Application of the Thermodynamics of Curved Boundary Layers to the Scaled Particle Theory of Hard-Sphere Fluids

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The thermodynamics of curved boundary layers, with the assumption that the distance between the surface of a fluid cavity and its surface of tension is a quadratic function of the cavity radius, is applied to the exact thermodynamic expression for G, the central function of scaled particle theory. The coefficients in the quadratic representation are determined so as to satisfy *all five* of the known exact conditions on G valid for cavity radii between one-half and one molecular diameter. The results of the calculation are displayed as the hard-sphere equation of state, the boundary tension associated with the surface of tension, and the distance between the cavity surface and the surface of tension. Although the hard-sphere equation of state obtained by this method using all five conditions on G is more accurate than in the case where only two or three conditions are used, the original scaled particle theory, in which G itself was represented simply by a quadratic function of inverse powers of cavity radius, still yields the more accurate equation of state. Nevertheless, the present approach limits approximations to the distance between the cavity surface and the surface of tension, a small quantity in itself. The path to a still more improved theory remains well

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defined, contingent upon the discovery of additional exact conditions, and does not depend, as in the original scaled particle theory, on a form for G arrived at in a somewhat ad hoc manner.

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1. INTRODUCTION

It has previously been established that through treatment of boundary effects in the vicinity of a microscopic spherical cavity,[1] the thermo-dynamics[2] and statistical thermodynamics[3,4] of curved boundary layers can be applied to the scaled particle theory of hard-sphere fluids.[5] In addition to the equation of state, the location of the surface of tension (SOT) and the boundary tension associated with the SOT are obtained as functions of cavity radius and the density.[4] With this approach, a physical assumption different from that originally introduced in scaled particle theory is used. The purpose of the present work is to fully test this alternative assumption using *all* of the applicable exact scaled particle theory conditions.

   Originally, it was assumed that G, the central function of scaled particle theory, defined by

$$W(x, y)/kT = 24y \int_0^x \zeta^2 G(\zeta, y)\, d\zeta \qquad (1)$$

(where W is the reversible work required to produce a cavity of radius ax in a fluid of hard-sphere particles of diameter a, number density $6y/\pi a^3$, and absolute temperature T, with k the Boltzmann constant), could be expanded as[1,5]

$$G(\zeta, y) = \sum_{n=0}^{\infty} G_n(y)(\zeta^{-1})^n \qquad (2)$$

The form of this expansion was based on what is now known[2,4] to be somewhat erroneous thermodynamic reasoning, and on the assumption that G is analytic in ζ for $\zeta > 1/2$ (not rigorously true). Various exact conditions on $G(\zeta, y)$ can then be used to determine several of the $\{G_n\}$ and hence an approximate equation of state from the exact relation

$$\phi = y + 4y^2 G(1, y) \qquad (3)$$

where $6kT\phi/\pi a^3$ is the fluid pressure in the system far from the cavity wall.

The exact conditions on $G(\zeta, y)$ are

$$G(1/2, y) = 1/(1 - y) \tag{4}$$

$$\partial G(1/2, y)/\partial \zeta = 6y/(1 - y)^2 \tag{5}$$

and

$$\frac{\partial^2 G(1/2, y)}{\partial \zeta^2} = \frac{24y}{(1 - y)^2} + \frac{72y^2}{(1 - y)^3} - \frac{48y}{1 - y} G(1, y) \tag{6}$$

at $\zeta = 1/2$;

$$G(\infty, y) = 1 + 4yG(1, y) \tag{7}$$

which is a connection between $G(\infty, y)$ and $G(1, y)$; and

$$y^2 G(1, y) + 1/4[\ln(1 - y) + y] = 6y^2 \int_{1/2}^{1} \zeta^2 G(\zeta, y)\, d\zeta$$

$$- 6 \int_0^y y'\, dy' \int_{1/2}^{1} \zeta^2 (G(\zeta, y')\, d\zeta \tag{8}$$

which is a connection between $G(1, y)$ and $G(\zeta, y')$ for $1/2 \leqslant \zeta \leqslant 1$ and $0 \leqslant y' \leqslant y$. Another condition, determined from the cycle equation,[1,3] is $G_3(y) = 0$.[2] The application of these conditions in the determination of the equation of state from Eqs. (2) and (3) is fully described in Ref. 1.

Later it was determined that the thermodynamic variables relevant to curved boundary layers are related to G through the exact thermodynamic equation[3]

$$yG(\zeta, y) = \phi(y) + [\sigma(\zeta, y)/u(\zeta, y)] \tag{9}$$

where ua is the location of the SOT and $3kT\sigma/\pi a^2$ is the associated boundary tension. These same thermodynamic variables are also related through a boundary analog of the Gibbs–Tolman–Koenig–Buff equation,[2]

$$(\partial \sigma/\partial \zeta)_y + \sigma p = \phi q \tag{10}$$

where

$$p = \frac{2}{u} \left[\left(\frac{\partial u}{\partial \zeta} \right)_y - \frac{\zeta^2}{u^2} \right] \tag{11}$$

and

$$q = -pu \tag{12}$$

Other exact equation (cycle equation,[1,3,4] compressibility equation,[4] and boundary analog of the Gibbs adsorption equation[2]) are also available but

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[2] For a different approach also leading to the result $G_3(y) = 0$, see Stillinger and Cotter.[8]

would involve the introduction of the location of the equimolecular dividing surface and the density derivatives of ϕ, σ, and u as additional unknowns.

In the next section, an approximate expression for the location of the SOT is used in conjunction with Eqs. (9) and (10) to determine $G(\zeta, y)$ and hence provide an alternative to Eq. (2) in the determination of the hard-sphere equation of state. In addition, the boundary tension associated with the SOT and its location, consistent with the equation of state, are determined as functions of density and cavity radius. In the third section, the hard-sphere equation of state obtained by the approximation for the location of the SOT is conpared with those obtained from Eq. (2).

2. THE HARD-SPHERE EQUATION OF STATE

It should be noted that if the dependence of the location of the SOT on cavity radius were known, the boundary tension could be determined exactly from Eq. (10) by using Eq. (9) and one of Eqs. (3)–(8) to eliminate G as the required boundary condition on the boundary tension. One could then use Eq. (9) for G and hence determine the equation of state directly from Eq. (3). Since the dependence of the location of the SOT on cavity radius is not known, this straightforward approach is not possible. Instead, we assume the location of the SOT can be represented as a power series of the form

$$u(\zeta, y) = \zeta + \delta(\zeta, y) \tag{13}$$

where

$$\delta(\zeta, y) = \sum_{n=0} a_n(y)(\zeta - 1)^n \tag{14}$$

is the distance between the cavity surface and the SOT. The y-dependent terms $\{a_n\}$ are treated as unknown parameters, so that $\sigma(\zeta, y)$ from Eq. (10) is determined in terms of the $\{a_n\}$ subject to the boundary condition obtained by eliminating $G(1/2, y)$ from Eqs. (4) and (9). As previously mentioned, other boundary conditions are possible, but the indicated choice turns out to be the most convenient for computation. We now have an expression for G in terms of the unknown coefficients $\{a_n\}$. This expression for G is then used to eliminate G from the remaining exact conditions and hence determine an approximate hard-sphere equation of state. This method was originally used with Eq. (14) in the form[3]

$$\delta = 0 \tag{15}$$

i.e., the SOT and the cavity surface are coincident, subject to Eqs. (3) and (4). Later, the method was used again in the form[4]

$$\delta = a_0(y) \tag{16}$$

i.e., the surface of tension and the cavity surface are separated by a distance that is a function of the fluid density alone, subject to Eqs. (3–5). Since Eq. (16) leads to a more accurate equation of state than does Eq. (15), it is desirable to fully test Eq. (14) with as many coefficients as scaled particle theory will permit.

We now use our expression for G in terms of the $\{a_n\}$ to eliminate G from Eq. (3),

$$\phi = [y/(1 - 4y)][1 + (4\sigma/u)]|_{\zeta=1} \tag{17}$$

from Eq. (5).

$$\phi(\partial u/\partial \zeta) = [6y^2u/(1 - y)^2] + [y(\partial u/\partial \zeta)/(1 - y)] - (\partial \sigma/\partial \zeta)|_{\zeta=1/2} \tag{18}$$

from Eq. (6),

$$\begin{aligned}
\phi = {}&[(1 - y)/12]\{[24y^2/(1 - y)^2] + [72y^3/(1 - y)^3] + [12y/(1 - y)] \\
&- (1/u)(\partial^2\sigma/\partial\zeta^2) + (2/u^2)(\partial u/\partial\zeta)(\partial\sigma/\partial\zeta) \\
&- (2\sigma/u^3)(\partial u/\partial\zeta)^2 + (\sigma/u^2)(\partial^2 u/\partial\zeta^2)\}|_{\zeta=1/2}
\end{aligned} \tag{20}$$

and from Eq. (8),

$$\begin{aligned}
\phi = {}&-\log(1 - y) + 24y \int_{1/2}^{1} \zeta^2 \left[\phi(y) + \frac{\sigma(\zeta, y)}{u(\zeta, y)}\right] d\zeta \\
&- 24 \int_{0}^{y} dy' \int_{1/2}^{1} \zeta^2 \left[\phi(y') + \frac{\sigma(\zeta, y')}{u(\zeta, y')}\right] d\zeta
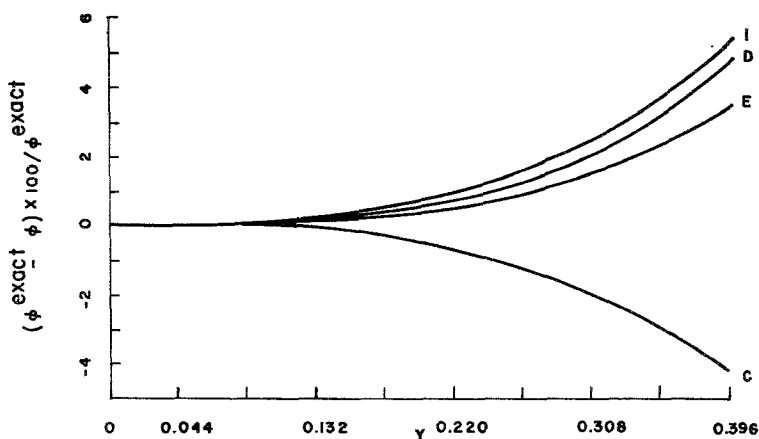\end{aligned} \tag{20}$$

Fig. 1. Percent deviation from exact hard-sphere equation of state as a function of density y. Curve 1, this paper; curves C, D, and E, Ref. 1.

Equation (4) has already been used as a boundary condition for the integration of Eq. (10); and Eq. (7), which includes terms at infinite radius, is inappropriate for the assumption of Eq. (14), whose approximate validity is probably, at best, limited to a small range of cavity radius. Each of Eqs. (17)–20) must give the same pressure so that we can form a system of equations of the form $(\Delta\phi_i = 0, i = 1, 2, 3$, where the only unknowns are the $\{a_n\}$. It is now clear that we are limited to three terms in the expansion of $\delta(\zeta, y)$ in Eq. (14). These three unknowns are determined as functions of of fluid density by the Newton–Raphson method[6] and then used to calculate the pressure (shown in curve 1 of Fig. 1 as the percent deviation from the exact hard-sphere equation of state[7]); and the boundary tension associated with the SOT and the distance between the SOT and the cavity surface, both as functions of cavity radius and fluid density (shown in Figs. 2 and 3, respectively, for several values of the density as a function of cavity radius).

3. COMPARISON OF METHODS AND CONCLUSIONS

The curves labeled C, D, and E (designated as in Ref. 1) represent the equations of state obtained from the assumption of Eq. (2). Each uses four terms in the expansion of G, with $G_3 = 0$, and Eqs. (3)–(5). In addition, C uses Eqs Eqs. (7) and (8), D uses Eqs. (6) and (7), and E uses Eqs. (6) an (7), $G_4 = 0$. The motivation for each of these choices is described in Ref. 1.
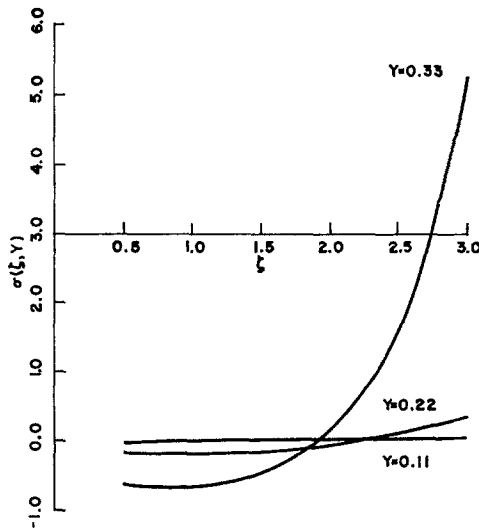

Fig. 2. The boundary tension associated with the surface of tension σ as a function of cavity radius ζ for several fluid densities y.

As shown in Fig. 1, each of the equations—C, D, and E—gives a more accurate equation of state than does the assumption of Eq. (14) using Eqs. (3)–(6) and (8), in spite of the fact that the assumption of Eq. (14) allows us to use all five of the known scaled particle theory conditions valid for $1/2 \leqslant \zeta \leqslant 1$; while each of C, D, and E uses only four of the five. Therefore, as expected, Eq. (14) with the first three coefficients and Eqs. (3)–(6) and (8) gives a better equation of state than the assumption of Eq. (16); but the improvement is not sufficient to surpass C, D, and E. The present results are however, significant since the path to a more improved theory is now well defined, contingent on the discovery of additional exact conditions. This limits assumptions concerning the form of G to the form of a small quantity δ and allows the use of the five exact conditions which do not require the introduction of another unknown.

These results lead to the conclusion that a quadratic representation of the location of the SOT is not sufficient to characterize its dependence on the cavity radius for radii between one-half and one molecular diameter, i.e., cavities of molecular dimension. The insufficiency of the quadratic represen-
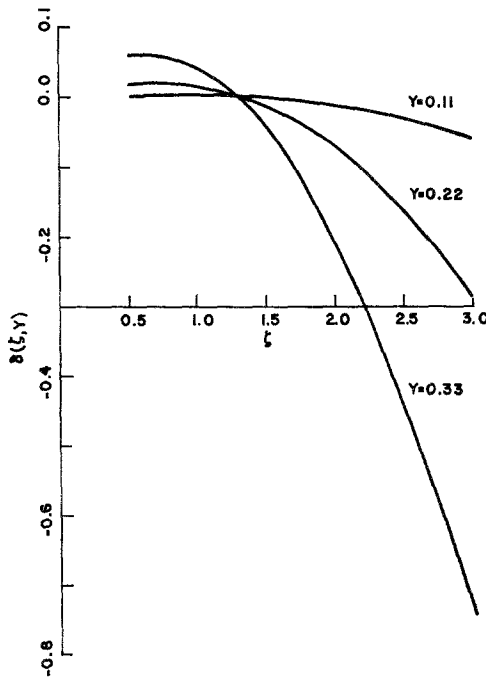

Fig. 3.   The distance between the cavity surface and the surface of tension ζ as a function of cavity radius ζ for several fluid densities y.

tation is indicated in Fig. 3, where the location of the mechanically equivalent SOT is within the cavity for $\zeta > 1.3$. Intuitively one feels that the surface mechanically equivalent to the transition layer lies within the fluid.

The assumption of Eq. (2) is sometimes described as an extrapolation of a macroscopic equation into a microscopic regime. Equation (14) does not involve this extrapolation, but it is physically reasonable to expect that in the limit of large cavities, the distance between the cavity and the SOT could be represented as

$$\delta(\zeta, y) = b_0(y) + [b_1(y)/\zeta] + [b_2(y)/\zeta^2] + \cdots \tag{21}$$

in which case the use of Eq. (21) for $1/2 \leqslant \zeta \leqslant 1$ would involve the extrapolation of a macroscopic equation into a microscopic regime. When this approach is tried, the numerical procedure that led to curve 1 of Fig. 1 and to the curves of Figs. 2 and 3 diverges, and we have not yet been able to devise a convenient program for handling Eq. (21). This could form the subject of further investigation.

A second numerical difficulty concerns the existence of a second isotherm possibly corresponding to the solid phase. A previous calculation[3] based on Eq. (15) shows that the equation of state has a singularity at $y = 1/2$ and an indication of solidlike behavior for $y > 1/2$. A second calculation[4] based on Eq. (16) confirmed the solidlike behavior and gave a qualitatively correct solid isotherm. This solid isotherm was not quantitatively correct and did not predict the solid–fluid phase transition. This second calculation was based on a one-dimensional search procedure generalized to three dimensions in order to obtain the three coefficients of Eq. (14) referring to the solid. This three-dimensional search procedure, when applied to our set of equations, $(\Delta \phi)_i = 0$, $i = 1, 2, 3$, became prohibitive due to the complexity of Eq. (20) and the fineness of the grid required to locate additional solutions. This difficulty is a consequence of the unknown behavior of $\delta(\zeta, y)$ for the solid as its density approaches zero. The unknown behavior makes the three-dimensional search procedure necessary and does not allow the use of the Newton–Raphson technique since, as applied to the fluid, the starting value of $\delta(\zeta, 0) = 0$, or $a_0 = a_1 = a_2 = 0$, is required. Therefore, the straightforward approach described here is incapable of obtaining the solution pertaining to the solid, so that the existence of a solid–fluid phase transition, as predicted by scaled particle theory, remains an open question.

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