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Modified Van der Waals theory of fluid interfaces

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A modified version of the Van der Waals theory of fluid interfaces is presented. The modified theory is shown to retain the qualitative simplicity of the original theory while yielding a much more quantitative description of fluid properties.

I. INTRODUCTION

Nearly a century ago, Van der Waals[1] introduced a theory of fluids which even today represents the simplest qualitatively correct molecular model of nonpolar fluids. The model yields explicit expressions for the thermodynamic functions, predicts the existence of metastable one-phase systems, and yields solvable equations for interfacial density profiles and interfacial tension of two-phase systems. The model is based on a series of approximations, all of which were necessary to obtain tractable results at the time of Van der Waas' original work. Recent developments in the molecular theory of fluids, however, allow one to eliminate some of the approximations of the Van der Waals model. The result is a quantitative improvement in the model with little sacrifice in the original simplicity. The purpose of this paper is to develop such a modified Van der Waals model, i.e., one in which the dispensable approximations are removed, and to use the model to investigate the interfacial properties of a liquid in equilibrium with its vapor.

II. GENERAL FEATURES OF THE MODIFIED VAN DER WAALS THEORY OF FLUID INTERFACES

We shall consider an inhomogeneous system, at temperature T and of volume V, containing N identical particles which interact via pairwise additive, centrally symmetric forces. The pair potential $u(r)$ will be expressed as the sum of two parts, $u_R(r)$ and $u_A(r)$, where $u_R(r)$ is the potential associated with the short-ranged strongly repulsive interactions. The precise forms of u_R and u_A may be left unspecified in the general results to be derived below. The canonical partition function for the system is of the form

$$Q=[q(T)]^N\frac{1}{N!}\times\int\cdots\int_V e^{-(u_R^N+u_A^N)/kT}d^3r_1\cdots d^3r_N\,, \tag{2.1}$$

where $q(T)$ denotes the contribution of the kinetic and internal energies to the partition function of a particle,

$$u_R^N\equiv\sum_{i>j=1}u_R(r_{ij})$$

the total repulsive potential, and

$$u_A^N\equiv\sum_{i>j=1}u_A(r_{ij})$$

the total attractive potential of the particles in a given configuration $\vec{r}_1,\ldots,\vec{r}_N$. The first assumption of the Van der Waals model is that the attractive potential u_A^N may be replaced by the average value $\langle u_A^N\rangle_R$ in Eq. (2.1), so that

$$Q\approx Q_R e^{-\langle u_A^N\rangle_R/kT}\,, \tag{2.2}$$

where Q_R, defined by

$$Q_R=\frac{[q(T)]^N}{N!}\int\cdots\int_V e^{-u_R^N/kT}d^3r_1\cdots d^3r_N\,, \tag{2.3}$$

is the partition function of a system of purely repulsive particles at the same temperature and having the same density profile $n(\vec{r})$ as the subject system. The subscript R on $\langle u_A^N\rangle_R$ indicates that the average of u_A^N is computed for an ensemble of the purely repulsive particles. Equation (2.2) represents a "mean-field" approximation, which is valid if the molecular configurations allowed by the repulsive interactions of the particles lie sufficiently close to the most probable or average molecular configuration. From the work of Lebowitz and Penrose[2] one can conclude that Eq. (2.2) is exact in the limit of infinitely long-ranged attractive interactions, and from the work of Weeks, Chandler, and Andersen,[3] the approximation of Eq. (2.2) (which can be shown to be closely related to the assumption that the fluid structure is primarily determined by the repulsive interactions) appears to be quite good for the Lennard-Jones 6-12 fluid at densities greater than twice the critical density. Unfortunately, we cannot give further justification for the mean-field approximation, although, as did Van der Waals, we shall take Eq. (2.2) as the starting point of the theory.

We remark that the true average value $\langle u_A^N \rangle$ could have been introduced as logically as $\langle u_A^N \rangle_R$ in the first assumption, Eq. (2.2), of the Van der Waals model. Since, however, only $\langle u_A^N \rangle_R$ can presently be computed conveniently, we shall not introduce the less restrictive assumption.

The Helmholtz free energy F corresponding to Eq. (2.2) is

$$F = F_R + U_A \, , \tag{2.4}$$

where

$$F_R = - kT \ln Q_R \, , \tag{2.5}$$

and

$$U_A = \langle u_A^N \rangle_R \, . \tag{2.6}$$

Thus, according to the mean-field approximation, the Helmholtz free energy of the subject fluid is equal to the sum of the Helmholtz free energy F_R of a reference fluid with the same density profile and composed of purely repulsive particles and the thermodynamic excess energy U_A arising from the attractive interactions of the subject-fluid particles.

For an inhomogeneous system, the free energy F_R may be written in the form

$$F_R = \int_V f_R(n(\vec{r}))\, d^3r \, , \tag{2.7}$$

where f_R is the local Helmholtz free-energy density of a reference system with the density profile $n(\vec{r})$. The second assumption of Van der Waals, and one that we shall also use, is that $f_R(n(\vec{r}))$ is equal to the Helmholtz free-energy density of the reference fluid at equilibrium at temperature T and with a uniform density equal to $n(\vec{r})$. In other words, it is assumed that the relationship between the local free-energy density $f_R(n(\vec{r}))$ and the local density $n(\vec{r})$ is the same as that between the equilibrium free-energy density and the density of a homogeneous reference fluid. This "local-equilibrium" assumption is expected to hold if the density profile varies sufficiently slowly over distances of the order of magnitude of the range of the repulsive forces. Thus, for vapor-liquid interfaces, this assumption of the Van der Waals model becomes exact as the critical temperature is approached. Although the domain of validity of the local-equilibrium approximation cannot be determined presently, it is the authors' opinion that the approximation underlying Eq. (2.2) is more likely to give error than the local-equilibrium approximation.

For an inhomogeneous system of N identical particles with an attractive potential of the form

$$u_A^N = \sum_{i>j=1} u_A(r_{ij}) \, ,$$

the quantity U_A may be expressed in the form

$$U_A = \tfrac{1}{2} \int\!\!\int_V n(\vec{r}) n(\vec{r}\,') g(\vec{r}, \vec{r}\,') u_A(|\vec{r} - \vec{r}\,'|)\, d^3r\, d^3r' \, , \tag{2.8}$$

where $g(\vec{r}, \vec{r}\,')$ is the pair-correlation function of a pair of particles at $\vec{r}$ and $\vec{r}\,'$, respectively. This form follows from Eq. (2.6) by noting that

$$\begin{aligned}\sum_{i>j=1}^{N} \langle u_A(r_{ij}) \rangle_R &= \frac{N}{2} (N-1) \langle u_A(r_{12}) \rangle_R \\ &= \frac{N}{2} (N-1) \int\!\!\int_V u_A(r_{12}) p_2(\vec{r}_1, \vec{r}_2)\, d^3r_1\, d^3r_2 ,\end{aligned}$$

where $p_2(\vec{r}_1, \vec{r}_2) d^3r_1 d^3r_2$ is the probability that a pair of particles are between $\vec{r}_1$ and $\vec{r}_1 + d\vec{r}_1$ and $\vec{r}_2$ and $\vec{r}_2 + d\vec{r}_2$, respectively. Defining the pair-correlation function by $g(\vec{r}_1, \vec{r}_2) = p_2(\vec{r}_1, \vec{r}_2) / p(\vec{r}_1) p(\vec{r}_2)$, where $p(\vec{r}_i) d^3r_i$ is the probability that a particle is located between $\vec{r}_i$ and $\vec{r}_i + d\vec{r}_i$, and noting that $n(\vec{r}_i) = N p(\vec{r}_i)$, we obtain Eq. (2.8).

Combining Eqs. (2.4), (2.7), and (2.8), we obtain the following expression for the mean-field approximation to the Helmholtz free energy of an inhomogeneous fluid with a given density distribution $n(\vec{r})$:

$$\begin{aligned} F = &\int_V f_R(n(\vec{r}))\, d^3r \\ &+ \tfrac{1}{2} \int\!\!\int_V n(\vec{r}) n(\vec{r}\,') g(\vec{r}, \vec{r}\,') u_A(|\vec{r} - \vec{r}\,'|)\, d^3r\, d^3r' \, . \end{aligned} \tag{2.9}$$

With the added assumption that $f_R(n)$ is equal to the free-energy density of the homogeneous reference system at n, Eq. (2.9) represents the starting point of Van der Waals theory. To obtain what is known as the Van der Waals model, the added approximations (a) that $g(\vec{r}, \vec{r}\,') \equiv 1$ and (b) that

$$f_R(n) \simeq -nkT[\ln q(T) + \ln(1/n - b) + 1] \qquad (2.10)$$

must be used. Equation (2.10) is based on the assumption that the repulsive interactions are rigid-sphere interactions *and* that the rigid-sphere-configuration partition function can be approximated by the relation $Z_N^R = (V - Nb)^N/N!$, obtained by analogy from the one-dimensional result. The quantity b represents the rigid-sphere excluded volume per molecule of the system. With approximations (a) and (b) one obtains for a homogeneous fluid $F = V[f_R(N/V) - (N^2/V^2)a]$, where

$$a = -\tfrac{1}{2}\int u_A(s)\,d^3s \;. \qquad (2.11)$$

This result, with Eq. (2.10), yields the well-known Van der Waals equation of state for a homogeneous fluid, namely,

$$(P + N^2a/V^2)(V - Nb) = NkT \;. \qquad (2.12)$$

In the improved version of Van der Waals theory (herein referred to as the modified Van der Waals theory), Eq. (2.9) is retained, but approximations (a) and (b) are replaced by a less severe approximation, namely, a "local-equilibrium" assumption for $g(\vec{r}, \vec{r}\,')$. We shall assume that the pair-correlation function may be approximated in Eq. (2.9) by the pair-correlation function of a homogeneous fluid at the density $n((\vec{r} + \vec{r}\,')/2)$ midway between the pair of particles. Thus, Eq. (2.9) becomes

$$F = \int_V f_R(n(\vec{r}))\,d^3r + \tfrac{1}{2}\int\int_V n(\vec{r})n(\vec{r}\,')\,g\left(|\vec{r} - \vec{r}\,'|\,;n\left(\frac{\vec{r} + \vec{r}\,'}{2}\right)\right)u_A(|\vec{r} - \vec{r}\,'|)\,d^3r\,d^3r' \,. \qquad (2.13)$$

Although the domain of validity of this approximation (which is quite similar to the local-equilibrium approximation introduced for f_R) is difficult to assess, it is clear that the broader and more slowly varying the interface the more accurate the approximation should be. Equation (2.13) is the basic equation of what is herein referred to as the modified Van der Waals theory.

Up to this point the density distribution has been left unspecified. However, for a closed system of N particles in a fixed volume V at a fixed temperature T, the equilibrium density distribution is determined by the condition that F be a minimum. Subject to the constraint that $\int_V n(\vec{r})\,d^3r = N$, the minimization condition for F is that the functional derivative of $F - \alpha\int_V n(\vec{r})\,d^3r$ with respect to $n(\vec{r})$ be zero for $n(\vec{r}) = n^s(\vec{r})$, where the superscript on n^s denotes an equilibrium or "stationary" density distribution and α is a Lagrange multiplier. *The quantity* α *can be shown to be the chemical potential of the system.* Taking the functional derivative of $F - \alpha\int_V n(\vec{r})\,d^3r$ with respect to $n(\vec{r})$ and setting it equal to zero, we obtain the following integral equation for $n^s(\vec{r})$:

$$\int\left(n^s(\vec{r} + \vec{s})\,g(s;n^s(\vec{r} + \tfrac{1}{2}\vec{s})) + \tfrac{1}{2}n^s(\vec{r} + \tfrac{1}{2}\vec{s})n^s(\vec{r} - \tfrac{1}{2}\vec{s})\,\frac{\partial g}{\partial n^s}(s;n^s(\vec{r}))\right)u_A(s)\,d^3s + f_R'(n^s(\vec{r})) - \alpha = 0 \;, \qquad (2.14)$$

where

$$f_R'(n) \equiv \frac{df_R(n)}{dn} \,. \qquad (2.15)$$

The Van der Waals limit of Eq. (2.14), obtained by setting $g \equiv 1$ and approximating f_R by Eq. (2.10), is

$$\int n^s(\vec{r} + \vec{s})u_A(s)\,d^3s + f_R'(n^s(\vec{r})) - \alpha = 0 \;. \qquad (2.16)$$

Van Kampen[4] has recently shown that Eq. (2.16) admits at all temperatures the homogeneous one-phase solutions ($n^s = N/V$), giving the usual Van der Waals equation of state, Eq. (2.12), and that, below the critical temperature, Eq. (2.16) admits inhomogeneous two-phase solutions along with the one-phase solutions. The two-phase solutions are identical to the coexistence states constructed from the one-phase equation of state by the Maxwell equal-area tie-line construction and are more stable (lower Helmholtz free energy) than the one-phase states allowed by Eq. (2.16) in the two-phase coexistence region. The same qualitative conclusions could be drawn from Eq. (2.14) for realistic models of g and f_R.

One of the systems we shall focus attention on in this paper is a two-phase gas-liquid system with a planar interface, i.e., one in which the density varies only along the x direction. We shall assume that the lengths of gas and liquid regions are long compared to the thickness of the interfacial region. The densities n_g and n_l of the bulk gas and liquid phases (far from the interfacial region) and the quantity α are determined from the conditions

$$f_R'(n_\gamma^s) + n_\gamma^s\int\left(g(s;n_\gamma^s) + \frac{n_\gamma^s}{2}\,\frac{\partial g}{\partial n_\gamma^s}(s;n_\gamma^s)\right)u_A(s)\,d^3s = \alpha,$$

$$\gamma = g \text{ and } l \qquad (2.17)$$

and

$$f(n_g) - \alpha n_g + \tfrac{1}{2} n_g^2 \int g(s, n_g) u_A(s)\, d^3s$$
$$= f(n_l) - \alpha n_l + \tfrac{1}{2} n_l^2 \int g(s, n_l) u_A(s)\, d^3s \; . \tag{2.18}$$

Equation (2.17) is obtained from Eq. (2.14) by requiring the density to approach the constant values n_g and n_l far from the interface and in the gas and liquid regions, respectively. To obtain Eq. (2.18), we have noted that the pressure P_B in a homogeneous bulk phase of a system whose free energy is of the form of Eq. (2.13) is given by

$$P_B(n) = -f_R(n) - \tfrac{1}{2} n^2 \int g(s, n) u_A(s)\, d^3s$$
$$+ n\Big(f_R'(n) + n \int g(s, n) u_A(s)\, d^3s$$
$$+ \tfrac{1}{2} n^2 \int \frac{\partial g}{\partial n}(s, n) u_A(s) d^3s\Big). \tag{2.19}$$

The quantity in the large parentheses of Eq. (2.19) is equal to the constant α according to Eq. (2.17). With this equality, the condition of hydrostatic equilibrium in a planar system, $P_B(n_l) = P_B(n_g)$, implies Eq. (2.18).

The surface tension for a planar interface may be determined from the thermodynamic relation

$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{T, V, N} , \tag{2.20}$$

where A is the area of the interface (normal to the x axis). Suppose the system is a rectangular parallelepiped of length L_x in the x direction and of area $L_y L_z$ normal to the x axis. Suppose also that the lengths L_x, L_y, and L_z are large compared to the range of $u_A(s)$ and to the width of the interfacial region [i.e., of the region in which $n(x)$ goes from n_l to n_g]. Suppose also that the interfacial region is far from the ends of the system in the x direction. Under these conditions, Eq. (2.13) becomes

$$F = L_y L_z \int_{-L_{x1}}^{L_{x2}} f_R(n(x))\, dx + \tfrac{1}{2} L_y L_z \iint_{-L_{x1}}^{L_{x2}} g(s; n(x + \tfrac{1}{2} s_x)) u_A(s) n(x) n(x + s_x)\, dx\, d^3s, \tag{2.21}$$

where $\vec{s} = \vec{r}' - \vec{r}$ and $-L_{x1}$ and L_{x2} are the lower and upper limits of x measured relative to an arbitrary origin. We shall evaluate the area derivative of F by varying L_z while L_y is kept constant so that $dA = L_y dL_z$. If we choose the origin such that $x = 0$ is located at the Gibbs dividing surface of zero excess matter, i.e., such that

$$L_y L_z \int_{-L_{x1}}^{L_{x2}} n(x)\, dx = L_y L_z (n_l L_{x1} + n_g L_{x2}) , \tag{2.22}$$

then the constraints of constant V and N on the area derivative in Eq. (2.20) yield the relations

$$\frac{dL_{x1}}{dL_z} = -\frac{L_{x1}}{L_z} , \quad \frac{dL_{x2}}{dL_z} = -\frac{L_{x2}}{L_z} \; . \tag{2.23}$$

Performing the area derivative of Eq. (2.20) with the aid of these relations, we obtain

$$\gamma = \int_{-L_{x1}}^{L_{x2}} [f_R(n(x)) - f_{gl}(x)]\, dx + \tfrac{1}{2} \iint_{-L_{x1}}^{L_{x2}} u_A(s)[g(s; n(x + \tfrac{1}{2} s_x)) n(x) n(x + s_x) - n_{gl}^{(2)}(s, x)]\, dx\, d^3s , \tag{2.24}$$

with the definitions

$$f_{gl}(x) = f_R(n_l)[1 - \eta(x)] + f_R(n_g)\eta(x) \tag{2.25}$$

and

$$n_{gl}^{(2)}(x) = n_l^2 g(s, n_l)[1 - \eta(x)] + n_g^2 g(s, n_g)\eta(x) , \tag{2.26}$$

where

$$\eta(x) = 0, \quad x < 0$$
$$= 1, \quad x > 0 \; . \tag{2.27}$$

Since the integrands in Eq. (2.24) are zero for x large compared to the width of the interfacial region, the limits L_{x2} and $-L_{x1}$ can be set equal to any computationally convenient values that are large compared to the width of the interfacial region. Once the equilibrium density profile $n^s(x)$ is determined from Eq. (2.14), the surface tension can be computed from Eq. (2.24).

For temperatures such that the density varies slowly over distances of the order of the range of u_A, Eq. (2.14) can be reduced to a differential equation with the aid of the expansions

$$\int n(\vec{r}+\vec{s})g(s;n(\vec{r}+\tfrac{1}{2}\vec{s}))u_A(s)\,d^3s=-n(\vec{r})w_0(n(\vec{r}))-[\nabla_{\vec{r}}^2 n(\vec{r})]\left(\frac{w_2}{2}(n(\vec{r}))+\frac{n(\vec{r})}{8}\frac{\partial w_2}{\partial n}(n(\vec{r}))\right)$$
$$-[\nabla_{\vec{r}}n(\vec{r})]^2\left(\frac{1}{2}\frac{\partial w_2}{\partial n}(n(\vec{r}))+\frac{n(\vec{r})}{8}\frac{\partial^2 w_2}{\partial n^2}(n(\vec{r}))\right)+O((\nabla_{\vec{r}}n)^4) \qquad (2.28)$$

and

$$\int n(\vec{r}+\tfrac{1}{2}\vec{s})n(\vec{r}-\tfrac{1}{2}\vec{s})\frac{\partial g}{\partial n}(s;n(\vec{r}))u_A(s)\,d^3s=-\frac{\partial w_0}{\partial n}n^2(\vec{r})-\frac{1}{4}\frac{\partial w_2}{\partial n}\{n(\vec{r})\nabla_{\vec{r}}^2 n(\vec{r})-[\nabla_{\vec{r}}n(\vec{r})]^2\}+O((\nabla_{\vec{r}}n)^4), \qquad (2.29)$$

where

$$w_0\equiv-\int u_A(s)g(s;n(\vec{r}))\,d^3s\ , \qquad (2.30)$$

$$w_2\equiv-\tfrac{1}{3}\int s^2u_A(s)g(s;n(\vec{r}))\,d^3s\ . \qquad (2.31)$$

Substituting Eqs. (2.28) and (2.29) into Eq. (2.14) and neglecting terms of order $(\nabla_r n)^4$, we find the following differential equation for the equilibrium density distribution:

$$\left(\frac{1}{4n}\frac{\partial(n^2w_2)}{\partial n}\right)\nabla_{\vec{r}}^2 n+\left[\frac{1}{8n^2}\frac{\partial}{\partial n}\left(n^3\frac{\partial w_2}{\partial n}\right)\right](\nabla_{\vec{r}}n)^2=\frac{\partial\Phi}{\partial n}(n)\ , \qquad (2.32)$$

where

$$\Phi(n)\equiv f_R(n)-\tfrac{1}{2}n^2w_0-n\alpha\ . \qquad (2.33)$$

In his work on interfacial density profiles, Van der Waals used Eq. (2.32) for the special case that $g(s;n)\equiv1$ and the f_R of Eq. (2.10).

For the special case of a planar interface, Equation (2.32) can be integrated directly and the corresponding surface tension can be written in an especially simple form. Multiplying Eq. (2.32) by dn/dx and rearranging the resulting left-hand side of the equation, we obtain for the planar case the result

$$\frac{d}{dx}\left[\frac{c(n)}{2}\left(\frac{dn}{dx}\right)^2\right]=\frac{d\Phi}{dx}\ , \qquad (2.34)$$

where we have introduced the definition

$$c(n)=\frac{1}{4n}\frac{\partial}{\partial n}(n^2w_2) \qquad (2.35)$$

and used the relation $d\Phi/dx=(\partial\Phi/\partial n)dn/dx$. Conditions (2.17) and (2.18) imply the following boundary conditions on $n(x)$:

$$n(x)\to n_l \text{ as } x\to-\infty\ ,$$
$$n(x)\to n_g \text{ as } x\to+\infty\ , \qquad (2.36)$$
$$\frac{dn}{dx}\to0 \text{ as } x\to\pm\infty\ .$$

The quantities α, n_l, and n_g are determined by the conditions

$$\Phi(n_g)=\Phi(n_l) \qquad (2.37)$$

and

$$\Phi'(n_g)=\Phi'(n_l)=0\ , \qquad (2.38)$$

where $\Phi'(n)\equiv\partial\Phi/\partial n$. Integrating Eq. (2.34), we find

$$\frac{c}{2}\left(\frac{dn}{dx}\right)^2-\Phi(n)=-\Phi(n_l)\ , \qquad (2.39)$$

or

$$\frac{dn}{dx}=-2^{1/2}\left(\frac{\Phi(n)-\Phi(n_l)}{c(n)}\right)^{1/2}. \qquad (2.40)$$

The sign convention in Eq. (2.40) is chosen so that the bulk gas phase lies in the positive x direction with respect to the bulk liquid phase. Equation (2.40) can be formally integrated to obtain

$$x-x_0=-\frac{1}{2^{1/2}}\int_{n(x_0)}^{n(x)}\left(\frac{c(n)}{\Phi(n)-\Phi(n_l)}\right)^{1/2}dn\ , \qquad (2.41)$$

a relatively simple formula for computing the density profile for a planar interface.

Combining Eqs. (2.21) and (2.28) for the planar case considered here, we may write F in the form

$$F=A\int_{-L_{x1}}^{L_{x2}}dx\left[f_R-\tfrac{1}{2}n^2w_0-\frac{1}{16n^2}\frac{\partial(n^4w_2)}{\partial n}\frac{d^2n}{dx^2}-\frac{1}{16n^2}\frac{\partial}{\partial n}\left(n^4\frac{\partial w_2}{\partial n}\right)\left(\frac{dn}{dx}\right)^2\right]$$
$$=A\int_{-L_{x1}}^{L_{x2}}dx\left[f_R-\tfrac{1}{2}n^2w_0+\frac{c(n)}{2}\left(\frac{dn}{dx}\right)^2\right]. \qquad (2.42)$$

To obtain the second form of the right-hand side of Eq. (2.42), we used the relation

$$\int_{-L_{x1}}^{L_{x2}} dx\, h(n) \frac{d^2n}{dx^2} = - \int_{-L_{x1}}^{L_{x2}} dx \frac{dh}{dn}\left(\frac{dn}{dx}\right)^2 , \tag{2.43}$$

which is obtained by integration by parts with the condition $(dn/dx)=0$ at $x=L_{x2}$ and $x=-L_{x1}$. Eliminating $f_R - \frac{1}{2}n^2 w_0$ from Eq. (2.42) with the aid of Eqs. (2.33) and (2.39), we find

$$F = A \int_{-\infty}^{\infty} c(n)\left(\frac{dn}{dx}\right)^2 dx + V\Phi(n_l) + N\alpha . \tag{2.44}$$

The limits L_{x1} and L_{x2} have been extended to infinity for convenience. Such an extension is valid as long as the linear dimensions of the system are large compared to the thickness of the interfacial region.

Equation (2.44), with the aid of the thermodynamic relation Eq. (2.20), yields for the surface tension the simple formula

$$\gamma = \int_{-\infty}^{\infty} c(n)\left(\frac{dn}{dx}\right)^2 dx . \tag{2.45}$$

According to this result, the variation of the density gradient across the interfacial region must be known in order to compute the surface tension. However, transforming the variable of integration from x to n, we can express γ in the *density-profile-independent* form

$$\gamma = \sqrt{2} \int_{n_g}^{n_l} \{c(n)[\Phi(n) - \Phi(n_l)]\}^{1/2} dn . \tag{2.46}$$

In the special case that $f_R(n)$ is given by Eq. (2.10) and that $c(n)$ is a constant, Eqs. (2.34)–(2.46) reduce to the results of what we are calling the original Van der Waals model.[1] As far as we have been able to ascertain, Lord Rayleigh[5] was the first to derive the profile and surface-tension expressions, Eqs. (2.34) and (2.45), for the case of constant $c(n)$. Later, other investigators, including members of the Van der Waals school, independently proposed the same equations. Orowan[6] provides a brief discussion of the history of the matter. As the Van der Waals school appears to have developed the implications of the theory most extensively and since even Lord Rayleigh's results were based on Van der Waals' equation-of-state model, we have chosen to refer to the early work as Van der Waals theory. Those seeking the proper historical perspective are urged to read the discussion and study the bibliography of Orowan's paper.

Incidentally, in the case of Van der Waals' original model, the general surface-tension formula, Eq. (2.24), can be reduced with the aid of Eq. (2.16) to the relatively simple form

$$\gamma = \int_{-\infty}^{\infty} \left(f_R(n(x)) - \frac{n(x)}{2} f_R'(n(x)) - \Phi(n_l) - \frac{\alpha}{2} n_{gl}(x) \right) dx , \tag{2.47}$$

where

$$n_{gl} = n_l[1 - \eta(x)] + n_g \eta(x) . \tag{2.48}$$

In Sec. III we shall apply Eqs. (2.41) and (2.46) for the original Van der Waals model and for the modified version given here. These expressions are based on the differential-equation approximation, Eq. (2.32), to the more general result, Eq. (2.14). This approximation, which is obviously accurate sufficiently close to the critical point, appears from preliminary studies on Eq. (2.14) to be quite accurate over the entire coexistence range of temperatures. The results of numerical investigations of Eq. (2.14) will be reported in a later paper. The small quantitative loss in going to the differential equation seems to us of minor importance when compared to the simplicity gained.

III. COMPUTATIONS

In the original Van der Waals model the quantity c is a constant and $f_R(n)$ is given by an expression, Eq. (2.10), containing the energy parameter a, Eq. (2.11), and the excluded-volume parameter b. It is convenient to eliminate a, b, and c from the thermodynamic equations by introducing the reduced parameters

$$n^* = nb, \quad T^* = \frac{bkT}{a}, \quad \gamma^* = \frac{b^2}{(ac)^{1/2}} \gamma, \quad \Phi^* = \frac{b^2}{a} \Phi, \quad x^* = \left(\frac{a}{c}\right)^{1/2} x . \tag{3.1}$$

In terms of these reduced parameters, the Van der Waals model yields for Eqs. (2.41) and (2.46)

$$x^* - x_0^* = -\frac{1}{\sqrt{2}} \int_{n_0^*}^{n^*(x^*)} \frac{dn^*}{[\Phi^*(n^*) - \Phi^*(n_l^*)]^{1/2}} \tag{3.2}$$

and

$$\gamma^* = \sqrt{2} \int_{n_g^*}^{n_l^*} [\Phi^*(n^*) - \Phi^*(n_l^*)]^{1/2} dn^* , \tag{3.3}$$

where

$$\Phi^* = n^*\zeta - n^*T^*[\ln(1/n^* - 1) + 1] - (n^*)^2 \tag{3.4}$$

and

$$\zeta = -\frac{b}{a}\,[kT\ln bq(T) + \alpha] \ . \tag{3.5}$$

Equations (2.37) and (2.38) yield the following conditions which determine n_l^*, n_g^*, and ζ as a function of T^*:

$$\Phi^*(n_l^*) = \Phi^*(n_g^*) \tag{3.6}$$

and

$$\zeta = T^*\ln\left(\frac{1}{n_\nu^*} - 1\right) - \frac{n_\nu^* T^*}{1 - n_\nu^*} + 2n_\nu^*, \quad \nu = l, g \ . \tag{3.7}$$

From the reduced expressions we conclude the well-known corresponding-states principle for a Van der Waals fluid: $n^*(x^*)$ is a universal function of x^* and T^*; i.e., it is the same for all Van der Waals fluids compared at the same x^* and T^*, and γ^* is a universal function of T^*.

Values of n_g^*, n_l^*, and ζ versus T^* obtained by solving Eqs. (3.6) and (3.7) are given in Table I. Choosing $x_0^* = 0$ for some arbitrary density n_0^* lying between n_g^* and n_l^*, one can compute isotherms of n^* versus x^* from Eq. (3.2). Such isotherms are presented in Fig. 1. The origin of the coordinate system used in Fig. 1 is the Gibbs dividing surface of zero excess matter. The position x_G^* of the dividing surface relative to an arbitrary origin for the abscissa x^* is obtained for each isotherm from the defining equation

$$\int_{-\infty}^{x_G^*} [n^*(x^*) - n_l^*]\,dx^* + \int_{x_G^*}^{\infty} [n^*(x^*) - n_g^*]\,dx^* = 0 \ . \tag{3.8}$$

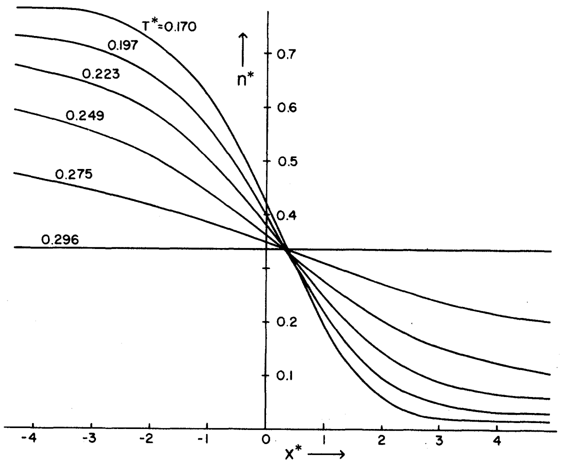

FIG. 1. Interfacial density profiles of the Van der Waals fluid [Eq. (3.2)]. $x^* = 0$ is located at the Gibbs dividing surface of zero excess matter.

TABLE I. Van der Waals reduced equation-of-state data for liquid-vapor system. n_g^*, n_l^*, and ζ are obtained by solving Eqs. (3.6) and (3.7) at several values of T^*. Values of γ^* are obtained from Eq. (3.3).

T^*	n_g^*	n_l^*	γ^*	ζ
0.170	0.0159	0.783	0.153	0.732
0.197	0.0331	0.735	0.110	0.723
0.223	0.0601	0.679	0.071	0.719
0.249	0.102	0.610	0.037	0.719
0.275	0.171	0.515	0.011	0.721
0.296	0.333	0.333	0	0.724

An examination of Fig. 1 shows that the isotherms follow the pattern that as T^* decreases the transition from gas to liquid is sharper, as it should be. Moreover, the isotherms exhibit the interesting feature of an approximate common point of intersection. The density at this common point corresponds to the reduced critical density. That the profiles do not cross at exactly the same point may have been caused by a computational error. Assuming a hyperbolic tangentlike form for the interfacial density Toxvaerd[7] has found a similar occurrence in the isotherms of a Lennard-Jones fluid. Since Van der Waals and Toxvaerd's models are quite different, the existence of a common intersection point at the critical density for all of the isotherms may be of thermodynamic significance. The intersection may be a corresponding-states principle, this principle being a common feature of the Van der Waals and Lennard-Jones models. It will be shown below that the modified Van der Waals theory applied for a Lennard-Jones model potential energy also yields a common point of intersection of the density isotherms at the critical density. In fact, the qualitative features of the density profiles predicted by the Van der Waals model are in good agreement with those predicted by the more realistic modified Van der Waals model and with those predicted by Toxvaerd's models. However, whereas the latter models yield profiles in substantial agreement with existing computer simulation results, the Van der Waals model predicts an interfacial region that is too broad. We shall return to this point below.

In Table II, the reduced surface tension predicted by Eq. (3.3) is given for several reduced temperatures. In order to convert the reduced tensions to tensions for a particular fluid, we must determine the value of the constants a, b, and c. The critical parameters T_c and P_c may be used to determine a and b through the relations $b = kT_c/8P_c$ and $a = 27(kT_c)^2/64P_c$ obtained from Eq. (2.12). We have obtained the values of

c for argon, carbon dioxide, propane, and benzene by fitting the theoretical surface tension to the experimental value at a reduced temperature corresponding to about $0.8T_c$ (except for propane, for which $0.6T_c$ was used because only limited data were available). The temperature for which c is determined is of course arbitrary and will affect agreement between theory and experiment at other temperatures to the extent that Van der Waals theory is not quantitatively accurate. Surface tensions predicted with aid of the fitted c's are compared with experiment in Table II. From the entries in the table we conclude that, if one is willing to tolerate an error of some 40%, the model provides a means of estimating from one measurement of the surface tension over a range of temperatures up to about $0.96T_c$.

TABLE II. Van der Waals predicted values compared with experimental values of the surface tension versus T_R ($=T/T_c$) for argon, carbon dioxide, benzene, and propane. The parameters a and b are determined from critical-point data. The parameter c is determined by fitting theoretical γ to experiment at the temperature indicated by an asterisk.

T_R	γ_{pred} (dyn/cm)	γ_{expt} (dyn/cm)
	Argon [a]	
0.56	16.10	13.45
0.66	10.91	9.40
0.76	6.60	6.01
*0.86	2.99	2.99
0.96	0.47	0.58
0.995	0.028	0.041
	Carbon dioxide [a]	
0.80	10.46	10.08
*0.83	8.06	8.06
0.87	5.86	6.14
0.90	3.90	4.34
0.93	2.21	2.67
0.95	1.49	1.90
0.96	0.86	1.19
0.98	0.36	0.57
0.997	0.03	0.07
	Benzene [b]	
0.48	40.1	31.7
0.57	30.7	24.7
0.66	22.0	18.8
0.75	14.15	12.86
*0.84	7.41	7.41
0.93	2.23	2.66
	Propane [a]	
0.50	19.08	17.07
0.55	16.28	15.34
*0.60	13.59	13.59
0.66	11.04	11.84
0.71	8.64	10.09
0.77	6.41	8.35

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The temperature dependence of the surface tension near the critical point may be determined easily from Eq. (2.46), which for constant c may be expressed in the form

$$\gamma = (2c)^{1/2} \int_0^u dy\, [\Phi(n_l) - \Phi(y + n_v)]^{1/2} , \qquad (3.9)$$

where $u \equiv n_l - n_g$. Expanding γ in a Taylor series in u, we find to lowest order

$$\gamma \simeq K u^3 = K (n_l - n_g)^3 . \qquad (3.10)$$

Combining Eq. (3.10) with Van Kampen's result,[4] namely, $n_l - n_g \simeq K'(T_c - T)^{1/2}$ in the vicinity of the critical point, we obtain the expression

$$\gamma \simeq K''(T_c - T)^{1.5} , \qquad (3.11)$$

valid near the critical point. The predicted critical exponent of 1.5, presented long ago by Van der Waals,[1] is to be compared to an exponent of 1.302 observed by Zollweg, Hawkins, and Benedek[8] for xenon and of 1.253 observed by Bouchiat and Meunier[9] for carbon dioxide. Since the quantity $c(n)$, Eq. (2.35), of the modified Van der Waals model is finite and continuous at T_c, this model too predicts a critical exponent of 1.5.

Let us now discuss some numerical result for the modified Van der Waals theory. We shall specialize to the 6-12 Lennard-Jones potential $u(r)$, which can be expressed in the form

$$u(r) = u_R(r) + u_A(r) , \qquad (3.12)$$

where the repulsive part is

$$\begin{aligned} u_R(r) &= 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \epsilon, \quad 0 < r < r_m \\ &= 0, \quad r > r_m \end{aligned} \qquad (3.13)$$

and the attractive part is

$$\begin{aligned} u_A(r) &= -\epsilon, \quad 0 < r < r_m \\ &= 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \quad r > r_m \end{aligned} \qquad (3.14)$$

The parameter r_m is determined by the condition

$$0 = \left[\frac{\partial u(r)}{\partial r}\right]_{r = r_m} . \qquad (3.15)$$

To apply the modified Van der Waals model, we need for the potential model just described the free-energy density $f_R(n)$ and the pair-correlation function. Recently, Weeks, Chandler, and Andersen[10] have found that $f_R(n)$ for the potential energy u_R may be well approximated by the free-energy density $f_R^{\mathrm{HS}}(n)$ of an equivalent hard-sphere system. The equivalent hard-sphere system is a fluid of hard spheres at the same density and temperature as the subject fluid, of diameter d determined by the equation

$$0 = \int [e^{-\beta u_R} - e^{-\beta u_d}] y_d(r) d^3 r , \tag{3.16}$$

where

$$\begin{aligned} u_d &= \infty, \quad r<d \\ &= 0, \quad r>d , \end{aligned} \tag{3.17}$$

and $y_d(r)$ is the hard-sphere limit of the correlation function $y(r) = e^{\beta u(r)} g(r)$. To determine the values of d for our calculations, we used the Percus-Yevick[11] theoretical values of $y_d(r)$. Then f_R^{HS} was calculated from the Carnahan-Starling formula,[12]

$$f_R^{\mathrm{HS}} = nkT\left(\eta \frac{(4-3\eta)}{(1-\eta)^2} + \ln n - 1 - \ln q(T)\right), \tag{3.18}$$

where

$$\eta = \tfrac{1}{6}\pi d^3 n . \tag{3.19}$$

The pair-correlation function we have used is of the form suggested by Weeks, Chandler, and Andersen[3] (WCA) for Lennard-Jones fluids, namely,

$$g(r) = e^{-\beta u_R(r)} y_d(r) . \tag{3.20}$$

WCA found that predictions of Eq. (3.20), with the Percus-Yevick values of y_d, agree well with molecular-dynamics results for fluid densities above $n = 0.65/\sigma^3$, a density about twice the critical value. Although Eq. (3.20) becomes inaccurate for densities below $0.65/\sigma^3$, for lack of an alternative source of analytical values of $g(r)$, we have chosen in the present calculations to use Eq. (3.20) for the entire density range. Thus, the liquid side of our predicted profiles are expected to be more accurate than the vapor side, except in the very-low-density region, where the fluid behavior is ideal and insensitive to $g(r)$.

With the Lennard-Jones model, it is convenient to introduce the dimensionless variables

$$\begin{aligned} &n_r = n\sigma^3, \quad T_r = kT/\epsilon, \quad \gamma_r = \sigma^2\gamma/\epsilon, \\ &P_r = \sigma^3 P/\epsilon, \quad x_r = x/\sigma . \end{aligned} \tag{3.21}$$

These variables obey the law of corresponding states: P_r, given by Eq. (2.19), is a universal function of n_r and T_r in the one-phase region and of T_r along the coexistence curve: γ_r is a universal function of T_r; n_r is a universal function of T_r and x_r.

The reduced gas and liquid densities, the quantity $\zeta_r = T_r \ln[q(T)\sigma^3] + \alpha/\epsilon$, and the reduced surface tension for the present model are given for various values of T_r in Table III. Isotherms of n_r versus x_r are shown in Fig. 2. The origin of the abscissa is again located at the Gibbs dividing surface of zero excess mass. Similarly to the profiles of the original Van der Waals theory, the density profiles of the modified Van der Waals theory are seen in Fig. 2 to intersect at the critical density at a constant distance from the Gibbs dividing surface.

Qualitatively, the profiles in Figs. 1 and 2 behave quite similarly. However, a comparison shown in Fig. 3 indicates that the modified Van der Waals model gives profiles in quantitative agreement with experiment while the original Van der Waals model does not. Using the potential energy parameters $\sigma = 3.4$ Å and $\epsilon/k = 119.4$ °K (corresponding to values often assumed for argon) Lee, Barker, and Pound[13] (LBP) determined by Monte Carlo methods the density profile for a Lennard-Jones liquid-vapor interface at 84 °K. The profile predicted by the modified Van der Waals model is seen in Fig. 3 to agree quite well with the profile computed by LBP (the reduced bulk-liquid density predicted by the model is 0.842 and found by LBP is 0.81). On the other hand, the profile predicted by the original Van der Waals model (for the argon used in computing γ in Table II) is much too broad and, as is already well known, gives a poor prediction of the bulk-liquid density.

A direct comparison between the shape of the modified Van der Waals model profiles and actual density profiles for a planar interface is not yet

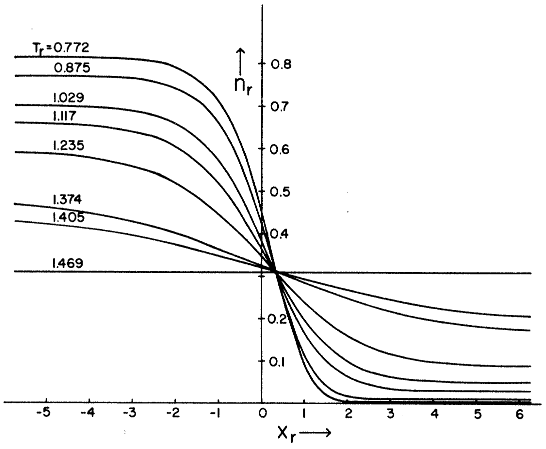

FIG. 2. Interfacial density profiles of the modified Van der Waals fluid [Eq. (2.41)] for the Lennard-Jones potential. $x_r = 0$ is located at the Gibbs dividing surface of zero excess matter.

possible, because of obvious experimental difficulties. However, we can compare for the model and experiment, the temperature dependence of an interfacial length which qualitatively characterizes the shape of a planar interfacial density profile. Let us define moments of the density profiles as follows:

$$\langle x^k \rangle_{\text{ave}} = -\frac{1}{n_l - n_g} \int_{-\infty}^{+\infty} x^k \frac{dn(x)}{dx}\, dx \,, \tag{3.22}$$

$$\mu_2^{1/2} = [\langle x^2 \rangle_{\text{ave}} - \langle x \rangle_{\text{ave}}^2]^{1/2} \,. \tag{3.23}$$

A plot of $\mu_2^{1/2}/\sigma$ versus $1/(1 - T/T_c)$ for the modified Van der Waals model shows that the data are closely approximated by

$$\frac{\mu_2^{1/2}}{\sigma} = \frac{K}{(1 - T/T_c)^{0.520 \pm 0.005}} \tag{3.24}$$

for a wide range of temperatures ($0.49 \leqslant T/T_c \leqslant 0.994$). The exponent of 0.52 in Eq. (3.24) is to be compared with an exponent of 0.66 determined from reflectivity measurements near the critical temperature by Wu and Webb[15] for the effective interfacial thickness $L'(T)$.

LPB determined from their computer data a surface tension of 16.5 ±2.3 dyn/cm. In fairly good agreement with this, the modified Van der Waals model yields 21.6 dyn/cm.

Although the LPB results appear to be the only source of Lennard-Jones "data" to compare the model with, we can test the model by comparing predictions with experimental results for argon. For the Lennard-Jones parameters, we shall use the set of parameters $\sigma = 3.37$ Å and $\epsilon/k = 116.41$ °K instead of the usual set of 3.4 Å and 119.4 °K. The former set was determined recently by Salter and Davis[16] by optimizing agreement between the experimental and theoretical pressure [using the WCA pair correlation function, Eq. (3.20)] for liquid argon between 84 and 106 °K. The two sets of parameters lead to quite similar results, the set of Salter and Davis perhaps giving slightly better over-all results. The critical parameters predicted by the model are $P_c = 78.5$ atm, $T_c = 171.0$ °K, and $n_c = 0.537$ g/cm^3. These may be compared to the observed values for argon: $P_c = 48.0$ atm, $T_c = 150.72$ °K, and $n_c = 0.531$ g/cm^3. We do not know whether the high predicted values result from a shortcoming of the modified Van der Waals theory or only from the known failure of the WCA pair-correlation function at densities lower than $n_r = 0.65$. It is interesting that in spite of the relatively high values predicted for P_c and T_c, the predicted dependence of the reduced vapor pressure $P_R = P/P_c$ on the reduced temperature T/T_c agrees well with experiment on argon and so also does the predicted dependence of γ on T/T_c. These comparisons are shown in Figs. 4 and 5.

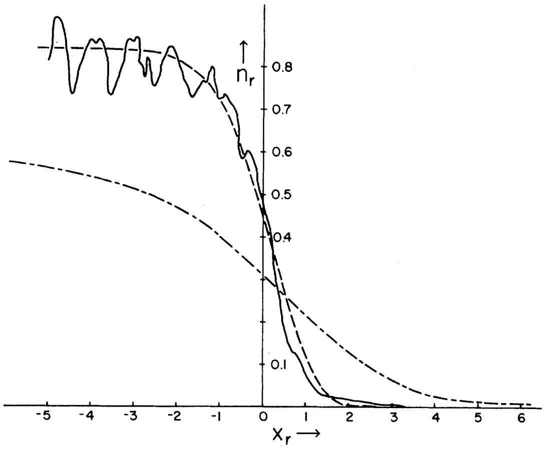

FIG. 3. Comparison of density profile of Monte Carlo computations (Ref. 13), the Van der Waals theory, and the modified Van der Waals theory. The Monte Carlo curve (solid line) and the modified-theory curve (dashed line) are for a Lennard-Jones potential model with argon-like parameters $\sigma = 3.4$ Å and $\epsilon/k = 119.4$°K. The parameters for the Van der Waals curve (dot-dashed line) were determined from argon data. In a more recent study (Ref. 14) it has been shown that the ripples in the Monte Carlo curve (solid line) are statistical artifacts of the computations.

TABLE III. Modified Van der Waals equation-of-state data for liquid-vapor system (for a Lennard-Jones potential). n_g^r, n_l^r, and ζ_r are obtained by solving Eqs. (2.37) and (2.38). $\zeta_r = T_r \ln[q(T)\sigma^3] + \alpha/\epsilon$. Values of γ_r are obtained from Eq. (2.46), reduced according to Eq. (3.21).

T_r	n_g^r	n_l^r	ζ_r	γ_r
0.772	0.0044	0.815	4.209	1.315
0.875	0.0112	0.771	4.010	1.032
1.029	0.0314	0.702	3.781	0.661
1.117	0.0502	0.660	3.681	0.475
1.235	0.0876	0.594	3.573	0.256
1.374	0.163	0.485	3.480	0.062
1.405	0.190	0.451	3.464	0.033
1.460	0.274	0.355	3.439	0.0014
1.469	0.310	0.310	3.443	0

IV. CONCLUSIONS

We have shown that a modified version of Van der Waals theory maintains the original simplicity of Van der Waals theory of bulk and interfacial properties but yields a much more quantitative description than the original theory. An obvious improvement on the calculations reported in Sec. III would be the introduction of a more accurate

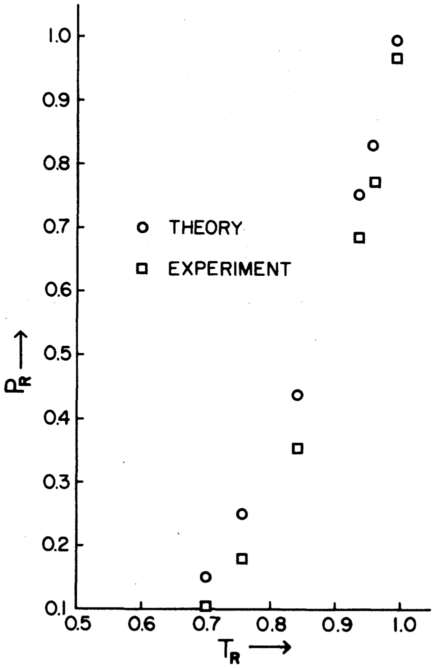

FIG. 4. Comparison of experimental and modified Van der Waals theoretical reduced vapor pressure ($P_R = P/P_c$) versus reduced temperature ($T_R = T/T_c$). Experimental data are for argon. Theoretical values are based on the Lennard-Jones potential with $\sigma = 3.37$ Å and $\epsilon/k = 116.4$°K.

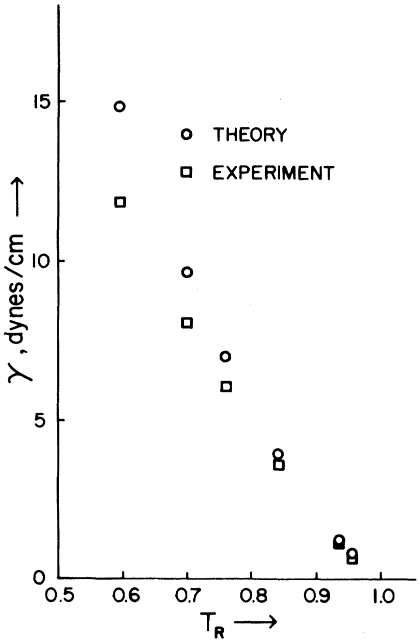

FIG. 5. Comparison of experimental (argon) and modified Van der Waals theoretical (Lennard-Jones potential, $\sigma = 3.37$ Å, $\epsilon/k = 116.4$°K) surface tension versus reduced temperature.

pair-correlation function than the WCA approximation of Eq. (3.20). Another improvement would be to solve the integral equation for the density profile instead of the differential-equation approximation. However, we have preliminary studies, to be reported later, that indicate little difference between the results of the integral and differential equations for the planar liquid-vapor interface.

The density profiles predicted by the modified Van der Waals theory are very similar to those predicted by Toxvaerd with two models, one[7] a perturbation theory with an assumed hyperbolic tangentlike profile and the other[17] a solution of the Yvon-Born-Green equation for a correlation-function model. The advantage of the modified Van der Waals model over those of Toxvaerd is that profile and surface-tension formulas of the former are much simpler and easier (cheaper) for computational purposes.

In closing, let us point out that Hill[18] and Plesner *et al.*[19-21] have previously developed variations of the Van der Waals theory. These investigators assumed a structureless fluid ($g \equiv 1$) and used a less quantitative theory of the repulsive fluid than the WCA theory. Thus, we feel the present theory represents the best available version of the Van der Waals theory.

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