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Nonadditivity contribution to the surface tension of simple liquids

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The Kirkwood-Buff formula has been extended to include three-body interactions by differentiation of the partition function with respect to the area. Assuming a step-function density profile (Fowler) and the superposition approximation (Kirkwood) for the triplet correlation function, the nonadditivity correction γ_3 to the surface tension is expressed as a septuple integral whose integrand contains the three-body interaction potential u_{123} and the radial distribution function of the liquid $g(r)$. We use the triple-dipole interaction (Axilrod-Teller) for u_{123} and the neutron diffraction data of Yarnell *et al.* for liquid Ar at 85°K to represent $g(r)$. It is necessary to make several changes of variable and inversions of the order of integration in order to transform the integral into a sextuple integral which can be programmed without incurring large errors due to cancellation. The result for Ar at 85°K is $\gamma_3 = -4.5$ erg/cm^2, which is not negligible when compared with the experimental surface tension (13.1 erg/cm^2). When γ_3 is combined with γ_2 [the surface tension computed in the Kirkwood-Buff-Fowler approximation from realistic pair potentials for Ar using the same $g(r)$ data], the total surface tension is significantly smaller than the experimental value.

I. INTRODUCTION

Molecular theories of surface tension based on radial distribution functions were first given by Fowler[1] and by Kirkwood and Buff.[2] Fowler assumed a step-function density profile at the interface, whereas Kirkwood and Buff allowed for a continuous decline in density in a surface layer 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}. It is very difficult to make a theoretical or experimental determination of $g(r_{12}, z_1, z_2)$. Fowler's approximation appears to be a reasonable one near the triple point, where the density falls off sharply, and recent calculations[3,4] on liquid Ar at 85°K give fairly good values for the surface tension γ but not for the surface energy (excess internal energy per unit area of the surface). Other noteworthy theories of surface tension are the significant-structures theory[5] and the Toxvaerd theory,[6] which is based on the Barker-Henderson[7] perturbation procedure. Lee *et al.*[8] have recently used Toxvaerd's method to calculate γ for liquid Ar with a realistic Ar-Ar pair potential, and they have included the triple-dipole three-body interaction. The purpose of this article is (i) to extend the Kirkwood-Buff formula to include nonadditivity effects and (ii) to evaluate the triple-dipole nonadditivity effect in the Fowler approximation, using the Kirkwood superposition approximation and experimental $g(r)$ data.

II. NONADDITIVITY EXTENSION OF THE KIRKWOOD-BUFF FORMULA

The Kirkwood-Buff formula was first derived by a hydrostatic-stress calculation.[2] A second derivation was later given by Buff[9] who, following Green's method[10] for calculating the vapor pressure, employed the purely statistical-mechanical procedure of differentiating the partition function with respect to the surface area. We shall generalize this derivation to include three-body interactions u_{ijk} in addition to the pair interactions u_{ij}. The surface tension γ is given by

$$\gamma = -kT\left(\frac{\partial \ln Z}{\partial A}\right)_{N,V,T}, \tag{1}$$

where A is the surface area and Z is the configuration integral ($\beta = 1/kT$)

$$Z = \int\cdots\int e^{-\beta U}\, dx_1 \cdots dz_N \tag{2}$$

and the potential energy U of the assembly is given by

$$U = \sum_{1\le i<j\le N} u_{ij} + \sum_{1\le i<j<k\le N} u_{ijk} = U_2 + U_3\,. \tag{3}$$

Transforming to Buff's dimensionless reduced coordinates

$$x_i = A^{1/2}x_i', \quad y_i = A^{1/2}y_i', \quad z_i = (V/A)z_i', \tag{4}$$

where the xy plane is parallel to the surface, one has

$$Z = V^N \int\cdots\int \exp[-\beta U(\vec{r}_i{}', V, A)]\, dx_1' \ldots dz_N', \tag{5}$$

and the limits are dimensionless. Thus

$$\left(\frac{\partial \ln Z}{\partial A}\right)_{N,V,T} = \frac{V^N}{Z}\int\cdots\int e^{-\beta U}\left[-\beta\left(\frac{\partial U}{\partial A}\right)_V\right] dx_1' \cdots dz_N', \tag{6}$$

where

$$\left(\frac{\partial U_2}{\partial A}\right)_V = \sum_{i<j} \frac{\partial u_{ij}}{\partial r_{ij}^2}\left(\frac{\partial r_{ij}^2}{\partial A}\right)_V , \tag{7}$$

$$\left(\frac{\partial U_3}{\partial A}\right)_V = \sum_{i<j<k}\left[\frac{\partial u_{ijk}}{\partial r_{ij}^2}\left(\frac{\partial r_{ij}^2}{\partial A}\right)_V + \frac{\partial u_{ijk}}{\partial r_{jk}^2}\left(\frac{\partial r_{jk}^2}{\partial A}\right)_V + \frac{\partial u_{ijk}}{\partial r_{ik}^2}\left(\frac{\partial r_{ik}^2}{\partial A}\right)_V\right]$$

$$= \sum_{i<j<k}\ \sum_{i\le l<m\le k} \frac{\partial u_{ijk}}{\partial r_{lm}^2}\left(\frac{\partial r_{lm}^2}{\partial A}\right)_V . \tag{8}$$

One readily finds that

$$A\left(\frac{\partial r_{ij}^2}{\partial A}\right)_V = x_{ij}^2 + y_{ij}^2 - 2z_{ij}^2 . \tag{9}$$

Let γ_2 be the part of γ that comes from $\partial U_2/\partial A$ in Eq. (6). Then

$$\gamma_2 = \frac{V^N}{Z}\int\cdots\int e^{-\beta U}\sum_{i<j}\frac{\partial u_{ij}}{\partial r_{ij}^2}\left(\frac{\partial r_{ij}^2}{\partial A}\right)_V dx_1'\cdots dz_N'$$

$$= \frac{N(N-1)}{2Z}\int\cdots\int e^{-\beta U}\frac{\partial u_{12}}{\partial r_{12}^2}\left(\frac{\partial r_{12}^2}{\partial A}\right)_V dx_1\ldots dz_N$$

$$= \frac{1}{2}\int d\tau_1\int d\tau_2\frac{\partial u_{12}}{\partial r_{12}^2}\left(\frac{\partial r_{12}^2}{\partial A}\right)_V$$

$$\times\frac{N(N-1)}{Z}\int\cdots\int e^{-\beta U}d\tau_3\cdots d\tau_N . \tag{10}$$

Introducing the pair correlation function in the surface layer, $\rho^{(2)}(\vec{r}_{12}, z_1)$, which depends on the three-body interactions since $U = U_2 + U_3$, Eq. (10) becomes

$$\gamma_2 = \frac{1}{2}\int d\tau_1\int d\tau_2\frac{\partial u_{12}}{\partial r_{12}^2}\left(\frac{\partial r_{12}^2}{\partial A}\right)_V \rho^{(2)}(\vec{r}_{12}, z_1) = \frac{1}{2}\int_{-\infty}^{\infty} dz_1\int d\tau_{12}\,\rho^{(2)}(\vec{r}_{12}, z_1)A\left(\frac{\partial r_{12}^2}{\partial A}\right)_V\frac{\partial u_{12}}{\partial r_{12}^2}$$

$$= \frac{1}{2}\int_{-\infty}^{\infty} dz_1\int d\tau_{12}\,\rho^{(2)}(\vec{r}_{12}, z_1)(x_{12}^2 + y_{12}^2 - 2z_{12}^2)\frac{\partial u_{12}}{\partial r_{12}^2}$$

$$= \frac{1}{4}\int_{-\infty}^{\infty} dz_1\int d\tau_{12}\,\rho^{(2)}(\vec{r}_{12}, z_1)\left(\frac{(x_{12}^2 + y_{12}^2 - 2z_{12}^2)}{r_{12}}\right)\frac{\partial u_{12}}{\partial r_{12}} . \tag{11}$$

From symmetry the term in y_{12}^2 is equal to the term in x_{12}^2, and the result is

$$\gamma_2 = \frac{1}{2}\int_{-\infty}^{\infty} dz_1\int d\tau_{12}\,\rho^{(2)}(\vec{r}_{12}, z_1)\left(\frac{x_{12}^2 - z_{12}^2}{r_{12}}\right)\frac{du_{12}}{dr_{12}} \tag{12}$$

$$= \frac{1}{2}\int_{-\infty}^{\infty} dz_1\,\rho(z_1)\int d\tau_{12}\,\rho(z_2)g(\vec{r}_{12}, z_1)\left(\frac{x_{12}^2 - z_{12}^2}{r_{12}}\right)\frac{du_{12}}{dr_{12}} , \tag{13}$$

where we have introduced the singlet densities $\rho(z_1)$ and $\rho(z_2)$ and the radial distribution function $g(\vec{r}_{12}, z_1)$ in the surface layer. Equation (13) is the Kirkwood-Buff formula. It is to be noted that Eqs. (12) and (13) contain the pair potentials explicitly but that the three-body (and higher-order) interactions are implicitly contained in $\rho^{(2)}(\vec{r}_{12}, z_1)$ and $g(\vec{r}_{12}, z_1)$.

We turn now to the explicit terms in u_{ijk}. Let γ_3 be the part of γ that comes from $\partial U_3/\partial A$ in Eq. (6). Then

$$\gamma_3 = \frac{V^N}{Z}\int\cdots\int e^{-\beta U}\sum_{i<j<k}\ \sum_{i\le l<m\le k}\frac{\partial u_{ijk}}{\partial r_{lm}^2}\left(\frac{\partial r_{lm}^2}{\partial A}\right)_V dx_1'\cdots dz_N'$$

$$= \frac{N(N-1)(N-2)}{3!Z}\int\cdots\int e^{-\beta U}\sum_{1\le l<m\le 3}\frac{\partial u_{123}}{\partial r_{lm}^2}\left(\frac{\partial r_{lm}^2}{\partial A}\right)_V dx_1\cdots dz_N$$

$$= \frac{1}{6}\int d\tau_1\int d\tau_2\int d\tau_3\sum_{l<m}\frac{\partial u_{123}}{\partial r_{lm}^2}\left(\frac{\partial r_{lm}^2}{\partial A}\right)_V \frac{N(N-1)(N-2)}{Z}\int\cdots\int e^{-\beta U}d\tau_4\cdots d\tau_N$$

$$= \frac{1}{6}\int d\tau_1\int d\tau_2\int d\tau_3\sum_{l<m}\frac{\partial u_{123}}{\partial r_{lm}^2}\left(\frac{\partial r_{lm}^2}{\partial A}\right)_V \rho^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) , \tag{14}$$

where $\rho^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ is the triplet correlation function in the surface layer. With the aid of Eq. (9), this becomes

$$\gamma_3=\frac{1}{6A}\int d\tau_1\int d\tau_2\int d\tau_3\sum_{l<m}(x_{lm}^2+y_{lm}^2-2z_{lm}^2)\frac{\partial u_{123}}{\partial r_{lm}^2}\,\rho^{(3)}(\vec{r}_1,\vec{r}_2,\vec{r}_3)$$

$$=\frac{1}{2A}\int d\tau_1\int d\tau_2\int d\tau_3(x_{12}^2+y_{12}^2-2z_{12}^2)\frac{\partial u_{123}}{\partial r_{12}^2}\,\rho^{(3)}(\vec{r}_1,\vec{r}_2,\vec{r}_3)$$

$$=\frac{1}{2A}\int d\tau_1\int d\tau_2\int d\tau_3\left(\frac{x_{12}^2-z_{12}^2}{r_{12}}\right)\frac{\partial u_{123}}{\partial r_{12}}\,\rho^{(3)}(\vec{r}_1,\vec{r}_2,\vec{r}_3), \tag{15}$$

where we have assumed u_{123} to be a symmetric function of the r_{lm} and have again taken the term in y_{12}^2 equal to the term in x_{12}^2. Finally

$$\gamma_3=\frac{1}{2}\int_{-\infty}^{\infty}dz_1\int d\tau_{12}\int d\tau_{13}\left(\frac{x_{12}^2-z_{12}^2}{r_{12}}\right)\frac{\partial u_{123}}{\partial r_{12}}\,\rho^{(3)}(\vec{r}_1,\vec{r}_2,\vec{r}_3)\,. \tag{16}$$

Equation (16) provides the nonadditivity extension of the Kirkwood-Buff formula to take explicit account of three-body interactions.

Equation (16) is intractable without further assumptions. We use the step-function approximation for the density profile and the superposition approximation for $\rho^{(3)}(\vec{r}_1,\vec{r}_2,\vec{r}_3)$. Taking the xy plane as the surface of discontinuity with the liquid of bulk number density n_l above and the vapor of density zero below, we assume for the singlet densities

$$\rho(z_i)=\begin{cases}n_l, & z_i>0\\ 0, & z_i<0\end{cases}\qquad i=1,2,3 \tag{17}$$

and for the triplet correlation function

$$\rho^{(3)}(\vec{r}_1,\vec{r}_2,\vec{r}_3)=\rho(z_1)\rho(z_2)\rho(z_3)g(r_{12})g(r_{23})g(r_{13}), \tag{18}$$

where $g(r)$ is the radial distribution function in the bulk liquid. Inserting Eqs. (17) and (18) in Eq. (16) then gives

$$\gamma_3=\frac{n_l^3}{2}\int_0^{\infty}dz_1\int_{-\infty}^{\infty}dx_{12}\int_{-\infty}^{\infty}dy_{12}\int_{-z_1}^{\infty}dz_{12}\int_{-\infty}^{\infty}dx_{13}\int_{-\infty}^{\infty}dy_{13}\int_{-z_1}^{\infty}dz_{13}\left(\frac{x_{12}^2-z_{12}^2}{r_{12}}\right)\frac{\partial u_{123}}{\partial r_{12}}\,g(r_{12})g(r_{13})g(r_{23})\,. \tag{19}$$

Equation (19) can be used to calculate γ_3 if u_{123} and $g(r)$ are known. It is reasonable to use the triple-dipole interaction for u_{123}, even for small r_{ij}, because of the cut-off provided by $g(r_{ij})$. The radial distribution function $g(r)$ will be taken from experiment.

III. EVALUATION OF THE SEPTUPLE INTEGRAL FOR γ_3

It is necessary to make several changes of variable and inversions of the order of integration in order to transform the septuple integral of Eq. (19) into a sextuple integral over z_1, r_{12}, z_{12}, r_{13}, z_{13}, and r_{23} which can be programmed for a computer without incurring large errors due to cancellation. The triple-dipole interaction is given by

$$u_{123}=\nu(r_{12}r_{23}r_{13})^{-3}(1+3\cos\gamma_1\cos\gamma_2\cos\gamma_3), \tag{20}$$

where r_{ij} are the sides and γ_i the interior angles of the triangular array and ν has been accurately calculated for rare-gas atoms.[11] We denote the threshold of the radial distribution function by d_0; this is often referred to as the distance of closest approach and can be determined approximately from diffraction experiments. We then assume that $g(r)=0$ for $r<d_0$, and it will be convenient to use d_0 as the unit of length. The coordinates in all the following formulas are dimensionless, e.g., x_{12} stands for x_{12}/d_0, etc. The integration is initially formulated in terms of cylindrical coordinates and x_{ij}, y_{ij} are replaced by the plane polar coordinates ρ_{ij}, ϕ_{ij}. It is convenient to introduce

$$F(r_{12},r_{23},r_{13})\equiv r_{12}^{-1}\frac{\partial u_{123}}{\partial r_{12}}\,g(r_{12})g(r_{23})g(r_{13}), \tag{21}$$

where F depends only on the sides r_{ij} of the triangle. Then

$$\gamma_3=\frac{n_l^3}{d_0^2}\int_0^{\infty}dz_1\int_{-z_1}^{\infty}dz_{12}\int_{-\infty}^{\infty}dx_{12}\int_{-\infty}^{\infty}dy_{12}\int_{-z_1}^{\infty}dz_{13}\int_0^{\infty}d\rho_{13}\,\rho_{13}\int_0^{\pi}d\phi_{23}\,(x_{12}^2-z_{12}^2)F. \tag{22}$$

In order to avoid errors due to cancellation, the integrals over x_{12}, y_{12}, and z_{12} are rewritten as

$$\int_{-z_1}^{\infty} dz_{12} \int_{-\infty}^{\infty} dx_{12} \int_{-\infty}^{\infty} dy_{12}(x_{12}^2 - z_{12}^2)F = \int_{-z_1}^{\infty} dz_{12} \int_{-z_1}^{\infty} dx_{12} \int_{-\infty}^{\infty} dy_{12}(x_{12}^2 - z_{12}^2)F + \int_{-z_1}^{\infty} dz_{12} \int_{-\infty}^{-z_1} dx_{12} \int_{-\infty}^{\infty} dy_{12}(x_{12}^2 - z_{12}^2)F. \tag{23}$$

The first integral on the right-hand side vanishes and the second integral, transformed to cylindrical coordinates, becomes

$$\int_{-z_1}^{\infty} dz_{12} \int_{z_1}^{\infty} d\rho_{12}\,\rho_{12} \int_{\pi-\alpha}^{\pi+\alpha} d\phi_{12}(\rho_{12}^2 \cos^2\phi_{12} - z_{12}^2)F = 2\int_{-z_1}^{\infty} dz_{12} \int_{z_1}^{\infty} d\rho_{12}\,\rho_{12}[(\tfrac{1}{2}\rho_{12}^2 - z_{12}^2)\alpha + \tfrac{1}{4}\rho_{12}^2 \sin 2\alpha]\,F, \tag{24}$$

where $\cos\alpha = z_1/\rho_{12}$. Since $r_{23}dr_{23} = \rho_{12}\,\rho_{13}\sin\phi_{23}\,d\phi_{23}$, Eq. (22) can then be rewritten as

$$\gamma_3 = \frac{2n_l^3}{d_0^2} \int_0^{\infty} dz_1 \int_{-z_1}^{\infty} dz_{12} \int_{-z_1}^{\infty} dz_{13} \int_{z_1}^{\infty} d\rho_{12}\,\rho_{12} \int_0^{\infty} d\rho_{13}\,\rho_{13} \int_{\max(r_{23}^-,\,1)}^{\max(r_{23}^+,\,1)} dr_{23}\,r_{23}G\ , \tag{25}$$

where

$$G = \frac{(\frac{1}{2}\rho_{12}^2 - z_{12}^2)\alpha + \frac{1}{4}\rho_{12}^2 \sin 2\alpha}{\rho_{12}\rho_{13}\sin\phi_{23}}\,F \tag{26}$$

and $r_{23}^{\pm} = [(z_{12} - z_{13})^2 + (\rho_{12} \pm \rho_{13})^2]^{1/2}$. If ρ_{12} is now replaced by r_{12} and ρ_{13} by r_{13}, Eq. (25) becomes

$$\gamma_3 = \frac{2n_l^3}{d_0^2} \int_0^{\infty} dz_1 \int_{-z_1}^{\infty} dz_{12} \int_{-z_1}^{\infty} dz_{13} \int_{\max[(z_1^2+z_{12}^2)^{1/2},\,1]}^{\infty} dr_{12}\,r_{12} \int_{\max(|z_{13}|,\,1)}^{\infty} dr_{13}\,r_{13} \int_{\max(r_{23}^-,\,1)}^{\max(r_{23}^+,\,1)} dr_{23}\,r_{23}G. \tag{27}$$

Equation (27) is in suitable form for computer programming. An alternative form of Eq. (27) is obtained by changing the order of integration. Thus

$$\gamma_3 = \frac{2n_l^3}{d_0^2} \int_0^{\infty} dz_1 \int_{\max(z_1,\,1)}^{\infty} dr_{12}\,r_{12} \int_{\max[-(r_{12}^2 - z_1^2)^{1/2},\,-z_1]}^{(r_{12}^2 - z_1^2)^{1/2}} dz_{12} \int_1^{\infty} dr_{13}\,r_{13} \int_{\max(-r_{13},\,-z_1)}^{r_{13}} dz_{13} \int_{\max(r_{23}^-,\,1)}^{\max(r_{23}^+,\,1)} dr_{23}\,r_{23}G. \tag{28}$$

In order to evaluate Eqs. (27) and (28) numerically, the integration domain is divided into blocks of finite size. The integration over each variable is then reduced to an N-point Gaussian approximation given by

$$\int_a^b f(x)\,dx \cong (b-a)\sum_{j=1}^{N} f[a + (b-a)x_j]\,\Delta x_j, \tag{29}$$

where the tabulated values of x_j and Δx_j depend only on N and not on the specific function $f(x)$. The Gaussian approximation becomes exact if $f(x)$ is a polynomial of degree less than $2N$ and, in other cases, it is accurate to the extent that $f(x)$ can be accurately approximated by a $2N$-1 degree polynomial. The summation of the contributions from all the blocks, with appropriate cut-off determined by the integration limits, leads to the following approximation for Eq. (27):

$$\begin{aligned}\gamma_3 \cong \frac{2n_l^3}{d_0^2} \sum_{j_1=0}^{N_1} \sum_{j_2=0}^{N_2} \sum_{j_3=0}^{N_3} \int_{aj_1}^{a(j_1+1)} dz_1 \int_{-z_1+bj_2}^{-z_1+b(j_2+1)} dz_{12} \int_{-z_1+cj_3}^{-z_1+c(j_3+1)} dz_{13} \\ \times \int_0^{\min[(z_1^2+z_{12}^2)^{-1/2},\,1]} r_{12}^3\,d(r_{12}^{-1}) \\ \times \int_0^{\min(|z_{13}|^{-1},\,1)} r_{13}^3\,d(r_{13}^{-1}) \\ \times \int_{\min[(r_{23}^+)^{-1},\,1]}^{\min[(r_{23}^-)^{-1},\,1]} r_{23}^3\,d(r_{23}^{-1})G;\end{aligned} \tag{30}$$

and for Eq. (28):

$$\gamma_3 \cong \frac{2n_l^3}{d_0^2} \sum_{j_1=0}^{N_1} \sum_{j_2=0}^{N_2} \sum_{j_3=0}^{N_3} \int_{aj_1}^{a(j_1+1)} dz_1 \int_{\max(z_1,\,1)+bj_2}^{\max(z_1,\,1)+b(j_2+1)} r_{12}\,dr_{12} \times \int_{1+cj_3}^{1+c(j_3+1)} r_{13}\,dr_{13} \int_{\max[-(r_{12}^2-z_1^2)^{1/2},\,-z_1]}^{(r_{12}^2-z_1^2)^{1/2}} dz_{12} \times \int_{\max(-r_{13},\,-z_1)}^{r_{13}} dz_{13} \int_{\max(r_{23}^-,\,1)}^{\max(r_{23}^+,\,1)} r_{23}\,dr_{23}\,G. \qquad (31)$$

In both Eqs. (30) and (31), the parameters a, b, and c which control the size of the blocks and the parameters N_1, N_2, and N_3 which specify the number of Gaussian points are selected by trial and error. The two formulas give results of comparable accuracy.

IV. RESULTS AND DISCUSSION

Up until recently x-ray and neutron diffraction experiments on liquids have been subject to large errors; these are partly manifested by large-amplitude ripples in $g(r)$ for small values of r at which the atoms overlap and $g(r)$ is expected to vanish. Recent neutron diffraction experiments of Yarnell *et al.*[12] on liquid Ar near the triple point provide data for $g(r)$ in which the spurious ripples are extraordinarily small (the estimated error in the structure factor is ~ 0.01). We have used these experimental data to calculate γ_3 for liquid Ar at 85 °K, where the density $n_l = 0.021\,25$ atoms/Å^3. The distance of closest approach or threshold of the $g(r)$ curve occurs at $d_0 = 3.20$ Å. The coefficient ν of the triple-dipole interaction, given by Eq. (20), has been found[11] to be 7.45×10^{-83} erg cm^9 for Ar.

The result for the nonadditivity correction γ_3 is -4.5 erg/cm^2 for liquid Ar at 85 °K. This is to be compared with the values[4] of γ_2 calculated by the Kirkwood-Buff-Fowler method for the same state of Ar using the same experimental $g(r)$ data[12] and two realistic pair potentials for Ar. The Morse-spline-van der Waals (MSV III) potential[13] gave $\gamma_2 = 15.0$ erg/cm^2 and the Barker-Fisher-Watts (BFW) potential[14] gave $\gamma_2 = 13.7$ erg/cm^2. The experimental value is 13.1 erg/cm^2. It is to be noted that part of the nonadditivity effect is taken into account through the use of the experimental $g(r)$ data in evaluating γ_2. The complete nonadditive surface tension $\gamma_2 + \gamma_3$, as obtained by the Kirkwood-Buff-Fowler method, is then 10.5 erg/cm^2 for the MSV III potential and 9.2 erg/cm^2 for the BFW potential. The agreement with experiment is not improved by the inclusion of γ_3. There is one other independent calculation of γ_3, that of Ref. 8, in which the triple-dipole potential was also used to represent the three-body interaction for all values of the distances r_{ij} and in which the superposition approximation was also used. This calculation was based on the Barker-Henderson perturbation theory, and the method is thus completely different from that used here. Nevertheless, the value of γ_3 obtained in Ref. 8 for liquid Ar at 84 °K is -4.0 erg/cm^2, which is remarkably close to the value we have obtained. The large value of $|\gamma_3|$ obtained in both calculations is not surprising in view of the large triple-dipole nonadditivity correction to the vapor pressure near the triple point where the correction[15] exceeds $n_l kT$. The singular behavior of the triple-dipole potential $[u_{123} \propto (r_{12}r_{23}r_{13})^{-3}]$ could lead to an excessively large contribution from small r_{ij} values. We have estimated the contribution to γ_3 from triangular arrays in which the r_{ij} are small by introducing a cut-off distance r^* such that the three-body interaction vanishes when *any* $r_{ij} < r^*$. If $r^* = 3.76$ Å (the minimum of the BFW pair potential), the value of γ_3 is reduced in magnitude to -2.5 erg/cm^2, but for $r^* = 3.5$ Å there is little change with $\gamma_3 = -4.2$ erg/cm^2. The contribution to γ_3 from triangles in which all sides are smaller than 3.76 Å is only -0.1 erg/cm^2. A large part of γ_3 comes from triangles with one side smaller than the separation at the minimum of the pair potential, and single-overlap three-body interactions should begin to play a role at these distances.

The three-body dipole-quadrupole interactions have been studied and found to make small but not negligible contributions to third virial coefficients and crystal energies.[16,17,18] There is no reliable calculation of three-body overlap interactions. We have essentially assumed that these interactions are absent and that the triple-dipole interactions can be used for distances r_{ij} greater than d_0, where u_{ijk} is cut off through the vanishing of $g(r_{ij})$. Although there is no theoretical justification for this procedure, it has been found to give satisfactory results in several cases. Third virial coefficients of noble gases, calculated from realistic pair potentials, are ~30% smaller than experimental values at low temperatures. Inclusion of the triple-dipole nonadditivity correction, in which u_{ijk} is cut off through the vanishing of the Boltzmann factors, gives results that are in very good agreement with experiment.[19] Calculations of solid-state and liquid-state properties of Ar, Kr, and Xe, using a realistic pair potential and including the triple-dipole interaction, have also given very good results.[14, 20, 21] A recent determination of the cohesive energy of fcc Kr, in which three independent semiempirical pair potentials adjusted to fit many two-body data were used and in which the triple-dipole interaction was included, gave excellent agreement with the experimental cohesive energy.[22]

The disagreement between the calculated values of $\gamma_2+\gamma_3$ and experiment could be due to the use of the step-function profile in obtaining γ_2. In Ref. 3 the effect of surface thickness was examined, and it was found that for surface thicknesses less than d_0 the value of γ_2 was inappreciably changed from the step-function result. We have also estimated the effect of surface thickness on γ_2 in a different way, using a cubic density profile and experimental $g(r)$ data, and obtained a similar result. Although there appears to be no reliable way of estimating surface thickness, there are some indications that the thickness near the triple point is of the order of the molecular diameter.[23] Therefore, the step-function approximation is probably fairly reliable.

The major approximations of this calculation, leading to uncertainties in the result, are (i) the neglect of n-body interactions with $n \geq 4$, (ii) the use of the triple-dipole potential to represent the three-body interaction for all values of the distances r_{ij}, (iii) the use of the superposition approximation for the triplet correlation function, and (iv) the use of the Fowler approximation. Inaccuracies in the $g(r)$ data and in the pair potentials used to calculate γ_2 should also be considered.[24]

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[24] J. A. Barker has made the following comments: "The Buff-Kirkwood-Fowler model (for pair interactions) involves two separate approximations: (i) the one-body density $\rho(r)$ is a step-function, (ii) the two-body distribution function is $\rho(r_1)\rho(r_2)g(R_{12})$, where g is the bulk liquid function. Freeman and McDonald [Ref. 3] and Present *et al.* [this work] show that approximation (i) is not too serious, but this says nothing about (ii). In fact, one would expect (ii) to be better for surface energy than surface tension, yet it gives surface energies which are too low, by about 7 erg cm^{-2} for argon at the triple point. Recent calculations by other methods—Monte Carlo: Ref. 8 and G. A. Chapela, G. Saville, and J. S. Rowlinson, Faraday Discuss. Chem. Soc. 59, 22 (1975); and perturbation theory: Refs. 6 and 8 and F. F. Abraham, J. Chem. Phys. 63, 157 (1975)—indicate that the Kirkwood-Buff-Fowler surface tension is also probably too low by something like 3 or 4 erg cm^{-2}," private communication.