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Further Application of the Statistical Thermodynamics of Curved Surfaces to Scaled Particle Theory

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The thermodynamics of curved boundary layers is combined with scaled particle theory to determine the rigid-sphere equation of state. In particular, the boundary analog of the Gibbs–Tolman–Koenig–Buff equation is solved for a rigid-sphere fluid, using the approximation that the distance between the surface of a cavity and its surface of tension is a function of the density only (the first-order approximation). This, in conjunction with several exact conditions on G, the central function of scaled particle theory, leads to an approximate rigid-sphere fluid equation of state and a qualitatively correct rigid-sphere solid equation of state. The fluid isotherm compares favorably with previous results (2.9% error in the fourth virial coefficient), but due to the inaccuracy of the solid isotherm, no phase transition is obtained. The theory described here is to be contrasted with previous approaches in that a less arbitrary functional form for G is assumed, and the surface of tension and cavity surface are not assumed to be coincident. The "cycle equation" of Reiss and Tully-Smith is rederived by a simpler route and shown to be correct to all orders of cavity curvature, rather than only first order as was originally thought. A new exact condition, obtained from the compressibility equation of state, is used as a boundary condition for the "cycle equation" to determine the location of the equimolecular surface. This molecular

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calculation compares favorably (discrepancy of $<2\%$) with a thermodynamic calculation based on the boundary analog of the Gibbs adsorption equation and indicates the accuracy and consistency of the first-order approximation.

KEY WORDS: Statistical thermodynamics of curved boundary layers; scaled particle theory; equation of state; cycle equation; fluid–solid phase transition.

1. INTRODUCTION

In a recent paper, Reiss and Tully-Smith(1) applied some ideas derived from the statistical thermodynamics of curved surfaces to scaled particle theory. In a later paper, Vieceli and Reiss(2) showed that Reiss and Tully-Smith had employed the thermodynamic formalism appropriate to *interfacial* layers, whereas they should have developed a formalism specific to the *boundary* layer involved in scaled particle theory. Although the entire philosophy of Ref. 1 and most of its conclusions retain their validity, some of the relations must be changed. These changes are not, however, quantitatively large. Vieceli and Reiss(2) developed the appropriate thermodynamic formalism for boundary layers in general. Some results of their development are: (1) a modified Gibbs-Tolman-Koenig-Buff equation, (2) a modified Gibbs adsorption equation, and (3) the elimination from the derivation of any dependence on edge effects associated with conical or wedge-shaped containers.

In the present paper, we reformulate the Reiss and Tully-Smith approach using the more appropriate boundary layer formalism and obtain the correct quantitative results. In addition, the theory is extended and analyzed beyond the point to which it was carried by Reiss and Tully-Smith. For example, we are now able to obtain two equations of state for rigid spheres, one of which, although necessarily very approximate (since the thermodynamic formalism is not designed for solid surfaces), corresponds to the solid phase. In addition, a new exact condition obtained from the compressibility equation of state is derived. Several other results of direct importance to the statistical thermodynamics of curved surfaces are also obtained and will be discussed in the body of the text.

2. SOME PRELIMINARY RELATIONS

Consider a system of N rigid spheres of diameter a in a spherical container of volume V, with radius R, at temperature T. A basic equation of scaled particle theory relating molecular and thermodynamic variables for this system is(3)

$$\partial W/\partial r = 4\pi r^2 kT\rho G(r, \rho) \tag{1}$$

In this equation, W is the reversible isothermal work required to produce a spherical cavity of radius r free of particle centers, ρ is the number density ($= N/V$) of rigid spheres, k is the Boltzmann constant, and $4\pi r^2 \rho G(r, \rho)\,dr$ is the probability that there is a particle center in the spherical shell between r and $r + dr$ when the cavity is known to be free of particle centers. Note that it has been customary to think of the cavity (an "r-cule") as being generated by another rigid sphere of diameter b, such that $r = (a + b)/2$. It is implicitly assumed that besides T, N and V are also held constant. Since the system is macroscopic, we can, without loss of generality, place the cavity at the center of the container, a sphere of radius R, and define the geometric variables

$$V_1 = \tfrac{4}{3}\pi(a_s^3 - r^3) \tag{2}$$

$$V_2 = \tfrac{4}{3}\pi(R^3 - a_s^3) \tag{3}$$

$$A_s = 4\pi a_s^2 \tag{4}$$

where a_s is the radius of another sphere, concentric with both the cavity and the container, which will play the role of a Gibbs dividing surface. In fact, the subscript s implies a particular dividing surface which, following Gibbs, we will call the "surface of tension". Clearly, V_1 is the volume between the cavity and the surface of tension, V_2 is the volume between the container wall and the surface of tension, while A_s is the area of the surface of tension. From Ref. 2, the change in Helmholtz free energy of a portion of the fluid contained within fixed a solid angle and having T and N fixed is given by

$$dF = -p_1\,dV_1 - p\,dV_2 + \gamma_s\,dA_s \tag{5}$$

where γ_s is the boundary tension associated with the surface of tension, and a_s has been *chosen* so that the following relation is true:

$$p_1 - p = 2\gamma_s/a_s \tag{6}$$

In Eqs. (5) and (6), p_1 and p are to be interpreted as the normal stresses exerted on the surfaces at r and R, respectively. Although under certain conditions, p_1 and p may be interpreted as (and in fact may be) the pressures within the volumes V_1 and V_2, respectively, they need not be, and their strict definitions remain the normal stresses referred to above (see Ref. 2). Under these conditions, the change in Helmholtz free energy is equal to the work dW appearing in Eq. (1), and under the condition of constant total volume, Eqs. (1), (5), and (6) may be combined to yield

$$\rho kTG(r, \rho) = p + (2\gamma_s/a_s) \tag{7}$$

This is an exact thermodynamic expression for G,(1) except when the physical situation does not allow a_s to be positive, in which case Eq. (7) is meaningless. Equation (7) contains the unknown quantities p, γ_s, and a_s, and for our purposes, replaces Eq. (1) as the basic scaled particle theory relation between molecular and thermodynamic variables.

In Ref. 3 [see Eqs. (14), (18), (19), (34), and (38)], several other exact relations involving $G(r, \rho)$ are derived. Two of these are

$$G(r, \rho) = 1/(1 - \tfrac{4}{3}\pi r^3 \rho), \qquad r \leq a/2 \tag{8}$$

$$\partial G(r, \rho)/\partial r = 4\pi r^2 \rho/(1 - \tfrac{4}{3}\pi r^3 \rho)^2, \qquad r \leq a/2 \tag{9}$$

The relation of G to the hard-sphere equation of state is obtained by noting the equivalence of $G(a, \rho)$ and the contact generic pair correlation function,(3)

$$p = \rho kT + \tfrac{2}{3}\pi kTa^3\rho^2 G(a, \rho) \tag{10}$$

From Ref. 2, the boundary layer analog of the Gibbs–Tolman–Koenig–Buff equation is

$$\left(p + \frac{2\gamma_s}{a_s}\right)\left[r^2 - a_s^2\left(\frac{\partial a_s}{\partial r}\right)_\rho\right] = a_s^2\left(\frac{\partial \gamma_s}{\partial r}\right)_\rho \tag{11}$$

The appropriate Gibbs adsorption equation, also derived in Ref. 2, will be discussed in Section 5 in connection with the "cycle equation" of Section 4.

Previously, two approaches have been used in determining the equation of state of a rigid-sphere fluid using scaled particle theory. The earliest approach(4) involved the assumption that G could be expanded in inverse powers of r (even though it was known that G was nonanalytic in r, having singularities in the second- and higher-order derivatives). Numerous exact boundary conditions on G [especially Eqs. (8)–(10)] were then used to determine the density-dependent coefficients in this expansion, and hence the equation of state. Although this approach gave very accurate virial coefficients, it did involve using a specific assumed functional form for $G(r, \rho)$. This form is known to be correct in the limit of large r but is otherwise of unkonwn validity. In addition, there is no way to extract the solid–fluid phase transition suggested by both Monte Carlo(5) and molecular dynamics computations.(6)

The later approach(1) endeavors to make no assumption (although it actually fails in this respect since some assumption must eventually be made) concerning the form of G, but instead attempts to rely on Eqs. (7)–(11) to specify that form. A seemingly more physically meaningful assumption (than that of expandability in inverse powers of r with truncation after the quadratic term) in connection with this set of equations is to assume that the surface of tension and cavity surface are coincident since there are independent indications that they differ in position by only a small fraction of a rigid-sphere diameter. When applied to Eqs. (7), (8), (10), and (11), this assumption predicts a boundary tension independent of cavity radius,

$$\sigma = -3y^2/2(1-y)(1-2y) \tag{12}$$

and an equation of state

$$\phi = y(1+y)/(1-y)(1-2y) \tag{13}$$

where we have used the dimensionless variables

$$\sigma = \pi a^2 \gamma_s/3kT \tag{14}$$

$$\phi = \pi a^3 p/6kT \tag{15}$$

$$y = \pi a^3 \rho/6 \tag{16}$$

Equation (13) gives the first three virial coefficients exactly and an error of approximately 20% in the fourth.[2] It also seems to indicate a thermodynamically unstable point at $y = 0.5^{(1)}$ and therefore a solid-fluid phase transition. The work described throughout the remainder of this paper is aimed at continuing this later approach employing a less severe approximation for the location of the surface of tension. Furthermore, we apply Eq. (9) as well as Eqs. (7), (8), (10), and (11).

In our treatment, we allow the surface of tension to be displaced by a reduced distance δ from the surface of the cavity, thus relaxing the severe restriction that the two surfaces be coincident. However, we assume that δ depends only on reduced density y and not upon cavity radius r. The justification for this assumption lies in the fact that we apply our equations only over a limited range of r between $r = a/2$ and a, where a is the diameter of the rigid-sphere molecule. Even so, δ is not strictly independent of r and errors are therefore generated. Further progress can be made by allowing δ to depend on r in a form which depends upon at least two additional functions of density; there is enough information in our set of equations to cover that case. However, we have not yet advanced the theory that far.

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[2] If virial coefficients are the only desired information, scaled particle theory, with an assumed form for G, gives the fourth and fifth virial coefficients with an accuracy of 2 and 7%, respectively (see Table II of Ref. 4, entry F). Note that a numerical error in Eq. (127) of Ref. 1 ($24.3y^4$ should be replaced by $22y^4$) led to a 32% error instead of the actual 20% error in the fourth virial coefficient. The fifth virial coefficient predicted by Eq. (13) is 63% too high.

In general, we work with a reduced cavity radius x ($= r/a$) and define

$$u = a_s/a = x + \delta(x, y) \tag{17}$$

In our approximation

$$u = x + \delta(y) \tag{18}$$

In the next section, this approximation is used in the determination of $\phi(y)$, $\delta(y)$, $G(x, y)$, $\sigma(x, y)$, and the virial coefficients. In Section 4, the "cycle equation" of Reiss and Tully-Smith(1) is rederived by a simpler route and is shown to be valid to all orders of curvature. In Section 5, the nature of the approximation in Eq. (18) is examined; the cycle equation and the boundary layer analog for the Gibbs adsoption equation are both used to determine the location of the equimolecular dividing surface.

3. DERIVATION OF THE EQUATION OF STATE

Equation (11) may be rewritten in terms of the dimensionless variables. If in this equation we employ Eq. (18) to substitute for u, the result is

$$\left(\frac{\partial\sigma}{\partial x}\right)_y + \frac{2(\delta^2 + 2\delta x)}{(x + \delta)^3}\,\sigma = -\frac{2\phi(\delta^2 + 2\delta x)}{(x + \delta)^2} \tag{19}$$

which can be solved through the use of the integrating factor,

$$F(x) = \exp\left[\frac{\delta^2}{(x + \delta)^2} - \frac{4\delta}{(x + \delta)}\right] \tag{20}$$

together with the boundary condition,

$$\sigma(\tfrac{1}{2}, y) = (\tfrac{1}{2} + \delta)\left(\frac{y}{1 - y} - \phi\right) \tag{21}$$

derived from Eqs. (7) and (8). The solution is

$$\sigma(x, y)F(x) = \sigma(\tfrac{1}{2}, y)F(\tfrac{1}{2}) - 2\phi I(x) \tag{22}$$

where

$$I(x) = \int_{1/2}^{x} \frac{\delta^2 + 2\delta t}{(t + \delta)^2}\,F(t)\,dt \tag{23}$$

Both Eqs. (7) and (9) may be expressed in terms of reduced variables, and Eq. (7) may be substituted into Eq. (9), eliminating G, so that an expression in $\sigma(\frac{1}{2}, y)$ and $\partial\sigma(\frac{1}{2}, y)/\partial x$ is obtained. Combining this equation with Eq. (19)

at $x = \frac{1}{2}$ and Eq. (21) so as to eliminate $\sigma(\frac{1}{2}, y)$ and $2\sigma(\frac{1}{2}, y)/\partial x$, we obtain an expression for the reduced pressure ϕ:

$$\phi = \frac{y + 2y^2(1 - 3\delta)}{(1 - y)^2} + \frac{8y\delta(1 + \delta)}{(1 - y)(1 + 2\delta)^2} \tag{24}$$

From Eqs. (7) and (10) together with Eq. (22), evaluated at $x = 1$, we may eliminate $\sigma(1, y)$ and obtain a second expression for ϕ:

$$\phi = \frac{y(1 - y)(1 + \delta)\,F(1) + 2y^2(1 + 2\delta)\,F(\frac{1}{2})}{(1 - 4y)(1 - y)(1 + \delta)\,F(1) + 2y(1 - y)(1 - 2\delta)\,F(\frac{1}{2}) + 8y(1 - y)\,I(1)} \tag{25}$$

Equations (24) and (25) were solved simultaneously for ϕ and δ at fixed y. Numerical solutions were obviously necessary and were limited to the range of δ between -0.5 and $+0.5$. The results are shown in Fig. 1 and 2, where three mechanically unstable solutions ($\partial\phi/\partial y < 0$ for all y) in the range $-0.5 < \delta < 0.5$ are not shown.

The relative positions of the two curves in Fig. 1 suggest that the upper curve corresponds to a fluid phase and the lower to a solid. Thus, as in Ref. 1, scaled particle theory again suggests the existence of two phases for a rigid-sphere fluid. At best, however, the curve representing the solid phase

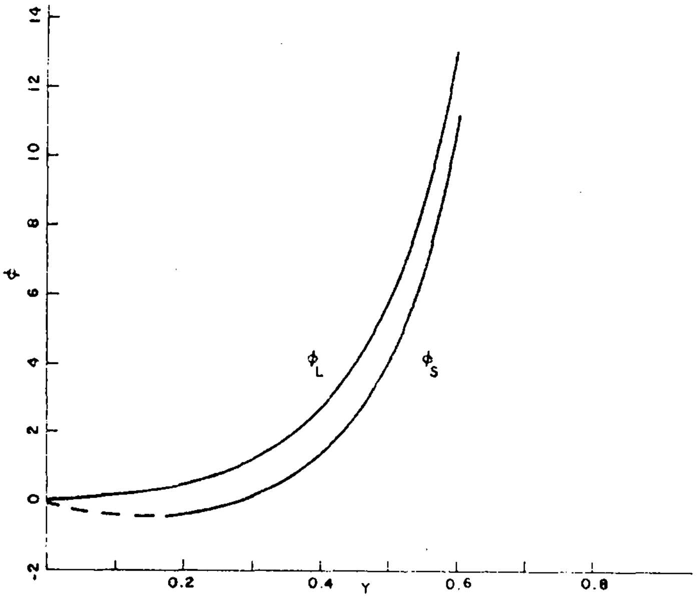

Fig. 1. The two stable pressure solutions of Eqs. (24) and (25). The broken portion of ϕ_s is excluded since it has $\partial\phi/\partial y < 0$ and is therefore mechanically unstable.

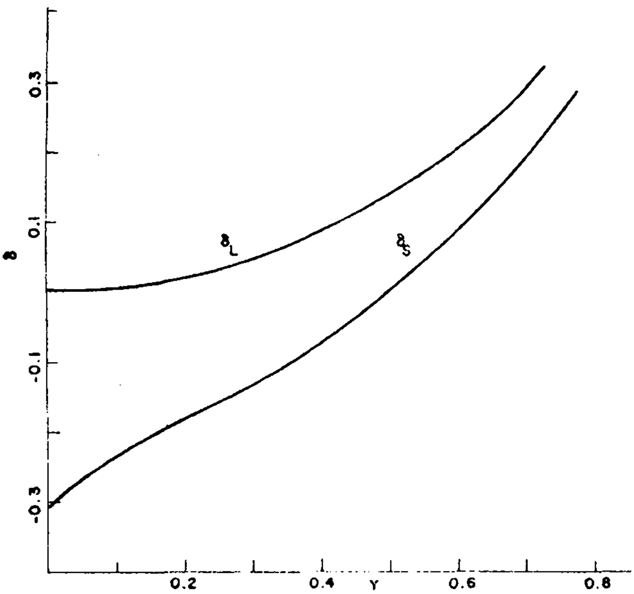

Fig. 2. The two δ solutions of Eqs. (24) and (25) corresponding to the two pressure solutions in Fig. 1.

must be very approximate since thermodynamic equations, such as Eq. (11), have been derived specifically for fluid phases.

The upper curve in Fig. 1 is readily established as an approximate version of the fluid equation of state through a comparison with machine computation results. The most convenient way to accomplish this is to compare directly with a Padé approximant(7) which reproduces the machine results. This expression for the reduced pressure of the fluid is

$$\phi_L = y + [(4y^2 + 16y^3 b + 64y^4 c)/(1 - 4yd + 16y^2 e)] \tag{26}$$

where $b = 0.063507$, $c = 0.017329$, $d = 0.561493$, and $e = 0.08131$. Alternatively, the upper curve of Fig. 1 may be represented as a power series in y and the first five coefficients may be compared with the known virial coefficients for a rigid-sphere fluid (Ref. 6, p. 111). In the virial expansion for ϕ_L,

$$\phi_L = \sum_{n=1} \phi_n y^n \tag{27}$$

$\phi_1 = 1$, $\phi_2 = 4$, $\phi_3 = 10$, $\phi_4 = 18.365$, and $\phi_5 = 28.24$ are the exact rigid-sphere virial coefficients.

The fluid curve in Fig. 1 is always slightly below the Padé approximant with an error of about 1.6% at the typical liquid density of $y = 0.25$, and 9.8% at $y = 0.45$ near the limit of validity of the Padé approximant.

In order to obtain the virial coefficients for the fluid curve in Fig. 1, it is necessary to represent δ_L and σ_L as power series in y,

$$\delta_L(y) = \sum_{n=1} \delta_n y^n \tag{28}$$

$$\sigma_L(x, y) = \sum_{n=0} \sigma_n(x)\, y^n \tag{29}$$

We note that $\delta_L \to 0$ as $y \to 0$, so that no constant term appears in Eq. (28). On the other hand, there is no *a priori* reason to exclude the constant term from Eq. (29), although we will find (as might be expected on physical grounds) that $\sigma_L \to 0$ as $y \to 0$. Equations (27)–(29) are now substituted for ϕ_L, δ_L, and σ_L in Eqs. (7)–(11), these equations of course being rewritten in terms of dimensionless variables. The coefficients in Eqs. (27)–(29) are then determined by equating equal powers of y and solving the set of simultaneous equations thereby generated. We find

$$\phi_L(y) = y + 4y^2 + 10y^3 + 17.841y^4 + 24.20y^5 + \cdots \tag{30}$$

$$\delta_L(y) = (3/8)y^2 + [(27/32) - (3/4)\ln 2]y^3 + \cdots \tag{31}$$

$$\begin{aligned} \sigma_L(x, y) = &-(3/2)y^2 - [(3/2)\ln 2x + (9/2)]y^3 - [(3\ln 2 - (75/8))\ln x \\ &-(9/4x) - (57/8) - (51/8)\ln 2 + 3(\ln 2)^2]y^4 + \cdots \end{aligned} \tag{32}$$

It is necessary to obtain only the third- and fourth-order terms in δ_L and σ_L, respectively, in order to obtain the fifth-order term in ϕ_L. From Eq. (30), we see that the first three virial coefficients are exact, the fourth is low by 2.9%, and the fifth low by 14%. This error in the fifth virial coefficient renders Eq. (30) less accurate than the result of the original scaled particle theory,[3,8] for which the equation of state is

$$\phi_L = y(1 + y + y^2)/(1 - y)^3 \tag{33}$$

Of course, we have used only part of the information available in the various differential equations and boundary conditions now at our disposal, and it is possible that further work in which the requirement that δ depend only on y is relaxed would lead to a better equation of state. On the other hand, the approximations in the original scaled particle theory are far more arbitrary and do not lead to an equation of state for the solid phase.

The negative portion of the solid-phase isotherm, with $\delta\phi/\delta y > 0$, indicates that a tensile stress is required to reduce the solid density below $y = 0.29$. The region for which $\partial\phi/\partial y < 0$, i.e., the broken portion of Fig. 1, is mechanically unstable and is excluded.

The appearance of two analytically distinct solutions[3] suggests the possibility of computing the position of the solid-fluid phase transition by calculating the chemical potentials of both the fluid and the solid and equating the chemical potentials and the pressures at the point of transition. Unfortunately, the isotherm for the solid phase, as indicated earlier, is very approximate and so it is not in fact possible to pursue this program in a meaningful way. An attempt to follow this procedure yielded no point at which the chemical potentials and pressures were simultaneously equal.

From the results contained in Figs. 1 and 2, we are able to examine the dependence of $\sigma(x, y)$ and $G(x, y)$ on x and y. These results are exhibited in Figs. 3–5, where Eq. (22) has been used for $\sigma(x, y)$ and the reduced form of Eq. (7),

$$yG(x, y) = \phi + \{\sigma(x, y)/[x - \delta(y)]\} \tag{34}$$

in order to specify $G(x, y)$. The results in Fig. 3 are typical of the boundary tension and illustrate several general trends; (1) For both the fluid and solid, larger values of reduced cavity radius are required in order to reach a relatively constant boundary tension as the density increases. (2) The fluid boundary tension is negative for all values of x and y ($\delta_L > 0$ for all y). (3) The solid boundary tension is positive for $y < 0.5$ and negative for $y > 0.5$ ($\delta_S < 0$ for $y < 0.5$ and $\delta_S > 0$ for $y \geq 0.5$). (4) Positive boundary

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[3] Integral equation approaches also give analytically distinct solutions for a hard-sphere system. See Alder and Hoover,(6) p. 100.

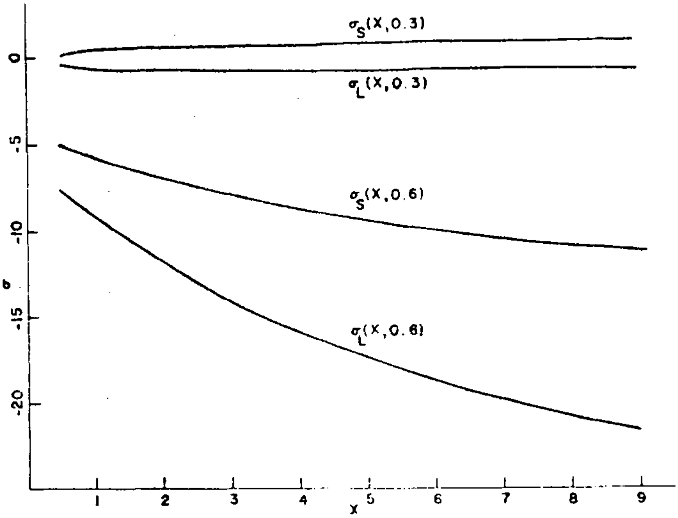

Fig. 3. The solid and fluid boundary tensions as a function of x for $y = 0.3$ and $y = 0.6$ from Eq. (22).

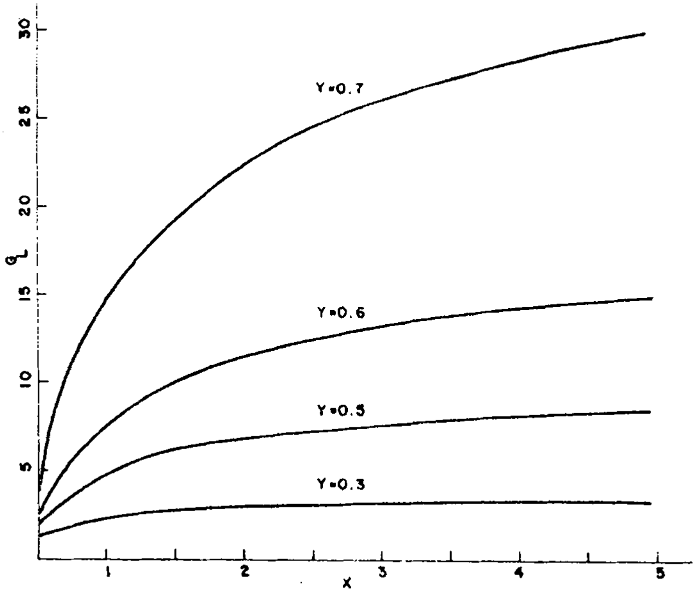

Fig. 4. The fluid G as a function of x from Eq. (34).

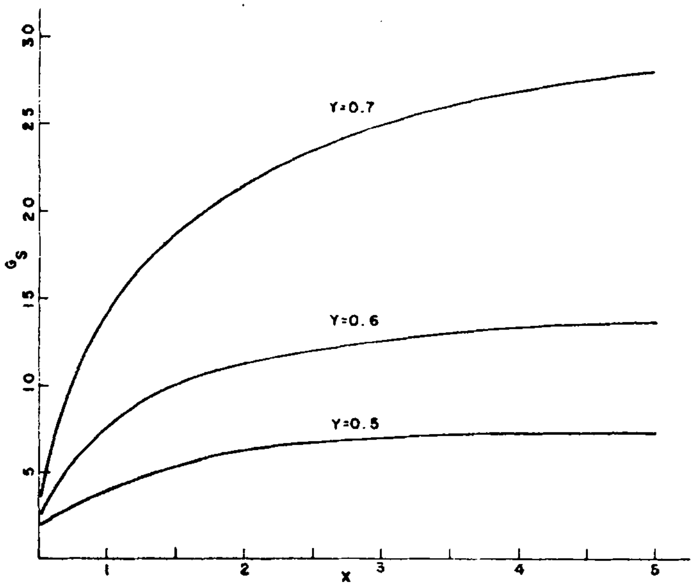

Fig. 5. The solid G as a function of x from Eq. (34).

tensions increase with increasing cavity radius and negative tensions decrease with increasing radius. The results in Figs. 4 and 5 show that as the density increases, larger values of the reduced cavity radius are required in order to reach a relatively constant value of G.

In the remainder of this paper, we discuss the cycle equation[1,4] and in particular how it and the boundary analog of the Gibbs adsorption equation[2] can be used to test the validity and consistency of our method, in which δ is assumed to depend only on r. We will call this method the first-order approximation, designating the approximation in which $\delta = 0$ as the zeroth-order approximation.

4. THE CYCLE EQUATION CORRECT TO ALL ORDERS OF CURVATURE

The following is the cycle equation as it appeared in an unmodified form [see Eq. (37) of Ref. 1]:

$$\begin{aligned}
\rho \int_0^r 4\pi(r')^2\, G(r',\rho)\, dr'
&= \tfrac{4}{3}\pi r^3 \left\{ \int_0^\rho [G(r,\rho') - \tfrac{2}{3}\pi a^3 \rho' G(a,\rho')]\, d\rho' + \tfrac{2}{3}\pi a^3 \rho^2 G(a,\rho) \right\} \\
&\quad + \tfrac{1}{3}\pi a^3 \int_0^\rho (d\rho'/\rho') \int d\mathbf{r}_1 \int N^2 [P_*^{(2)}(r_1, \mathbf{a}, \rho') - P^{(2)}(a,\rho')] \sin\theta_{12}\, d\theta_{12} \\
&\quad - 4\pi r^2 \tfrac{2}{3}\pi a^3 \int_0^\rho (\Gamma_r{}^*/\rho') \{\partial[(\rho')^2\, G(a,\rho')]/\partial\rho'\}\, d\rho'
\end{aligned} \tag{35}$$

In this equation,

$$\Gamma_r{}^* = \rho'(r^3 - a_0{}^3)/3r^2 \tag{36}$$

is the superficial density of matter adsorbed on the dividing surface coincident with the surface of the cavity and a_0 is the radius of the equimolecular dividing surface defined by

$$N = \tfrac{4}{3}\pi(R^3 - a_0{}^3)\rho' \tag{37}$$

$P_*^{(2)}$ and $P^{(2)}$ are pair specific distribution functions with the cavity present and absent, respectively. All terms in Eq. (35), except the second on the right, are treated exactly as before, i.e., Eqs. (7), (10), and (36) are used to eliminate $G(r,\rho')$, $G(a,\rho')$, and $\Gamma_r{}^*$, respectively. The second term on the right of Eq. (35) is rewritten as

$$\frac{4\pi}{3kT} \int_0^\rho \frac{d\rho'}{\rho'}\, I \tag{38}$$

where

$$I = \tfrac{1}{2}a^3kT \int_r^R r_1^2\, dr_1 \int N^2[P_*^{(2)}(r_1, \mathbf{a}, \rho') - P^{(2)}(a, \rho')] \sin\theta_{12}\, d\theta_{12}\, d\phi_{12} \tag{39}$$

In this equation, r_1 represents the distance of one of the particles involved in the pair specific distribution function from the center of the cavity, while θ_{12} and ϕ_{12} are the polar and azimuthal angles locating particle 2 in a spherical coordinate system centered on particle 1 with z axis parallel to $\mathbf{r}_1$, and $\mathbf{a}$ is a vector of lenght a whose direction is given by θ_{12} and ϕ_{12}. The integration over the angles is over the complete sphere.

In Ref. 1, I was evaluated in terms of thermodynamic quantities under the restriction that the cavity was large enough so that only first-order contributions of curvature to the boundary tension had to be considered. In the present section, we shall not only evaluate I by a simpler method, but the final result will be shown to be correct to all orders of curvature.

In Ref. 1, for the system under consideration, the derivative of the Helmholtz free energy was evaluated by two independent routes leading to the expressions

$$\frac{\partial F}{\partial r} = \frac{8\pi r^2}{a_s}\gamma_s - \frac{4\pi}{r}(R^3 - r^3)p \tag{40}$$

$$\frac{\partial F}{\partial r} = -\frac{3NkT}{r} - \frac{a^3kT}{2r}\int d\mathbf{r}_1 \int N^2P_*^{(2)}(r_1, \mathbf{a}, \rho') \sin\theta_{12}\, d\theta_{12}\, d\phi_{12} \tag{41}$$

In Ref. 1, these equations were Eqs. (47) and (59), respectively. Now consider a homogeneous reference system containing N_2 particles whose Helmholtz free energy we denote by F_2. This system is chosen so that its uniform density is the same as the local density which prevails far from the cavity in the system in which the cavity is present. For the homogeneous system, we may write

$$\frac{\partial F_2}{\partial r} = -\frac{3N_2kT}{r} - \frac{a^3kT}{2r}\int d\mathbf{r}_1 \int N_2^2P^{(2)}(a, \rho') \sin\theta_{12}\, d\theta_{12}\, d\phi_{12} \tag{42}$$

or

$$\frac{\partial F_2}{\partial r} = -\frac{4\pi(R^3 - r^3)}{r}p \tag{43}$$

Equations (40)–(43) may be combined to yield

$$\frac{8\pi r^2}{a_s}\gamma_s = -\frac{3kT}{r}(N - N_2) - \frac{a^3kT}{2r}\int d\mathbf{r}_1 \int [N^2P_*^{(2)} - N_2^2P^{(2)}] \sin\theta_{12}\, d\theta_{12}\, d\phi_{12} \tag{44}$$

Since

$$N - N_2 = 4\pi r^2\Gamma_r^* \tag{45}$$

Eq. (44) may be rewritten as

$$I = 3r^2\Gamma_r{}^*kT\left(1 - \frac{2p}{\rho kT}\right) - \frac{2r^3\gamma_s}{a_s} \tag{46}$$

In this equation, terms have been neglected of order N, $(\Gamma_r{}^*)^2$ and $\Gamma_r{}^*$ relative to terms of order N^2 and $\Gamma_r{}^*N$, and terms of order $(\Gamma_r{}^*)^2$ relative to terms of order N. The detailed arguments involving this neglect may be found in Ref. 1, p. 1684. Equation (46) is identical to the corresponding equation [Eq. (90)] derived in Ref. 1. There, however, an intermediate step of the derivation was involved whose validity was limited to situations in which only first-order contributions from curvature were important. Thus, in Ref. 1, it was assumed that Eq. (46) [Eq. (90) in Ref. 1] was also limited in validity to situations involving first-order contributions from curvature. However, the derivation we have presented leading to Eq. (46) is in no way limited, so that in fact it is now evident that Eq. (46) is generally valid even though it is identical to the corresponding equation derived in Ref. 1.

Now, Eq. (35) may be rewritten as

$$\frac{\gamma_s r^2}{a_s kT} = \int_0^\rho d\rho' \left[1 - \frac{1}{2kT}\frac{\partial p}{\partial \rho'} - \frac{p}{\rho' kT}\right]\left[r^2 - a_0{}^2\left(\frac{\partial a_0}{\partial r}\right)_{\rho'}\right] \tag{47}$$

where we have used Eq. (7) to eliminate $G(r, \rho')$, Eq. (10) to eliminate $G(a, \rho')$, Eq. (36) to eliminate $\Gamma_r{}^*$, Eqs. (38) and (46) for the second term on the right side of Eq. (35), and finally differentiated the result with respect to r. Equation (47) is equivalent to Eq. (94) of Ref. 1. It may be rewritten in more convenient form by differentiating with respect to ρ; using dimensionless variables, we find

$$\frac{x^2}{u}\left(\frac{\partial \sigma}{\partial y}\right)_x - \frac{x^2}{u^2}\left(\frac{\partial u}{\partial y}\right)_x \sigma = 2\left[x^2 - v^2\left(\frac{\partial v}{\partial x}\right)_y\right]\left[1 - \frac{\phi}{y} - \frac{1}{2}\frac{\partial \phi}{\partial y}\right] \tag{48}$$

where

$$v = a_0/a = x + \delta_0(x, y) \tag{49}$$

We now refer to Eq. (48) as the cycle equation.

5. USE OF OTHER EQUATIONS IN CONNECTION WITH THE FIRST-ORDER APPROXIMATIONS; CONCLUSIONS

Both the accuracy of the first-order approximation, Eq. (18), and the internal consistency of the various exact differential equations and boundary conditions thus far provided by scaled particle theory may be tested by attempting to generate similar results by using some of the relations not yet employed for this purpose. For example, to determine v, the reduced radius of the equimolecular surface, we can use Eqs. (30)–(32) with Eq. (48), or with the boundary layer analog of the Gibbs adsorption equation,[2]

$$\frac{1}{2}\left(\frac{\partial \sigma}{\partial y}\right)_x + \frac{\partial \phi}{\partial y}\left(\frac{u^3 - v^3}{3u^2}\right) = -\left(\frac{\partial u}{\partial y}\right)_x\left(\phi + \frac{\sigma}{u}\right) \tag{50}$$

In particular, both Eqs. (48) and (50) can be used to determine the x dependence of v_n in the density expansion

$$v(x, y) = x + \sum v_n(x)\, y^n \tag{51}$$

The method involves once again expressing all the dependent variables as power series in y, equating coefficients of the same power, and solving the resulting simultaneous equations. The first two coefficients from Eq. (48) are

$$v_1(x) = -\frac{3}{2} + \frac{l}{x^2} \tag{52}$$

and

$$v_2(x) = \frac{147}{8} - \frac{9}{4}\ln 2x - \frac{9}{4x} + \frac{m}{x^2} + \frac{3l}{x^3} - \frac{l^2}{x^5} \tag{53}$$

where l and m are integration constants. These are determined from a new exact condition derived from the compressibility equation of state,[9]

$$\frac{\partial p}{\partial \rho} = \frac{kT}{1 + \int_0^\infty [\rho g^{(2)}(r_{12}) - \rho]\, 4\pi r_{12}^2\, dr_{12}} \tag{54}$$

where r_{12} $(= |\mathbf{r}_2 - \mathbf{r}_1|)$ is the distance between the first particle at $\mathbf{r}_1$ and the second particle at $\mathbf{r}_2$, while $g^{(2)}(r_{12})$ is the generic pair correlation function. Since $g^{(2)}(r_{12}) = 0$ for $r_{12} < a$ and

$$\int_a^\infty [\rho g^{(2)}(r_{12}) - \rho]\, 4\pi r_{12}^2\, dr_{12} = 4\pi a^2 \Gamma_r{}^*(a) \tag{55}$$

Eq. (54) may be rewritten, using dimensionless variables and Eq. (36), as

$$\partial\phi/\partial y = 1/[1 - 8yv^3(1, y)] \tag{56}$$

This is a *new* exact condition and another indication that so many exact conditions can be generated within the context of scaled particle theory that there may be others that have not yet been discovered. From Eq. (56), by equating coefficients of powers of y, we find

$$v_1(1) = -17/12 = -1.42 \tag{57}$$

and

$$v_2(1) = (431/144) - \ln 2 \simeq 2.30 \tag{58}$$

so that

$$l = 1/12 \tag{59}$$

and

$$m = (5/4) \ln 2 - (963/72) \tag{60}$$

The x derivative of v is not involved in Eq. (50). As a result, we obtain directly

$$v_1(x) = -3/2 \tag{61}$$

and

$$v_2(x) = (51/8) - (9/4) \ln 2x - (9/4x) \tag{62}$$

in which there are no integration constants. At $x = 1$,

$$v_1(1) = -3/2 \simeq -1.50 \tag{63}$$

and

$$v_2(1) = (33/8) - (9/4) \ln 2 \simeq -2.57 \tag{64}$$

Comparison of Eqs. (48) and (50) is now made by using Eqs. (57) and (58) [obtained from Eq. (48)] and Eqs. (63) and (64) [obtained from Eq. (50)] to determine the distance $\delta_0(x, y)$ between the cavity surface and the equimolecular surface at $x = 1$ and the typical liquid density $y = 0.25$. From Eq. (48),

$$\delta_0(1, 1/4) \simeq -0.211 \tag{65}$$

and from Eq. (50),

$$\delta_0(1, 1/4) \simeq -0.214 \tag{66}$$

The agreement is remarkably good and indicates that the first-order approximation is useful for the calculation not only of bulk properties but also of surface properties.

As indicated earlier, the present theory might be improved by going to a higher order, i.e., by allowing δ to depend on x through some functional form involving as many as two unknown functions of y. One method for accomplishing this might involve taking higher-order x-dependent terms in the expansion of u. For each additional term in u, one additional condition on G would be required. This procedure might result in a better fluid equation of state.

A second possibility involves making no assumption at all, but attempting to solve the set of partial differential equations (11), (48), and (50) using the boundary conditions (8)–(10) and (56). If this program could be carried out, it would amount to an exact determination of the rigid-sphere equation of state.

We believe, at this point, that such a program cannot be carried out with the equations thus far presented. Note that in the more familiar integral equation approaches, it is clearly very difficult to generate additional fundamental equations, but it is not immediately obvious that scaled particle theory suffers from the same limitation, especially when the interplay between thermodynamics and molecular theory is considered. It is now of primary importance to determine what additional information is required and if scaled particle theory is capable of supplying it.

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REFERENCES

1. H. Reiss and D. M. Tully-Smith, *J. Chem. Phys.* **55**:1674 (1971).
2. J. J. Vieceli and H. Reiss, *J. Chem. Phys.* **57**:3745 (1972).
3. H. Reiss, *Adv. Chem. Phys.* **9**:1 (1965).
4. D. M. Tully-Smith and H. Reiss, *J. Chem. Phys.* **53**:4015 (1970).
5. W. W. Wood, in *Physics of Simple Fluids*, H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke, eds., Chapter 5, Wiley, New York, 1968.
6. B. J. Alder and W. G. Hoover, in *Physics of Simple Fluids*, H. N. Temperley, J. S. Rowlinson, and G. S. Rushbrooke, eds., Chapter 4, Wiley, New York, 1968.
7. F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **40**:939 (1964).
8. H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**:369 (1959).
9. T. L. Hill, *Statistical Mechanics*, McGraw-Hill, New York, 1956, p. 236.