.90
1.0	13.74	2.89	13.73	2.89
1.5	13.78	2.88	13.75	2.89
2.0	13.82	2.87	13.78	2.88
2.5	13.84	2.87	13.81	2.88
3.0	13.82	2.87	13.83	2.87
3.5	13.75	2.89	13.82	2.87
4.0	13.59	2.92	13.79	2.88
4.5	13.35	2.97	13.72	2.89
5.0	13.05	3.04	13.61	2.92
5.5	12.72	3.12	13.45	2.95
6.0	12.36	3.21	13.26	3.00
6.5	12.00	3.31	13.04	3.05
7.0	11.64	3.41	12.80	3.10
7.5	11.28	3.52	12.54	3.17
8.0	10.93	3.63	12.28	3.23
8.5	10.60	3.75	12.01	3.31
9.0	10.28	3.86	11.74	3.38
9.5	9.98	3.98	11.47	3.46
10.0	9.69	4.10	11.21	3.54

TABLE II. Dependence of the location of the surface of tension z_G of Ar at 85 K on the zone width d using MSV-III potential (Ref. 25) ($\delta = -z_G$).

d	Linear profile		Cubic profile	
(Å)	γ(dyn/cm)	δ(Å)	γ(dyn/cm)	δ(Å)
0.0	15.00	2.79	15.00	2.79
0.5	15.00	2.79	15.00	2.79
1.0	15.00	2.79	15.00	2.79
1.5	14.99	2.79	14.99	2.79
2.0	14.97	2.79	14.99	2.79
2.5	14.93	2.80	14.98	2.79
3.0	14.84	2.82	14.94	2.80
3.5	14.70	2.85	14.89	2.81
4.0	14.47	2.89	14.80	2.83
4.5	14.18	2.95	14.68	2.85
5.0	13.83	3.03	14.52	2.88
5.5	13.45	3.11	14.31	2.92
6.0	13.06	3.20	14.08	2.97
6.5	12.67	3.30	13.82	3.03
7.0	12.27	3.41	13.55	3.09
7.5	11.90	3.52	13.26	3.16
8.0	11.53	3.63	12.97	3.23
8.5	11.18	3.74	12.68	3.30
9.0	10.84	3.86	12.39	3.38
9.5	10.52	3.98	12.10	3.46
10.00	10.21	4.10	11.81	3.54

A thermodynamic property related to the location of surface of tension is so-called excess surface-mass density Σ (or superficial number density defined in Ref. 1). This quantity Σ, originally introduced in Gibbs's adsorption formula $d\gamma = -\Sigma d\mu$ (μ being the chemical potential), is said to depend upon the choice of the dividing surface.[28] Following the Kirkwood-Buff theory of expressing the location of Gibbs surface of tension z_G, the excess surface-mass density Σ with respect to the dividing surface $z = z_G$ can be formulated by using Eq. (4), i.e.,

$$\Sigma = \int_{-\infty}^{z_G} [\rho(z) - \rho_l]\, dz + \int_{z_G}^{\infty} [\rho(z) - \rho_v]\, dz$$
$$= -\rho_l z_G = \rho_l \delta\,. \tag{22}$$

This simple exact relation provides a different physical interpretation by defining δ as the ratio

TABLE III. Comparison of the present calculation with the result previously reported.

	T(K)	δ(Å)
Kirkwood, Buff (1949) (Ref. 1)	90	3.63
Hill (1952) (Ref. 18)	90	2.81
	84	2.67
Plesner, Platz (1968) (Ref. 19)	84	2.01
Toxvaerd (1973) (Ref. 20)	89.85	9.28
	101.83	10.53
	119.80	13.93
Rao, Berne (1979) (Ref. 21)	110	3.27
Present work	85	3.00 (recommended)

of excess surface-mass density to bulk-liquid density ($\delta = \Sigma/\rho_l$), if Σ can be determined from certain thermodynamic functions.[29] In the relation of Eq. (17) for the product of $\delta(d)\gamma(d)$, a similar expression has been given by Lekner and Henderson[7c] in the cases of slow varying-density profiles (approaching the critical point or some polymer at ordinary temperature[30]). At the large-d limit, the surface tension is approximately equal to

$$\gamma(d) \simeq \frac{A(\rho_l - \rho_v)^2}{d} \int_0^\infty dr\, r^5 u'(r) g_l(r)\,, \tag{23}$$

where A is a dimensionless parameter depending on profile shape. Combining Eqs. (17) and (23) shows that δ is proportional to the interface thickness d. This is a highly satisfactory result. In fact, one can simply plot the linearity relation at large-d limit to verify the conclusion.

IV. CURVATURE (SIZE) DEPENDENCE OF SURFACE TENSION

One of the important applications in the evaluation of the location of the Gibbs surface of tension in the transition region is for consideration of the curvature (or size) dependence of the surface tension of a droplet or a liquid microcluster. An approximate relation for spherical surface tension derived from the Gibbs-Tolman-Koenig-Buff[14] expression for a *large* liquid cluster is

$$\gamma(R) = \gamma_\infty\left(1 - \frac{2\delta}{R} + \frac{3\delta^2}{R^2} \cdots\right), \tag{24}$$

where one restricts the treatment to a droplet with radius R large compared with the thickness d (equivalent to δ) of the interface layer. γ_∞ is the surface tension of planar interface (zero curvature).

Near the tripole point, a liquid droplet may be further approximated as a homogeneous spherical saturated cluster. Assuming the number of particles n is

$$n \simeq \tfrac{4}{3}\pi\rho_l R^3\,, \tag{25}$$

then (24) becomes

$$\gamma(n) = \gamma_\infty(1 - c_1 n^{-1/3} + c_2 n^{-2/3} \cdots) \tag{26}$$

with

$$c = \frac{2\delta}{(3/4\pi\rho_l)^{1/3}}\,, \quad c_2 = \tfrac{3}{4}c_1^2\,. \tag{27}$$

For instance, taking $\delta = 3.0$ Å and $\rho_l = 0.021\,25/\text{Å}^3$ in the present work, one finds $\gamma(n)$ at 85 K is

$$\gamma(n) = \gamma_\infty(1 - 2.68 n^{-1/3} + 5.38 n^{-2/3} \cdots)\,. \tag{28}$$

Because of initial limitation in deriving Eq. (24), Eq. (28) cannot be applicable for the cluster-size range relevant to nucleation conditions (n is $10^2 \sim 10^3$). The stronger dependence of γ on n in Eq. (28) was discussed by Nishioka,[31] who gave a similar equation by a least-squares fit of a Monte Carlo study of cluster free energy. For example, at 84 K Nishioka obtained

$$\gamma(n) = \gamma_\infty(1 - 0.67 n^{-1/3} + 5.56 n^{-2/3} \cdots)\,. \tag{29}$$

Asymptotic behaviors of Eqs. (28) and (29) are compared in Table IV. As suggested by Nishioka, the difficulty in calculating δ may be one of the many factors which result in a significant discrepancy of the c_1 coefficient in Eq. (26). In our judgment, the thickness effect on the δ-value determination probably gives a c_1 coefficient with at most ±5% uncertainty.

TABLE IV. Asymptotic behavior of the size dependence of the surface tension $\gamma(n)$ given in the ratio of $\gamma(n)/\gamma_\infty$.

n	R(Å)	$\gamma(n)/\gamma_\infty$ Eq. (29), 84 K	Eq. (28), 85 K
10^4	48	0.981	0.887
10^6	224	0.994	0.974
10^8	483	0.999	0.994
10^{10}	4825	1.000	0.999

V. CONCLUSION

Using the extended Kirkwood-Buff formula, the effect of the transition-zone width on the location of the surface of tension of argon near the triple point is formulated. To evaluate those formulas, we employed two realistic potentials, two simple single-density profiles, and an experimental radial-distribution function of the bulk liquid for the transition zone. Both the BFW and the MSV-III potentials, and the linear and the cubic density profiles lead to the mild dependence for the location of the surface of tension as a functions of the zone width. If only pairwise additive potentials are considered, the Gibbs surface of tension is located about one molecular size on the bulk-liquid side of the equimolecular dividing surface. This is in good agreement with those results reported previously.

ACKNOWLEDGMENTS

The author is very grateful to Professor W. C. Stwalley for reading this manuscript and clarifying several statements. Acknowledgment is also made to the Donors of the Petroleum Research Fund administered by the American Chemical Society for support of this work.

---

[1] J. G. Kirkwood and F. P. Buff, J. Chem. Phys. 17, 338 (1949).

[2] C. C. Shih and Y. H. Uang, Phys. Rev. A 17, 377 (1978); 15, 355 (1977).

[3] J. Goodisman, Phys. Rev. A 19, 1717 (1979).

[4] See, for example, H. S. Green, *The Molecular Theory of Fluids* (Interscience, New York, 1952), p. 70.

[5] K. S. C. Freedman and I. R. McDonald, Mol. Phys. 26, 529 (1973).

[6] R. W. Pastor and J. Goodisman, J. Chem. Phys. 68, 3654 (1978).

[7] J. Lekner and J. R. Henderson, (a) Physica (Utrecht) 94A, 545 (1978); (b) J. Low Temp. Phys. 31, 763 (1978); (c) Mol. Phys. 34, 333 (1977).

[8] J. R. Henderson and J. Lekner, Phys. Rev. A 20, 621 (1979).

[9] J. Miyazaki, J. A. Barker, and G. M. Pound, J. Chem. Phys. 64, 3364 (1976).

[10] J. M. Haile, C. G. Gray, and K. E. Gubbins, J. Chem. Phys. 64, 2569 (1976).

[11] R. C. Tolman, J. Chem. Phys. 16, 758 (1948); 17, 118 (1949); 17, 333 (1949).

[12] F. O. Koenig, J. Chem. Phys. 18, 449 (1950).

[13] F. P. Buff and J. G. Kirkwood, J. Chem. Phys. 18, 991 (1950).

[14] For a general review, see S. Ono and S. Kondo, *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1960), Vol. 10, p. 134; and F. P. Buff, *ibid.*, p. 281.

[15] F. F. Abraham, *Homogeneous Nucleation Theory* (Academic, New York, 1974), Chap. 2.

[16] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), Chap. 5, p. 351.

[17] R. H. Fowler, Proc. R. Soc. London Ser. A 159, 229 (1937).

[18] T. L. Hill, J. Chem. Phys. 20, 141 (1952).

[19] I. W. Plesner and O. Platz, J. Chem. Phys. 48, 5361 (1968).

[20] S. Toxvaerd, Mol. Phys. 26, 91 (1973).

[21] M. Rao and B. J. Berne, Mol. Phys. 37, 455 (1979).

[22] D. D. Fitts, Ph.D. dissertation, Yale University, 1957 (unpublished); Physica (Utrecht) 42, 205 (1969).

[23] Y. H. Uang, Ph.D. dissertation, University of Tennessee, 1977 (unpublished).

[24] J. A. Barker, R. A. Fisher, and R. O. Watts, Mol. Phys. 21, 657 (1971); J. K. Lee, J. A. Barker, and G. M. Pound, J. Chem. Phys. 60, 1976 (1974).

[25] J. M. Parson, P. E. Siska, and Y. T. Lee, J. Chem. Phys. 56, 1511 (1972).

[26] J. L. Yarnell, M. J. Katz, R. G. Wentzel, and S. H. Koenig, Phys. Rev. A 7, 2130 (1973).

[27] R. D. Present and C. T. Chen, J. Chem. Phys. 60, 5133 (1974); C. E. Upstill and R. Evans, J. Phys. C 10, 2791 (1977).

[28] J. W. Gibbs, *Scientific Papers* (Dover, New York, 1961).

[29] D. O. Edwards, J. R. Eckhardt, and F. M. Gasparini, Phys. Rev. A 9, 2070 (1974).

[30] S. T. Hwang (private communication).

[31] K. Nishioka, Phys. Rev. A 16, 2143 (1977).