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Nonadditivity contribution to the surface energy of a simple liquid

Yea H. Uang and Chia C. Shih

Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37916

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The nonadditivity contribution to the surface energy (excess internal energy per unit area of the surface) is derived from statistical mechanics as an integral involving intermolecular potentials and molecular distribution functions. Using Fowler's step-function density profile for the vapor-liquid system, Kirkwood's superposition approximation for the triplet-correlation function, Axilrod-Teller's triple-dipole potential for the three-body interaction potential u_{123}, and neutron-diffraction data of Yarnell *et al.* for the radial distribution function, one can calculate a sextuple integral to obtain the three-body correction $U_3^{(s)}$, which is about -2.4 ± 0.1 erg/cm^2 for liquid Ar at 85°K (near the triple point). This contribution is opposite in sign to the correction needed to improve the two-body contribution $U_2^{(s)}$ obtained from Fowler's formula with the same $g(r)$ data and Barker's realistic potential. Thus the combined value 23.9 erg/cm^2 of $U_2^{(s)}$ and $U_3^{(s)}$ is in worse disagreement with the experimental value of 34.9 erg/cm^2 than $U_2^{(s)}$ itself.

I. INTRODUCTION

Fowler's formula,[1] with the approximation of a density discontinuity between two phases, is found to be fairly good for the surface tension and poor for the surface energy of liquid argon at 85 °K in recent calculations[2,3] ($\gamma_{\text{exp}} = 13.1$ dyn/cm and $U_{\text{exp}}^{(s)} = 34.9$ erg/cm^2). Based on statistical-mechanical theory, Kirkwood and Buff[4] modified Fowler's formula by a hydrostatic treatment to include a continuous transition zone where the radial distribution function $g(r_{12}, z_1, z_2)$ depends on the positions z_1 and z_2 along the normal, as well as on the intermolecular distance r_{12}. More recently, taking the nonadditivity contribution into account, Present, Shih, and Uang[5,6] extended the Kirkwood-Buff molecular theory of surface tension to include the three-body interaction. They found that the agreement with the experimental result for the surface tension is not improved by the inclusion of γ_3 ($= -4.5$ dyn/cm) to γ_2 ($= +13.70$ dyn/cm). In a new Monte Carlo calculation, Miyazaki, Barker, and Pound[7] calculated both the surface tension and surface energy based on a direct evaluation of free energy (by relaxing the surfaces), which gave the larger values of 18.3 dyn/cm for γ_2 and 38.9 erg/cm^2 for $U_2^{(s)}$ and gave the combined values of $\gamma_2 + \gamma_3$ and $U_2^{(s)} + U_3^{(s)}$ closer to the experimental values. On the other hand, a more recent molecular-dynamics calculation of γ_2 by Rao and Levesque[8] gave 12.2 dyn/cm instead.

In the following, one uses a completely different approach, starting from the definition[9,10] of surface energy. $U^{(s)}$ is obtained by subtracting the internal energies of two individual bulk phases from the actual total internal energy of the inhomogeneous system. The main purposes for this work are (i) to extend the Kirkwood-Buff surface-energy formula to include nonadditivity effects and (ii) to evaluate the triple-dipole nonadditivity effect in Fowler's approximation, using the Kirkwood superposition approximation and experimental $g(r)$ data.

II. DEFINITION AND EXTENDED FORMULATION

Suppose that the surface of separation has been assigned in such a way as to divide the total volume V into a part V_l occupied by the liquid and a part $V_v = V - V_l$ occupied by the saturated vapor. Let ρ_l and U_l represent the number density and internal energy per molecule in the bulk liquid, and ρ_v and U_v represent the same in the bulk vapor. The total internal energy ignoring all surface effects is $\rho_l V_l U_l + \rho_v V_v U_v$. The difference U_A between the actual total energy U_T of the vapor-liquid inhomogeneous system and the above quantity is defined as the total excess surface energy, i.e.,

$$U_A = U_T - (\rho_l V_l U_l + \rho_v V_v U_v) . \tag{1}$$

Taking the Gibbs dividing surface as the $z = 0$ plane, by its definition,

$$0 = \int_{-\infty}^{0} [\rho(z) - \rho_v]\, dz + \int_{0}^{\infty} [\rho(z) - \rho_l]\, dz \tag{2}$$

and

$$U_A = A \int_{-\infty}^{0} [\rho(z) U(z) - \rho_v U_v]\, dz + A \int_{0}^{\infty} [\rho(z) U(z) - \rho_l U_l]\, dz , \tag{3}$$

where $\rho(z)$ and $U(z)$ are the actual number density and internal energy per molecule, respectively, and A is the total area of the dividing surface.

In the canonical ensemble, the internal energy per unit volume is given by[11,12]

$$\rho_l U_l = \tfrac{3}{2}\rho_l kT + \frac{1}{2}\int u_{12}(r_{12})\rho_l^{(2)}(\vec{r}_1, \vec{r}_2)\, d\tau_2 + \frac{1}{6}\iint u_{123}(r_{12}, r_{13}, r_{23}) \times \rho_l^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3)\, d\tau_2 d\tau_3 + \cdots , \tag{4}$$

$$\rho_v U_v = \tfrac{3}{2}\rho_v kT + \frac{1}{2}\int u_{12}(r_{12})\rho_v^{(2)}(\vec{r}_1, \vec{r}_2)\, d\tau_2 + \frac{1}{6}\iint u_{123}(r_{12}, r_{13}, r_{23}) \times \rho_v^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3)\, d\tau_2 d\tau_3 + \cdots , \tag{5}$$

$$\rho(z_1)U(z_1) = \tfrac{3}{2}\rho(z_1)kT + \frac{1}{2}\int u_{12}(r_{12})\rho^{(2)}(\vec{r}_1, \vec{r}_2)\, d\tau_2 + \frac{1}{6}\iint u_{123}(r_{12}, r_{13}, r_{23}) \times \rho^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3)\, d\tau_2 d\tau_3 + \cdots , \tag{6}$$

where $u_{12\ldots n}$ stands for the n-body interaction potential, $\rho_l^{(n)}$ and $\rho_v^{(n)}$ stand for the n-body correlation function in the bulk liquid and the bulk vapor, respectively, and $\rho^{(n)}$ stands for the n-body correlation function in the inhomogeneous system. The integration is over the whole volume and $r_{ij} = |\vec{r}_i - \vec{r}_j|$.

Since the surface energy is the excess internal energy per unit area, upon substituting (4)–(6) into (3), the kinetic-energy term vanishes and

$$U^{(s)} \equiv U_A/A = U_2^{(s)} + U_3^{(s)} + \cdots , \tag{7}$$

where

$$U_2^{(s)} = \frac{1}{2}\int_{-\infty}^{0} dz_1 \int u_{12}(r_{12})[\rho^{(2)}(\vec{r}_1, \vec{r}_2) - \rho_v^{(2)}(\vec{r}_1, \vec{r}_2)]\, d\tau_2 + \frac{1}{2}\int_0^{\infty} dz_1 \int u_{12}(r_{12})[\rho^{(2)}(\vec{r}_1, \vec{r}_2) - \rho_l^{(2)}(\vec{r}_1, \vec{r}_2)]\, d\tau_2 , \tag{8}$$

$$U_3^{(s)} = \frac{1}{6}\int_{-\infty}^{0} dz_1 \iint u_{123}(r_{12}, r_{13}, r_{23})[\rho^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) - \rho_v^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3)]\, d\tau_2 d\tau_3 + \frac{1}{6}\int_0^{\infty} dz_1 \iint u_{123}(r_{12}, r_{13}, r_{23})[\rho^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) - \rho_l^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3)]\, d\tau_2 d\tau_3 . \tag{9}$$

Here, $U_2^{(s)}$ is in agreement with the expression given by Kirkwood and Buff.[4]

In order to calculate the $U_2^{(s)}$ and $U_3^{(s)}$, we should know the behavior of $\rho^{(2)}$ and $\rho^{(3)}$ in the surface region. As there is no accurate and explicit theory for this behavior, we adopt the same approximations as in Ref. 6.

The pair number density function is then

$$\rho^{(2)}(\vec{r}_1, \vec{r}_2) = \rho^{(1)}(z_1)\rho^{(1)}(z_2)g^{(2)}(z_1, z_2, r_{12}) , \tag{10}$$

and the superposition approximation gives

$$\rho^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \rho^{(1)}(z_1)\rho^{(1)}(z_2)\rho^{(1)}(z_3) \times g^{(2)}(z_1, z_2, r_{12})g^{(2)}(z_1, z_3, r_{13}) \times g^{(2)}(z_2, z_3, r_{23}) , \tag{11}$$

where $g^{(2)}(z_1, z_2, r_{12})$ stands for the two-body radial distribution function in the transition zone.

Taking the Fowler step-function density-profile model, we have

$$\rho^{(1)}(z) = \begin{cases} 0 , & z < 0 \\ \rho_l , & z \geq 0 \end{cases} \tag{12}$$

and

$$g^{(2)}(z_1, z_2, r_{12}) = \begin{cases} 0 , & z_1 < 0 \text{ or } z_2 < 0 \\ g^{(2)}(r_{12}) , & z_1 \geq 0 \text{ and } z_2 \geq 0 \end{cases} \tag{13}$$

where $g^{(2)}(r_{ij})$ is the radial distribution function in the bulk liquid.

The three-body correction term has only three contributions for which at least one particle is in the vapor phase. $U_3^{(s)}$ then becomes

$$\begin{aligned} U_3^{(s)} = {} & \frac{1}{6}\int_0^{\infty} dz_1 \int_{-\infty}^{-z_1} dz_{12} \int_{-\infty}^{\infty} dx_{12} \int_{-\infty}^{\infty} dy_{12} \int_{-\infty}^{-z_1} dz_{13} \int_{-\infty}^{\infty} dx_{13} \int_{-\infty}^{\infty} dy_{13}\, u_{123}[-\rho_l^3 g^{(2)}(r_{12})g^{(2)}(r_{13})g^{(2)}(r_{23})] \\ & + \frac{1}{6}\int_0^{\infty} dz_1 \int_{-z_1}^{\infty} dz_{12} \int_{-\infty}^{\infty} dx_{12} \int_{-\infty}^{\infty} dy_{12} \int_{-\infty}^{-z_1} dz_{13} \int_{-\infty}^{\infty} dx_{13} \int_{-\infty}^{\infty} dy_{13}\, u_{123}[-\rho_l^3 g^{(2)}(r_{12})g^{(2)}(r_{13})g^{(2)}(r_{23})] \\ & + \frac{1}{6}\int_0^{\infty} dz_1 \int_{-\infty}^{-z_1} dz_{12} \int_{-\infty}^{\infty} dx_{12} \int_{-\infty}^{\infty} dy_{12} \int_{-z_1}^{\infty} dz_{13} \int_{-\infty}^{\infty} dx_{13} \int_{-\infty}^{\infty} dy_{13}\, u_{123}[-\rho_l^3 g^{(2)}(r_{12})g^{(2)}(r_{13})g^{(2)}(r_{23})] , \end{aligned} \tag{14}$$

where the last two terms are equal. By using cylindrical coordinates, $U_3^{(s)}$ becomes

$$U_3^{(s)} = -\frac{\rho_l^3}{3}\int_0^\infty dz_1 \int_{-\infty}^{-z_1} dz_{12}\int_0^\infty d\rho_{12}\,\rho_{12}\int_0^{2\pi} d\phi_{12}\int_{-\infty}^{-z_1} dz_{13}\int_0^\infty d\rho_{13}\,\rho_{13}\int_0^\pi d\phi_{23}\,G$$

$$-\frac{2\rho_l^3}{3}\int_0^\infty dz_1 \int_{-z_1}^{\infty} dz_{12}\int_0^\infty d\rho_{12}\,\rho_{12}\int_0^{2\pi} d\phi_{12}\int_{-\infty}^{-z_1} dz_{13}\int_0^\infty d\rho_{13}\,\rho_{13}\int_0^\pi d\phi_{23}\,G\,, \tag{15}$$

where

$$G = u_{123}\,g^{(2)}(r_{12})\,g^{(2)}(r_{13})\,g^{(2)}(r_{23})\,. \tag{16}$$

Replacing ρ_{12} by r_{12}, and ρ_{13} by r_{13}, we have

$$U_3^{(s)} = -\frac{2\pi\rho_l^3}{3}\int_0^\infty dz_1\int_{-\infty}^{-z_1} dz_{12}\int_{-\infty}^{-z_1} dz_{13}\int_{|z_{12}|}^\infty dr_{12}\,r_{12}\int_{|z_{13}|}^\infty dr_{13}\,r_{13}\int_{r_{23}^-}^{r_{23}^+} dr_{23}\,r_{23}F$$

$$-\frac{4\pi\rho_l^3}{3}\int_0^\infty dz_1\int_{-z_1}^{\infty} dz_{12}\int_{-\infty}^{-z_1} dz_{13}\int_{|z_{12}|}^\infty dr_{12}\,r_{12}\int_{|z_{13}|}^\infty dr_{13}\,r_{13}\int_{r_{23}^-}^{r_{23}^+} dr_{23}\,r_{23}F\,, \tag{17}$$

where we have used the relations

$$r_{23}\,dr_{23} = \rho_{12}\,\rho_{13}\sin\phi_{23}\,d\phi_{23}\,, \tag{18}$$

$$r_{23}^{\pm} = [(z_{12}-z_{13})^2 + (\rho_{12}\pm\rho_{13})^2]^{1/2}\,, \tag{19}$$

$$F = G/\rho_{12}\,\rho_{13}\sin\phi_{23}\,. \tag{20}$$

We have assumed $g(r)=0$ for $r \le d_0$, where d_0 is the distance of closest approach. It is very convenient to take d_0 as the unit of length and change the variables of integration to dimensionless quantities. Then, following the method of Ref. 6,

$$U_3^{(s)} = -\frac{2\pi\rho_l^3}{3d_0^2}\int_0^\infty dz_1\int_{\max(1,z_1)}^\infty dr_{12}\,r_{12}\int_{\max(1,z_1)}^\infty dr_{13}\,r_{13}\int_{-r_{12}}^{-z_1} dz_{12}\int_{-r_{13}}^{-z_1} dz_{13}\int_{\max(r_{23}^-,1)}^{\max(r_{23}^+,1)} dr_{23}\,r_{23}F$$

$$-\frac{4\pi\rho_l^3}{3d_0^2}\int_0^\infty dz_1\int_1^\infty dr_{12}\,r_{12}\int_{\max(1,z_1)}^\infty dr_{13}\,r_{13}\int_{\max(-r_{12},-z_1)}^{r_{12}} dz_{12}\int_{-r_{13}}^{-z_1} dz_{13}\int_{\max(r_{23}^-,1)}^{\max(r_{23}^+,1)} dr_{23}\,r_{23}F\,. \tag{21}$$

III. RESULTS AND DISCUSSION

The numerical evaluation of the above sextuple integrals is done by using the N-point Gaussian integration and is similar to the method described in Ref. 6. The triple-dipole interaction potential is given by[13]

$$u_{123} = \nu(r_{12}r_{13}r_{23})^{-3}(1 + 3\cos\theta_1\cos\theta_2\cos\theta_3)\,, \tag{22}$$

where r_{ij} are the sides and θ_i are the interior angles of the triangular array and ν is 7.45×10^{-83} erg cm^9 for Ar.[14] We have taken the neutron-diffraction experimental data of Yarnell *et al.*[15] for the radial distribution function. By carefully examining the experimental data, we have taken d_0 to be 3.20 Å. The density of liquid argon at 85 °K is taken to be $\rho_l = 0.021\,25$ atoms/Å^3.

The result for the nonadditivity correction $U_3^{(s)}$ is -2.4 ± 0.1 erg/cm^2 for liquid Ar at 85 °K. $U_2^{(s)}$ is 26.3 erg/cm^2 for both the Barker-Fisher-Watts and Morse-spline-van der Waals (MSV III) potentials[3] using the same $g(r)$ data and the Fowler approximation. $U_3^{(s)}$ gives a negative contribution to the total surface energy. The resulting combined value of $U_2^{(s)}$ and $U_3^{(s)}$ is 23.9 erg/cm^2 as compared to the experimental value of 34.9 erg/cm^2.[16] A larger value for $U_2^{(s)} + U_3^{(s)}$ was indicated by Miyazaki *et al.*[17]

Error in estimating the nonadditivity correction may come from the assumption of the Fowler approximation, the superposition approximation in the triplet correlation function, the use of the triple-dipole potential to represent the three-body interaction for all values of the distance r_{ij}, or possible inaccuracy in the experimental $g(r)$ data. Nevertheless, these factors are very unlikely to change the sign and magnitude of $U_3^{(s)}$ sufficiently to bring $U_2^{(s)} + U_3^{(s)}$ close to the experimental value. Higher-order n-body interaction or dipole-quadrupole interactions may also contribute. But these contributions are typically small for other thermodynamical properties and therefore not expected to be large.

The large discrepancy between the experimental value of surface energy and the $U_2^{(s)}+U_3^{(s)}$ most likely comes from $U_2^{(s)}$ instead $U_3^{(s)}$. Using a more realistic density profile and an approximate correlation function in the interfacial zone,[18] one can calculate the effects due to the nonzero width transition zone on the surface energy $U_2^{(s)}$. The results will be reported in another article.

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