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Theory of Surface Tension and Its Application to Simple Fluids

V. A. Kuz,[1] M. A. Vila,[1] A. N. Garazo,[1] and G. J. Zarragoicoechea[1]

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We consider a liquid–vapor interface in thermal equilibrium. The tangential component of the pressure tensor is supposed to depend explicitly upon the position and the density profile. Under this hypothesis the mechanical definition of surface tension becomes a finite summation of $N+1$ terms related directly to the local compressibility. When the inhomogeneous compressibility equation is considered, the theory provides a microscopic expression of the surface tension coefficient. A calculation for argon near the critical point is done; the agreement with experiment is satisfactory.

KEY WORDS: Surface tension; compressibility; argon; critical point.

1. INTRODUCTION

We sketch a theory of surface tension based on the idea that the tangential component P_T of the pressure tensor $\tilde{P}$ is an explicit function of the position z and the density $\rho(z)$ within the inhomogeneous interfacial region. This assumption, suggested recently by Percus,(1) can be seen as a generalization of the Tolman(2) and Ono and Kondo(3) hypothesis. Following this idea, in section 2 the surface tension σ is written as a sum of N integrals involving the partial derivatives with respect to the position of $\partial P_T/\partial\rho$, plus a contribution containing the partial derivative $\partial^{N+1}P_T/\partial z^{N+1}$ only. As $\partial P_T/\partial\rho$ is related to the "local compressibility," we follow the so-called "compressibility route" instead of the pressure route investigated by Kirkwood(4) and others.(5),[2]

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[1] Instituto de Física de Líquidos y Sistemas Biológicos, Universidad Nacional de la Plata, La Plata (1900), Argentina.

[2] Reference 5 extends the pressure tensor to mixtures.

In order to give a microscopic expression for the surface tension, in Section 3, we obtain the local transverse compressibility from the generalized local thermodynamic and the first Yvon equations. Then the local compressibility is expressed in terms of the one- and two-particle distribution functions. Section 4 is devoted to checking the theory, calculating approximately the surface tension of argon near the critical point. In the light of the numerical results for different density profiles, a comparison with other theories and experimental values is performed.

2. SURFACE TENSION

The mechanical definition of surface tension σ for a flat liquid–vapor interface at the $z=0$ plane is$^{(6)}$

$$\sigma=\int_{-\infty}^{\infty}(p-P_T)\,dz \tag{1}$$

where p is the equilibrium pressure and P_T is assumed here to be strictly locally dependent on z and $\rho(z)$. This dependence removes the vanishing of σ produced in the point-thermodynamic approximation,$^{(2,3,6)}$ when the density profile $\rho(z)$ is the step function, for any $P_T(\rho)$. If, e.g., $P_T(z,\rho(z))=p+A(\rho(z))\,\delta(z)$, where $A(\rho(z))$ is any function of $\rho(z)$ different from zero at $z=0$, and $\delta(z)$ is the delta "function," then $\sigma\neq 0$ for the step density function.

Equation (1) can be written, after a partial integration,$^{(7)}$

$$\sigma=\int_{-\infty}^{\infty}z\,dP_T(z,\rho(z)) \tag{2}$$

The total differential of P_T is

$$dP_T=\left(\frac{\partial P_T}{\partial\rho}\right)_z d\rho+\left(\frac{\partial P_T}{\partial z}\right)_\rho dz$$

Thus, Eq. (2) becomes

$$\sigma=\int_{-\infty}^{\infty}z\left(\frac{\partial P_T}{\partial\rho}\right)_z\rho'\,dz+\frac{1}{2}\int_{-\infty}^{\infty}\left(\frac{\partial P_T}{\partial z}\right)_\rho dz^2 \tag{3}$$

The second term of the equation can be integrated by parts:

$$\int_{-\infty}^{\infty}\left(\frac{\partial P_T}{\partial z}\right)_\rho dz^2=\left[z^2\left(\frac{\partial P_T}{\partial z}\right)_\rho\right]_{-\infty}^{\infty}-\int_{-\infty}^{\infty}z^2\,d\left[\left(\frac{\partial P_T}{\partial z}\right)_\rho\right] \tag{4}$$

By applying l'Hôpital's rule, we find that the first term of the rhs is null if $z(P_T-p)\to 0$ and $z(\rho(z)-\rho_{L,V})\to 0$ when $z\to\pm\infty$.

The total differential $d[(\partial P_T/\partial z)_\rho]$ is

$$d\left[\left(\frac{\partial P_T}{\partial z}\right)_\rho\right] = \frac{\partial}{\partial z}\left(\frac{\partial P_T}{\partial \rho}\right)_\rho \rho'\,dz + \frac{\partial^2 P_T}{\partial z^2}\,dz$$

Substituting the above relation in Eqs. (3) and (4), we obtain

$$\sigma = \int_{-\infty}^{\infty} z\left(\frac{\partial P_T}{\partial \rho}\right)_z \rho'\,dz - \frac{1}{2}\int_{-\infty}^{\infty} z^2 \frac{\partial}{\partial z}\left(\frac{\partial P_T}{\partial \rho}\right)_z \rho'\,dz - \frac{1}{2}\int_{-\infty}^{\infty} z^2 \frac{\partial^2 P_T}{\partial z^2}\,dz \quad (5)$$

By carrying out $(N-2)$ times similar operations to those performed in Eqs. (3)–(5), we finally get

$$\sigma = \sum_{n=0}^{N} \frac{(-1)^n}{(n+1)!}\int_{-\infty}^{\infty} z^{n+1}\frac{\partial^n}{\partial z^n}\left(\frac{\partial P_T}{\partial \rho}\right)_z \rho'\,dz + \frac{(-1)^N}{(N+1)!}\int_{-\infty}^{\infty} z^{N+1}\left(\frac{\partial^{N+1} P_T}{\partial z^{N+1}}\right)_\rho dz \quad (6)$$

where, as before, by l'Hôpital's rule, the first term in each partial integration is null.

The summation in Eq. (6) contains the local compressibility via $\partial P_T/\partial \rho$ and for any value of N we have an expression for the surface tension.

If the explicit dependence on z proposed here is identified with that considered in mean-field theories, i.e.,

$$P_T(z, \rho(z)) \equiv P_T(\rho', \rho'', \ldots, \rho(z))$$

the operator $\partial/\partial z$ is identified with

$$\frac{\partial}{\partial z} \equiv \frac{\partial}{\partial \rho'}\rho'' + \frac{\partial}{\partial \rho''}\rho''' + \cdots$$

So, in this context, Eq. (6) would include the square density gradient and higher order derivatives.

3. INHOMOGENEOUS COMPRESSIBILITY EQUATION AND SURFACE TENSION

Let us consider a fluid, inhomogeneous in the z direction and in thermal equilibrium. In the grand canonical ensemble the single density $\rho^{(1)}$ is

$$\rho^{(1)}(\bar{r}_1) = \Xi^{-1} \sum_{N \geqslant 1} \frac{e^{\mu N}}{\Lambda^{3N}(N-1)!}\int \exp\left(\frac{-U_N + V_N}{k_B T}\right) d\bar{r}_2\,d\bar{r}_3 \cdots d\bar{r}_N \quad (7)$$

where Ξ is the grand partition function, μ is the chemical potential, $\Lambda = (h^2/2\pi m k_B T)^{1/2}$ is the de Broglie thermal length, k_B is the Boltzmann constant, and T is the absolute temperature. U_N is the configurational energy of the N moleculas and V_N is the external potential.

V_N can be written as

$$V_N = \sum_{i=1}^{N} v_i(\bar{r}) \tag{8}$$

Let us consider $\rho^{(1)}$ as a functional of $v_i(\bar{r})$ for a given chemical potential μ:

$$\rho^{(1)} = \rho_\mu^{(1)}[v_i(\bar{r})] \tag{9}$$

From the first Yvon equation[8] it follows that

$$-k_B T \frac{\delta\rho^{(1)}(\bar{r}_1)}{\delta v(\bar{r}_2)} = \rho^{(1)}(\bar{r}_2)\,\delta(\bar{r}_1 - \bar{r}_2) + \rho^{(2)}(\bar{r}_1, \bar{r}_2) - \rho^{(1)}(\bar{r}_1)\,\rho^{(1)}(\bar{r}_2) \tag{10}$$

This equation enable us to find the change $\delta\rho$ for any change δv.

$$\delta\rho^{(1)}(\bar{r}_1) = \int \frac{\delta\rho^{(1)}(\bar{r}_1)}{\delta v(\bar{r}_2)}\,\delta v(\bar{r}_2)\,d\bar{r}_2 \tag{11}$$

If we choose a particular change of v such that $\delta v_0 = d\mu$, then from Eq. (7) we get

$$\rho_\mu^{(1)}[v(\bar{r}) + \delta v_0] = \rho_{\mu+d\mu}^{(1)}[v] \tag{12}$$

Using Eqs. (11) and (12), we obtain

$$d\rho^{(1)}(\bar{r}_1) = d\mu \int \frac{\delta\rho^{(1)}(\bar{r}_1)}{\delta v(\bar{r}_2)}\,d\bar{r}_2 \tag{13}$$

then by substitution of Eq. (10) into (13) we have

$$\frac{d\rho^{(1)}}{d\mu} = -\frac{1}{k_B T}\left\{\rho^{(1)}(\bar{r}_1) + \int [\rho^{(2)}(\bar{r}_1, \bar{r}_2) - \rho^{(1)}(\bar{r}_1)\,\rho^{(1)}(\bar{r}_2)]\,d\bar{r}_2\right\} \tag{14}$$

As we want to evaluate the surface tension from Eq. (6), it is necessary to know $\partial P_T/\partial\rho$. This quantity can be obtained using some relations from local thermodynamics.

On evaluating the work done on the system to change its area, it is easy to find a relation between the inverse local compressibility $\rho(\partial P_T/\partial\rho)$ and the chemical potential μ[6]:

$$(1/\rho)\,\partial P_T/\partial\rho = \partial\mu/\partial\rho \tag{15}$$

The rhs of this equation can be evaluated by using Eq. (14):

$$\frac{\partial P_T(z, \rho(z))}{\partial \rho(z)} = k_B T \left\{ 1 + \int d\bar{r}_{12}\, \rho(z_2)[g(r_{12}, z_1) - 1] \right\}^{-1} \tag{16}$$

where $\rho^{(2)}(\bar{r}_1, \bar{r}_2) = \rho^{(1)}(z_1)\, \rho^{(1)}(z_2)\, g(r_{12}, z_1)$ and $\rho^{(1)}$ is only a function of z_1.

On substitution of Eq. (16) into (6), one obtains the surface tension:

$$\begin{aligned} \sigma = \sum_{n=0}^{N} \frac{(-1)^n}{(n+1)!} k_B T \int_{-\infty}^{\infty} z^{n+1} \left\{ 1 + \int \rho(z_2)[g(r, z_1) - 1]\, d\bar{r} \right\}^{-1} \\ \times \rho'(z_1)\, dz_1 + \frac{(-1)^N}{(N+1)!} \int_{-\infty}^{\infty} z^{N+1} \frac{\partial^{N+1} P_T}{\partial z^{N+1}}\, dz \end{aligned} \tag{17}$$

The surface tension given by Eq. (17) is functionally dependent on the function $\rho(z)$, $g(r, z_1)$, and $\partial P_T/\partial z$ and its successive derivatives. It does not depend explicitly on the intermolecular potential.

4. SURFACE TENSION EVALUATION

We will calculate the surface tension for argon near the critical point using Eq. (17) for $N = 1$, by approximating the anisotropic radial distribution function and using some trial density profiles.

For $N = 1$, Eq. (6) is

$$\begin{aligned} \sigma = \int_{-\infty}^{\infty} z \left(\frac{\partial P_T}{\partial \rho} \right)_z \rho'\, dz - \frac{1}{2} \int_{-\infty}^{\infty} z^2 \frac{\partial}{\partial z} \left(\frac{\partial P_T}{\partial \rho} \right)_z \rho'\, dz \\ - \frac{1}{2} \int_{-\infty}^{\infty} z^2 \frac{\partial^2 P_T}{\partial x^2}\, dz \end{aligned} \tag{18}$$

The second term of this equation was calculated via Eq. (16) by using the identity

$$\frac{\partial}{\partial z} \left(\frac{\partial P_T}{\partial \rho} \right)_z = \frac{d}{dz} \left(\frac{\partial P_T}{\partial \rho} \right)_z - \frac{\partial}{\partial \rho} \left(\frac{\partial P_T}{\partial \rho} \right)_z \rho'$$

and considering that $\rho(z + z_1) \approx \rho(z_1)$ holds near the critical point.[9] The last term of this equation has been rejected. However, in order to weight its contribution, we have used a van der Waals-like equation of state[6]

$$P_T = p + W(\rho) - \tfrac{1}{2} m \rho'^2$$

Considering the operator $\partial/\partial z$ equivalent to $(\partial/\partial\rho')\rho'' + (\partial/\partial\rho'')\rho''' + \cdots$, then

$$\frac{\partial^2 P_T}{\partial z^2} = -\frac{m}{2}\frac{d^2}{dz^2}(\rho'^2)$$

and using the van der Waals expression for σ,

$$\sigma^{\text{vW}} = m \int_{-\infty}^{\infty} \rho'(z)^2 \, dz$$

we find that the last term of Eq. (18) is of the order $\sigma^{\text{vW}}/2$. Then, for a van der Waals fluid, our numerical results will be affected by this error.

The anisotropic radial distribution function $g(r, z_1)$ is approximated by the following interpolated relation:

$$g(r, z_1) = a_V(z_1)\, g_V(r) + a_L(z_1)\, g_L(r) \tag{19}$$

where $g_L(r)$ and $g_V(r)$ are the radial distribution functions of the liquid and vapor phases, respectively, weighted by z_1-dependent coefficients:

$$a_V(z_1) = \frac{\rho_L - \rho(z_1)}{\rho_L - \rho_V}; \qquad a_L(z_1) = \frac{\rho(z_1) - \rho_V}{\rho_L - \rho_V}$$

We use the experimental values for $g_L(r)$ and $g_V(r)$ obtained by Mikolaj and Pings$^{(10)}$ at the coexistence temperature $T = 148.16$ K, with densities $\rho_L = 0.780$ g/cm^3 and $\rho_V = 0.280$ g/cm^3 of pure phases, respectively.[3]

Three different z-dependent trial density profiles were employed, namely Fisk–Widom (FW), error function (ERF), and hyperbolic tangent (TANH),$^{(12)}$ whose analytical expressions are

$$\rho(z) = \rho_+ + \rho_- \frac{\sqrt{2}\tanh(z\sqrt{6}/L_1)}{[3 - \tanh^2(z\sqrt{6}/L_1)]^{1/2}} \tag{FW}$$

$$\rho(z) = \rho_+ + \rho_- \operatorname{erf}\left(\frac{z\sqrt{\pi}}{L_2}\right) \tag{ERF}$$

$$\rho(z) = \rho_+ + \rho_- \tanh\left(\frac{2z}{L_3}\right) \tag{TANH}$$

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[3] The work of Eisenstein and Gingrich$^{(11)}$ gives experimental values of g_L and g_V, but they are inadequate for our calculation because the compressibility equation is very sensitive to the tail of the distribution functions. The mentioned work does not provide sufficient information in this region. A confirmation of this assertion was given by calculating the surface tension and the liquid and vapor compressibilities for Ar employing Ping's distribution functions truncated at the same interval covered by Eisenstein's measurements. The obtained values showed a discrepancy of several orders of magnitude from experimental results at the same temperature.

where $\rho_+ = \rho_L + \rho_V$ and $\rho_- = \rho_L - \rho_V$ and L_1, L_2, and L_3 are the respective interfacial widths defined as $L_i = \rho - [\partial\rho(z)_i/\partial z]_{z=0}$. At temperatures near the critical point Wu and Webb masured the reflectivity at the surface for SF_6. The critical index ν, corresponding to the divergence of the interfacial width, was determined using the mentioned trial profiles. The values of ν obtained were found to be $\nu = 0.62 \pm 0.01$ (ERF) and $\nu = 0.66 \pm 0.02$ (FW). The classical profile (TANH) gave $\nu = 0.80 \pm 0.05$. Thus, the ERF and FW profiles give essentially better fits than the classical profile and the values of ν are both close to the exponent for the divergence of the correlation length at the critical point.

The interfacial width L for Ar at $T = 120$ K is known by experiment for the ERF profile(13); then, using the relation(14)

$$L^{\mathrm{Ar}} = L_0^{\mathrm{Ar}}(1 - T/T_c)^{-\nu} \tag{20}$$

and considering $\nu = 0.62 \pm 0.01$(12) (a universal constant), and $T_c = 150.73$ K, we obtain L_0^{Ar} (which is substance-dependent), and finally $L^{\mathrm{Ar}}(148.16\ \mathrm{K})$. As far as we know, measurements of the interfacial width for Ar when the density profile is represented by FW or TANH profiles are unavailable. However, the interfacial width for SF_6 as a function of T for each of the three mentioned profiles is known.(12) Then, assuming, at a given temperature, the constancy of the interfacial width per molecular diameter (L/σ_d), irrespective of the considered substance and knowing the molecular diameters $\sigma_d(SF_6)$ and $\sigma_d(\mathrm{Ar})$,(15) we calculate L_1, L_2, and L_3. Values obtained by the procedure just outlined are gathered in Table I.

Table I. Interfacial Width L for Argon at $T = 148.16$ K Obtained from L for SF_6 at the Same Temperature[a]

	Value for given profile		
	TANH	ERF	FW
SF_6	$L_1 = 17$ Å	$L_2 = 117$ Å	$L_3 = 100$ Å
$n = L(SF_6)/\sigma_d(SF_6)$	9	21	18
Ar	$L_1 = 30.65$ Å	$L_2 = 71.51$ Å	$L_3 = 61.29$ Å

[a] n is the number of molecular diameters. $\sigma_d(SF_6) = 5.51$ Å is the molecular diameter for SF_6 obtained from the second virial coefficient. For argon the corresponding value is $\sigma_d(\mathrm{Ar}) = 3.405$ Å.(15) Then L_1, L_2, and L_3 for Ar are calculated by the expression $L_i = n * \sigma_d(\mathrm{Ar})_i$. Using the expression $L = L_0(1 - T/T_c)^{-\nu'}$ from the values of Ref. 12 for an ERF profile at $T = 120$ K, we extrapolated the following result at $T = 148.16$ K:

$$L(148.16\ \mathrm{K}) = 5.907\ \text{Å} \cdot (1 - 148.16/150.86)^{-0.62} = 71.55\ \text{Å}$$

which is virtually the same as the tabulated value obtained by using the universality criterion.

With the aproximations done on $g(\bar{r}, z_1)$, the "experimental" $\rho(z_1)$ and the respective interfacial widths, we evaluate the first two terms of Eq. (16). The numerical results are gathered in Table II.

Finally, we discuss the adequacy of Eq. (19). Triezenberg and Zwanzig (TZ) derived an expression for the surface tension that involves the direct correlation function $c(\bar{r}_1, \bar{r}_2)$. So, if we were able to calculate $c(\bar{r}, z_1)$ corresponding to Eq. (19), we could make the desired test via the TZ equation.

It is well known that the Ornstein–Zernike equation links $c(\bar{r}, z_1)$ to $g(\bar{r}, z_1)$. A local approximation is

$$c(r_{12}, z_1) = h(r_{12}, z_1) - \int \rho(z_3)\, c(r_{13}, z_1)\, h(r_{23}, z_1)\, d\bar{r}_3 \tag{21}$$

Local homogeneity around z leads to

$$\begin{aligned} c(r_{12}, z_1) = h(r_{12}, z_1) &- \rho(z_1)\, a_L(z_1) \int_{-\infty}^{\infty} c(r_{13}, z_1)\, h_L(r_{23})\, d\bar{r}_3 \\ &- \rho(z_1)\, a_V(z_1) \int_{-\infty}^{\infty} c(r_{13}, z_1)\, h_V(r_{23})\, d\bar{r}_3 \end{aligned} \tag{22}$$

Table II. Experimental and Theoretical Surface Tension Values for Argon.

Temperature (K)	σ (exp) (dynes/cm)	σ (theor) (dynes/cm)
149.0	0.16[a]	5.28[c] 4.85[d] 1.52[e]
148.16	0.20[b]	1.62, 0.71, 0.64[f] 0.68, 0.31, 0.36[g]
145.0	0.57	2.10[h]
143.8	0.73	1.80[i]
135.0	2.10	4.60[j]

[a] Experimental value reported by Stansfield.(23)

[b] Extrapolation using $\sigma_{\text{exp}}(149\ \text{K})$ as a reference value.

[c] Using $g(r)$ given by Zwanzig *et al.*(24) and a Lennard-Jones intermolecular potential.

[d] Using $g(\alpha r)$, given by Zwanzig *et al.*,(21) where α is a correction factor.

[e] Following MacLellan's approximation.(22)

[f] Results corresponding to Eq. (17) from our theory using the TANH, ERF, and FW profiles, respectively.

[g] Results corresponding to Eq. (25), using the TZ expression for σ, and the TANH, ERF, and FW trial density profiles respectively.

[h] By computer simulation using MC method.(18)

[i] Perturbation theory.(20)

[j] By computer simulation using MC and MD methods.(19)

where we have used $g(r, z_1)$ given by Eq. (19) and the fact that $g(r_{12}) = h(r_{12}) + 1$.

Fourier transforming Eq. (22), we get

$$\tilde{c}(k; z_1) = \tilde{h}(k; z_1)/[1 + \tilde{h}(k; z_1)] \tag{23}$$

where

$$\tilde{h}(k; z_1) = a_L(z_1)\frac{i_L(k)}{\rho_L} + a_V(z_1)\frac{i_V(k)}{\rho_V}$$

$i_L(k)$ and $i_V(k)$ are the experimental x-ray scattering intensities of the liquid and gas phases, respectively,$^{(10)}$ given by

$$i(k) = \rho \int_0^\infty 4\pi r^2 h(r)\frac{\sin(kr)}{kr}\,dr$$

The inverse Fourier transform of Eq. (23) gives the desired anisotropic direct correlation function

$$c(r; z_1) = \frac{1}{2\pi^2 r}\int_0^\infty k\frac{\tilde{h}(k; z_1)\sin(kr)\,dk}{1 + \rho(z_1)\,\tilde{h}(k; z_1)} \tag{24}$$

In the evaluation of the last expression we have included the correction for small-angle scattering ($k \to 0$) suggested by Mikolaj and Pings.$^{(10)}$

By substitution of Eq. (24) into the approximated TZ equation for σ,$^{(6)}$ we get

$$\sigma \simeq \frac{2\pi}{3}k_B T\int_{-\infty}^\infty dz_1\,[\rho'(z_1)]^2\int_0^\infty dr\,r^4 c(r; z_1) \tag{25}$$

In the numerical calculation of σ given by Eq. (25) we employed the same density profiles mentioned above. The numerical results are also included in Table II.

5. SUMMARY AND COMMENTS

An expression has been obtained for the surface tension coefficient; Eq. (17) contains integrals that are functions of the inverse local compressibility. We believe that this approach helps clarify the link between the surface tension and an elastic property such as the local isothermal compressibility. Baus,$^{(16)}$ using a microscopic approach to the elastic interfacial behavior, expressed the surface tension also as a particular combination of adiabatic surface elastic coefficients.

Our expression for surface tension, like that derived by Triezenberg and Zwanzig,(17) involves the density profile and the two-particle distribution function. In neither case is there explicit reference to the intermolecular potential (as there is in those obtained by the virial route(4)); both approaches make use of the fluctuation theory. The expression of Triezenberg and Zwanzig is obtained by calculating the change in free energy associated with an increase of surface area caused by the fluctuations in density, while we focus attention on the connection between the surface tension and the local compressibility, the last being expressed through the first Yvon equation.

A semiempirical calculation of the surface tension of Ar at $T = 148.16$ K for three different density profiles (FW, ERF, and TANH) has been done using Eq. (17). The first term of this equation gives the essential contribution, the second is only a minor correction, and the last is rejected.

The approximation used in the anisotropic correlation function given by Eq. (19) is a reliable one. The corresponding direct correlation function [Eq. (24)] was used together with the same trial density profiles, via the TZ equation. The numerical values obtained for σ are of the same order of magnitude as those given by experiment.

Table II shows a discrepancy between the numerical results of the surface tension evaluated via Eq. (17) and the TZ expression. It must be kept in mind that our calculation has rejected a term of the order of $\sigma^{\mathrm{vW}}/2$. The same data show that the ERF and FW profiles are more suitable than the classic TANH profile. Wu and Webb(12) also observed that these two profiles give better values of the critical exponent than the TANH profile.

Finally, we also include in Table II results from computer simulations,(18,19) perturbation theory,(20) the modified Kirkwood–Buff equation,(21,22) and an experiment reported by Stansfield.(23)

It is remarkable that our formula, which is a "local" one, provides a value of surface tension of the order of the experimental data for argon at temperatures of order 100 K, where collective modes (capillary waves) are expected to control the phenomenon. Nevertheless, this is not strange, because we include fluctuations in a way in that experience has shown is successful when the system is not too far from the critical point.

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