

Microscopic theory of surface tension

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We show that the interfacial surface tension, for two phases of the same substance, can be expressed exactly in terms of bulk correlation functions in the two phases. This is accomplished by an examination of area corrections to stress tensor averages for hard-wall boundary conditions, together with an examination of the equilibrium between the two phases and the hard wall. There is also an examination of critical behavior, together with a simple model exploration to illustrate the method.

I. INTRODUCTION

Previous work on interfacial surface tension, either classically or for quantum systems, concentrates on a local analysis.¹⁻¹² (See particularly the review papers, Refs. 11 and 12.) By this we mean that the microscopic explanation of surface properties appears to require detailed information about correlation functions in the neighborhood of the interface. In particular, one may either introduce very complicated two-phase local correlation functions, which can be related to the familiar bulk correlation functions only by approximations which are difficult to analyze or justify, or one may invoke classical arguments to make plausible assumptions about the nature of local density and pressure in the interfacial region. In this paper, we avoid the local description by calculating corrections to the average stress tensor with hard-wall boundary conditions. These corrections can then be directly related to interfacial surface tension by examining the equilibrium between two phases and the hard wall.

In the introductory remarks below, we first describe briefly some of the earlier work, and describe in more detail the motivation for this paper.

Suppose we have translational invariance in the (x,y) plane, and that the thermodynamic Gibbs dividing surface between two phases occurs at $z=0$. In the early classical work of Kirkwood and Buff,⁵ the interfacial surface tension is then given by

$$\gamma = \int_{-\infty}^{\infty} [P - p'(z)] dz, \quad (1.1)$$

where P is the macroscopic uniform pressure in either phase, and $p'(z)$ is a function which approaches this pressure far in the interior of either phase (large $|z|$), but is in general a function of the *local* particle density and pair correlation function in the interfacial region. The Kirkwood-Buff analysis for $p'(z)$ involves several approximations and classical caveats, but the exact results of Toda can be put in the same form. Toda's formulation⁶ requires a knowledge of the local one- and two-particle distribution functions in the interfacial region, but it is not limited to classical systems. The work of Brout and Nauenberg¹ is similar in spirit, also requires local distribution functions, but defines surface tension in such a way that an exact correspondence with the usual definition is

possible only at zero temperature. For comparison with the results of this paper, and to emphasize the local nature of the required correlation functions in earlier work, we note that Toda's result⁶ for γ can be written:

$$A\gamma = \frac{2 \text{Tr} \left[-\frac{\hbar^2}{2m} \sum_{j=1}^N \left(\frac{\partial^2}{\partial z_j^2} - \frac{\partial^2}{\partial x_j^2} \right) \rho_1(\mathbf{x}, \mathbf{x}') \right]}{\text{Tr}[\rho_1(\mathbf{x}, \mathbf{x}')]}$$

$$+ \int \int \frac{(x_{12}^2 - z_{12}^2)}{2r_{12}} \frac{dV(r_{12})}{dr_{12}} \rho_2(\mathbf{r}_1, \mathbf{r}_2) d^3r_1 d^3r_2,$$

where $\rho_1(\mathbf{x}, \mathbf{x}')$ is a density matrix for states with a definite liquid film of area A perpendicular to the z axis, and ρ_2 is a pair distribution function in the inhomogeneous two-phase system. In this form, the theory is not classical and can be shown to exhibit certain correct limiting behavior. However, because of its complexity, the theory has not been widely applied.

Still another approach, which again requires local properties, is the density functional analysis.⁷ This method begins with the notion of local thermodynamic equilibrium and a local free-energy functional, modeled in terms of a density gradient expansion, usually truncated after a few terms. This approach is particularly useful in the critical region, and has been applied to ⁴He near the λ point.⁸ There are other formulations specially designed for superfluid helium.¹³⁻¹⁵

The classical Kirkwood-Buff analysis⁵ is based on the mechanical definition of surface tension in terms of the stress transmitted across a strip of unit width normal to the Gibbs dividing surface. In many respects, this is similar to the analysis of the pressure itself in terms of normal forces of containing walls in a large volume. That is, if the system Hamiltonian contains a "wall" potential $U_w(\mathbf{r})$, which confines the particles to a fixed volume V , then the pressure is given by

$$P = \frac{1}{3V} \int d^3r \langle \rho(\mathbf{r}) \rangle_w \mathbf{r} \cdot \nabla U_w(\mathbf{r}), \quad (1.2)$$

where $\langle \rho(\mathbf{r}) \rangle_w$ is the *local* density in the confined system. If we make the system translationally invariant in (x,y) , and suppose the confining walls to be at $z = \pm L/2$, then the pressure is

$$P = \frac{1}{L} \int_{-L/2}^{L/2} dz \langle \rho(z) \rangle_w z \frac{dU_w(z)}{dz}, \quad (1.3)$$

where again $\langle \rho(z) \rangle_w$ is the local density, calculated in a finite slab. $U_w(z)$ becomes large and $\langle \rho(z) \rangle_w$ becomes small in the neighborhood of the wall. The integral of this very complicated product indeed gives the pressure. In fact, Eq. (1.3) is exact in the limit of large L . However, (1.2) or (1.3) require a knowledge of local quantities, and we know perfectly well that the pressure in a bulk thermodynamic system can be obtained in a much simpler manner. Equations (1.2) and (1.3) emphasize the equivalence between thermodynamic pressure and force per unit area on the walls, but one does not generally regard these expressions as a useful starting point for the calculation of pressure in a many-body system.

To obtain the familiar alternative to (1.2) or (1.3), consider the thermodynamic potential Ω and the grand partition function Z ,

$$e^{-\beta\Omega} = Z = \text{Tre}^{-\beta\mathcal{H}}, \quad \mathcal{H} = H - \mu N, \quad (1.4)$$

together with the averages of operators with respect to the density matrix $(1/Z)e^{-\beta\mathcal{H}}$,

$$\langle O \rangle_w \equiv \frac{1}{Z} \text{Tre}^{-\beta\mathcal{H}} O, \quad (1.5)$$

where $\langle \rangle_w$ refers to the situation where the Hamiltonian contains an explicit "wall" potential $U_w(\mathbf{r})$. If this potential confines the system to volume $L_x L_y L_z$, then

$$H_w = \int d^3r \rho(r) U_w(xe^{-\epsilon_1}, ye^{-\epsilon_2}, ze^{-\epsilon_3}) \quad (1.6)$$

confines that system to volume $L_x L_y L_z$, with $L_i = L_i^0 e^{\epsilon_i}$. Variation with respect to volume (or to L_x , L_y , and L_z separately) can be accomplished by variation of the ϵ_i parameters, usually setting $\epsilon_i = 0$ at the end of the calculation.¹⁶ Since $\Omega = -(1/\beta)\ln(Z)$, we see that

$$\frac{\partial\Omega}{\partial\epsilon_i} \Big|_{\beta,\mu} = -\frac{1}{\beta} \frac{\partial}{\partial\epsilon_i} \ln(Z) \Big|_{\beta,\mu} = \left\langle \frac{\partial\mathcal{H}}{\partial\epsilon_i} \right\rangle_w, \quad (1.7)$$

but we recognize that any unitary transformation can be applied to the density matrix before taking the trace to obtain $\ln(Z)$. Thus, we have

$$\frac{\partial\Omega}{\partial\epsilon_i} \Big|_{\beta,\mu} = \left\langle G^\dagger \left[\frac{\partial}{\partial\epsilon_i} (G\mathcal{H}G^\dagger) \right] G \right\rangle_w, \quad (1.8)$$

where G is any unitary transformation. If we apply (1.7) directly, noting that ϵ_i appears only in the wall term of the full Hamiltonian, we find

$$\frac{\partial\Omega}{\partial\epsilon_i} \Big|_{\beta,\mu} = - \int d^3r \langle \rho(r) \rangle_w x_i \nabla_i U_w. \quad (1.9)$$

Now, in the large-volume thermodynamic limit, we know that the grand potential Ω is $-PV$. Hence, in that limit $\partial\Omega/\partial\epsilon_i|_{\beta,\mu} = -PV$, and we obtain

$$P = \frac{1}{V} \int d^3r \langle \rho(r) \rangle_w x_i \nabla_i U_w.$$

In this limit, any ϵ_i could have been chosen, and we can

take $\frac{1}{3}$ the sum over i . The result is Eq. (1.2). As observed previously, this expression establishes the familiar force per area and pressure equivalence, but presents an awkward nonlocal form for the calculation of P .

If, however, we employ a simple scale transformation on the fields

$$G\psi(r)G^\dagger = \exp \left[\frac{1}{2} \sum_i \epsilon_i \right] \psi(xe^{-\epsilon_1}, ye^{-\epsilon_2}, ze^{-\epsilon_3}), \quad (1.10)$$

then the wall parameters ϵ_i are shifted from H_w to the internal part of the Hamiltonian, and the application of Eq. (1.8) results in

$$\frac{\partial\Omega}{\partial\epsilon_i} \Big|_{\beta,\mu} = - \langle \bar{T}_{ii} \rangle_w, \quad (1.11)$$

where the \bar{T}_{ii} is the diagonal element of the integrated stress tensor operator.¹⁷ This diagonal element has the form

$$\begin{aligned} \bar{T}_{ii} = & \int d^3r_1 \psi^\dagger(r_1) \left[\frac{-\hbar^2 \nabla_{i1}^2}{2m} \right] \psi(r_1) \\ & - \frac{1}{2} \int \int d^3r_1 d^3r_2 \frac{(r_{12})_i^2}{r_{12}} \frac{dV(r_{12})}{dr_{12}} \\ & \times \psi^\dagger(r_1) \rho(r_2) \psi(r_1), \end{aligned} \quad (1.12)$$

with $\mathbf{r}_{12} \equiv \mathbf{r}_1 - \mathbf{r}_2$.

The simplest application of (1.11) and (1.12) is to the large-volume limit, where $\Omega = -PV$. In this case, we have

$$P = \frac{1}{V} \langle \bar{T}_{ii} \rangle_w = \frac{1}{3V} \sum_i \langle \bar{T}_{ii} \rangle_w \quad \text{as } V \rightarrow \infty, \quad (1.13)$$

and we may, to lowest order in this large-volume limit, now replace the average $\langle \rangle_w$ with the average in the translationally invariant system, where the wall term in H is omitted. This is permissible *only* in the usual thermodynamic limit, in which all but the volume part of system thermodynamic averages is neglected. Much of the analysis in Sec. IV is devoted to a calculation of corrections to this limit.

In this $V \rightarrow \infty$ limit, Eqs. (1.12) and (1.13) yield the familiar Virial theorem

$$P = \frac{2}{3} \frac{\langle E_{\text{kin}} \rangle}{V} - \frac{2\pi}{3} \int_0^\infty dr r^3 V'(r) \rho^2 g(r), \quad (1.14)$$

where $\langle E_{\text{kin}} \rangle/V$ is the average kinetic energy per unit volume

$$\frac{\langle E_{\text{kin}} \rangle}{V} = \int d^3k \frac{1}{(2\pi)^3} \frac{\hbar^2 k^2}{2m} n(k), \quad (1.15)$$

and $g(r)$ is the radial distribution function. In contrast to (1.2), Eq. (1.14) now permits determination of P from only bulk correlation functions [$n(k)$ and $g(r)$]. Of course, in this familiar large-volume limit, other thermodynamic functions can be calculated from the same correlation functions, and P can then be deduced from simple thermodynamic relations. In practice, the virial theorem

can be used as a self-consistency requirement on approximation schemes which produce the equation of state by other methods.

Since Eq. (1.11) is correct even before the large-volume limit is taken, we would like to use it in the case where surface contributions have been included explicitly in the analysis of Ω . In Sec. II, we discuss these surface terms and show how they are related to a single-phase surface tension, for a single phase of arbitrary density in contact with a hard wall. This highly artificial mathematical problem, which is seemingly unrelated to any physical situation, is shown in Sec. III to allow direct calculation of the interfacial surface tension of two phases of the same substance in thermodynamic equilibrium with a hard wall. At the same time, we are able to make a connection between the interface location, the quantum-mechanical depletion of particles at the hard-wall surface, and the interfacial surface tension. We also explore the question of interfacial surface-tension critical behavior. With this information, we return in Sec. IV to explicit calculation of the single-phase surface tension, using the integrated stress tensor operator above. We also obtain then the final form for the interfacial tension. In Sec. V, in order to show more clearly how our theoretical framework can be applied, we explore a simple classical model, using the familiar van der Waals model of the gas-liquid transition for this purpose. Section VI contains concluding remarks.

II. THERMODYNAMICS AND STATISTICAL MECHANICS: SURFACE TERMS

We would like to introduce area terms in the usual thermodynamic analysis, for a one-component single-phase system. The "thermodynamic limit" now assumes that we keep both terms of order volume V and of order area A , but ignore smaller terms. We begin by including the work done by the system on its surroundings in a volume-independent change of area. That is,

$$\delta \mathcal{W} = PdV - \alpha dA. \quad (2.1)$$

The inclusion of this area term then leads, by familiar analysis, to the following thermodynamic equations:

$$\begin{aligned} \mu dN &= dE - TdS + PdV - \alpha dA, \\ \mu N &= E - TS + PV - \alpha A, \end{aligned} \quad (2.2)$$

from which the Gibbs-Duhem relation,

$$Nd\mu = -SdT + VdP - Ad\alpha, \quad (2.3)$$

follows.

These equations show that the appropriate grand potential Ω , which will appear naturally in the statistical mechanics, is

$$\begin{aligned} E - TS - \mu N &= \Omega = -PV + \alpha A, \\ d\Omega &= -SdT - Nd\mu - PdV + \alpha dA. \end{aligned} \quad (2.4)$$

The "nonintensive" variables, those which depend on the size of the system, will contain both volume and area contributions:

$$O = O_V + O_A, \quad O = N, E, S, \dots, \quad (2.5)$$

where O_V is proportional to volume and O_A is proportional to area. We regard this as $\langle O \rangle$, in an explicit expansion for large volume and area. Higher-order terms, for example those proportional to some circumferential length, are to be neglected. Consequently, the volume and area thermodynamics can be uniquely separated (Eqs. 2.2) to yield

$$\mu N_V = E_V - TS_V + PV, \quad \mu N_A = E_A - TS_A - \alpha A, \quad (2.6)$$

$$\mu dN_V = dE_V - TdS_V + PdV, \quad \mu dN_A = dE_A - TdS_A - \alpha dA.$$

Equation (2.1) identifies α as the thermodynamic surface tension, while Eq. (2.4) relates it to the surface contribution in the thermodynamic potential Ω .

The volume thermodynamics is the usual one. From the area contributions, we then have

$$d\alpha = -s_A dT - n_A d\mu, \quad s_A = \frac{S_A}{A}, \quad n_A = \frac{N_A}{A}. \quad (2.7)$$

The intensive variables μ and T link the volume and area terms, since the usual Gibbs-Duhem relation is

$$dP = s_V dT + \rho_V d\mu, \quad s_V = \frac{S_V}{V}, \quad \rho_V = \frac{N_V}{V}. \quad (2.8)$$

From the areal thermodynamics, we find immediately the following relations:

$$\begin{aligned} n_A &= - \left. \frac{\partial \alpha}{\partial \mu} \right|_T, \\ s_A &= - \left. \frac{\partial \alpha}{\partial T} \right|_\mu, \\ \epsilon_A &= \alpha - T \left. \frac{\partial \alpha}{\partial T} \right|_\mu - \mu \left. \frac{\partial \alpha}{\partial \mu} \right|_T, \quad \epsilon_A \equiv \frac{E_A}{A}, \end{aligned} \quad (2.9)$$

so that, in principle, the function $\alpha(T, \mu)$ determines the other areal thermodynamic quantities. In fact, if α is known as a function of T and ρ_V , we see that

$$\begin{aligned} n_A &= \rho_V^2 K_T \left. \frac{\partial \alpha}{\partial \rho_V} \right|_T = -\rho_V \left. \frac{\partial \alpha}{\partial \rho_V} \right|_T / \left. \frac{\partial P}{\partial \rho_V} \right|_T, \\ s_A &= - \left. \frac{\partial \alpha}{\partial T} \right|_{\rho_V} + \frac{n_A}{\rho_V} \left[s_V - \frac{\alpha_P}{K_T} \right], \end{aligned} \quad (2.10)$$

where K_T is the bulk isothermal compressibility and α_P is the bulk thermal-expansion coefficient.

From Eq. (2.4), we have

$$\Omega = -PL_x L_y L_z + 2\alpha(L_x L_y + L_y L_z + L_x L_z) \quad (2.11)$$

for a large box with side lengths L_x, L_y, L_z . If $L_i = L_i^0 e^{\epsilon_i}$, we obtain

$$\left. \frac{\partial \Omega}{\partial \epsilon_i} \right|_{\beta, \mu} = -PL_x L_y L_z + 2\alpha L_i (L_j + L_k) = -\langle \bar{T}_{ii} \rangle_{\text{box}} \quad (2.12)$$

where the indices (i, j, k) are cyclic, and we have used Eq. (1.11) to identify this derivative with the average of \bar{T}_{ii} in

the "wall" or "box" system. The leading term is in accord with the familiar discussion in Sec. I [see Eq. (1.13)]. It is clear that we can extract α from Eq. (2.12) by subtraction of any two distinct $\langle \bar{T}_{ii} \rangle$ components. That is,

$$\alpha = \frac{\langle \bar{T}_{xx} - \bar{T}_{yy} \rangle_{\text{box}}}{2L_z(L_y - L_x)} = \frac{\langle \bar{T}_{xx} - \bar{T}_{zz} \rangle_{\text{box}}}{2L_y(L_z - L_x)} = \frac{\langle \bar{T}_{yy} - \bar{T}_{zz} \rangle_{\text{box}}}{2L_x(L_z - L_y)}, \quad (2.13)$$

where we suppose a large L limit and retain only the lowest-order (in this case area) contribution to the averages on the right-hand side. In this limit, α is the proper (intensive) thermodynamic quantity, and we return to its explicit evaluation in Sec. IV. We also may note here that the full particle number is given by

$$N = N_V + N_A, \quad (2.14)$$

where N_A (proportional to area) will be a negative quantity for hard-wall boundary conditions, representing the fact that the system wave function goes to zero at the walls.

III. EQUILIBRIUM: TWO PHASES AND CONFINING WALLS

We want to relate the surface quantity α , discussed in Sec. II, to the physical quantity γ , the interfacial surface tension of a two-phase, one-component system. For simplicity, imagine a liquid phase and a gas phase. To establish such a relation, we first introduce a solid wall in addition to the two phases. In equilibrium, the contact angle θ is defined as the angle between the surface of the liquid and the plane surface of the solid. It is given by the "contact-angle formula"^{18,19}

$$\cos\theta = \frac{\alpha_{g,w} - \alpha_{l,w}}{\alpha_{g,l}}, \quad (3.1)$$

where $\alpha_{g,w}$, $\alpha_{l,w}$, and $\alpha_{g,l}$ are surface-tension coefficients for the gas-wall, the liquid-wall, and the gas-liquid, respectively. $\alpha_{g,w}$ and $\alpha_{l,w}$ depend on the nature of the wall, whereas $\alpha_{g,l}$ is the interfacial surface tension γ and is independent of the nature of the wall.

For an infinitely hard wall, we want to argue that the contact angle is known, and that therefore $\alpha_{g,l} = \gamma$ can be determined from this known angle together with the hard-wall α 's for the two phases. The argument is as follows.

Consider a liquid and vapor in equilibrium with a wall whose long-range, attractive component is much smaller than the interparticle forces in the liquid and is small compared to the interparticle forces in the vapor. Under these conditions, the vapor will be more strongly attracted to the wall than will the liquid, since the counterbalancing interparticle force is stronger in the liquid than in the vapor. Thus, one would have an obtuse contact angle, as shown in Fig. 1.

If the attractive component of wall potential is increased in strength, it will begin to overcome the interparticle attractions in the liquid. At some point, the effective

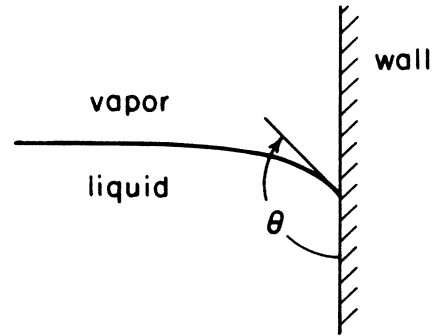


FIG. 1. Contact angle.

wall potential (attractive plus hard core) will be the same for liquid and vapor, so that the contact angle becomes $\pi/2$.

If the attractive wall component is increased still further, the effective wall potential for the vapor becomes repulsive. The hard core dominates; a single particle "overshoots" the equilibrium position of the attractive well and is repulsed by the hard core at the wall. For moderate well strengths, this effect is stronger in the vapor than in the liquid, and the result is an acute contact angle.

The above physical picture illustrates how the contact angle ranges from obtuse, through $\pi/2$ to acute, as the attractive part of the fluid-wall interaction becomes larger. For absolutely zero attractive component (pure hard wall) the most obtuse angle possible will be attained. That is, $\theta = \pi$. Consequently, the appropriate expression for γ is

$$\gamma(T) = \alpha_{l,hw}(\rho_l(T), T) - \alpha_{g,hw}(\rho_g(T), T), \quad (3.2)$$

where $\alpha_{l,hw}$ and $\alpha_{g,hw}$ are the values of the hard-wall surface tensions for the liquid and gas phases, respectively. This means that in $\alpha_{l,hw}$ ($\alpha_{g,hw}$) one sets ρ equal to its liquid (gas) value on the phase coexistence curve. Thus γ is a function of T only.

In addition to the contact-angle formula (3.1), the conditions for equilibrium require a small pressure difference between the two phases, given by the Laplace formula²⁰

$$P[\rho_l(T), T] - P[\rho_g(T), T] = \gamma(T) \left[\frac{1}{R_1} + \frac{1}{R_2} \right], \quad (3.3)$$

where R_1 and R_2 are the principal radii of curvature for the interfacial surface. (The radii are taken as positive when drawn into the more dense medium; the pressure in the liquid is greater than that in the gas when the liquid has a convex surface.)

Now, consider our equilibrium hard-wall situation, where we have observed that the contact angle is π . In this case, the vapor is in contact with the wall everywhere. We can visualize this condition in a large spherical volume. The liquid forms a smaller sphere, radius R_l , in contact with the spherical hard wall (radius R_w) at one point. The contact angle is π , so that Eq. (3.2) holds. Equilibrium then requires

$$P[\rho_l(T), T] - P[\rho_g(T), T] = \frac{2\gamma(T)}{R_l}, \quad (3.4)$$

$$\mu[\rho_l(T), T] - \mu[\rho_g(T), T] = 0,$$

where we have included the additional requirement of equality in the chemical potentials for the two phases. The usual phase boundary in the infinite system, described by the functions $\rho_l^0(T)$ and $\rho_g^0(T)$, are then given by

$$P[\rho_l^0(T), T] - P[\rho_g^0(T), T] = 0, \quad (3.5)$$

$$\mu[\rho_l^0(T), T] - \mu[\rho_g^0(T), T] = 0,$$

and the corrections $\delta\rho_{l,g} = \rho_{l,g}(T) - \rho_{l,g}^0(T)$ are then obtained from (3.4) and (3.5). We find

$$R_l \delta\rho_l = \rho_l^2 K_T \frac{2\gamma(T)}{\rho_l^0(T) - \rho_g^0(T)}, \quad (3.6)$$

$$R_l \delta\rho_g = \rho_g^2 K_T \frac{2\gamma(T)}{\rho_l^0(T) - \rho_g^0(T)},$$

where K_T is the isothermal compressibility.

Thus, the densities of both liquid and gas are increased over the values they would have had in the infinite, translationally invariant, system. R_l is the radius of the liquid "bubble" in contact with the wall. This radius clearly depends on both the total number of particles in the fixed total volume V as well as the temperature. In fact, if we do not concern ourselves with area corrections, we have $N = \rho_l^0 V_l^0 + \rho_g^0 V_g^0$, with $V = V_l^0 + V_g^0$, so that the "lever rule"

$$\frac{V_l^0}{V}(\rho, T) = \frac{\rho - \rho_g^0(T)}{\rho_l^0(T) - \rho_g^0(T)} = \left[\frac{R_l^0}{R_w} \right]^3 \equiv x^3 \quad (3.7)$$

gives the ratio of liquid-occupied volume to total volume, when $\rho_l^0(T) \geq \rho \geq \rho_g^0(T)$. R_w is the (fixed) radius of the containing volume. The radius R_l^0 can be used in (3.6). Note that both R_l^0 and $\delta\rho_{l,g}$ depend on the average density, while their product depends only on the temperature.

To make a simple picture, we can detach the liquid bubble from the wall. That is, having understood that the equilibrium conditions (3.2) and (3.6) are met, the actual location of the liquid sphere is irrelevant. If the liquid sphere and the confining spherical volume are taken to have a common center, then a profile of the local density looks something like Fig. 2.

The dashed vertical line is at R_l , the radius of the liquid sphere. About this radius is an interfacial region. Both the interfacial thickness and R_l location are imprecisely defined at this point. We know that both ρ_l and ρ_g are slightly increased over ρ_l^0 and ρ_g^0 , respectively, and that there is a depletion in the gas phase at the hard wall. We also expect that R_l differs from R_l^0 , the location previously defined by the lever rule. The total number of particles is given by

$$N = \rho_l V_l + \rho_g V_g + (N_l^f - N_l^i) + N_g^w, \quad (3.8)$$

where the interface contributions are given by integrals

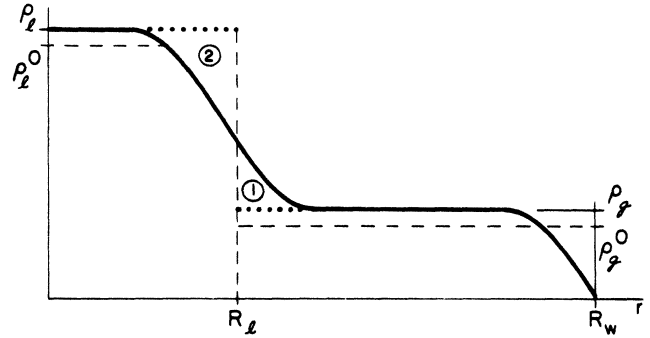


FIG. 2. Local-density profile.

representing the regions 1 and 2 in the diagram. They clearly depend on details of the local density in the interface region. That is,

$$N_l^f \equiv \int_1 [\rho(r) - \rho_g] d^3r, \quad (3.9)$$

$$N_l^i \equiv \int_2 [\rho_l - \rho(r)] d^3r.$$

The sizes of the integration regions are not precisely defined, since we have not specified a "thickness" for the interface. We do require that $N = \rho_l^0 V_l^0 + \rho_g^0 V_g^0$ and that the total volume remains fixed. Therefore, Eq. (3.8) demands

$$0 = \rho_l^0 \delta V_l + \rho_g^0 \delta V_g + \delta\rho_l V_l + \delta\rho_g V_g + (N_l^f - N_l^i) + N_g^w. \quad (3.10)$$

Each of the terms in (3.10) is proportional to area. For example, in the notation of Sec. II, $N_g^w = A_w n^A(\rho_g(T), T)$, where A_w is the hard-wall area. The quantities $\delta V_{l,g}$ result from the difference between R_l and R_l^0 , while the $\delta\rho_{l,g}$ are given by Eq. (3.6). We divide Eq. (3.10) by the total wall area and collect terms to obtain

$$\{[\rho_l^0(T) - \rho_g^0(T)]\Delta R + (n_l^f - n_l^i) + \frac{1}{3}(R_l^0 \delta\rho_l - R_l^0 \delta\rho_g)\}x^2 + \frac{1}{3}R_l^0 \delta\rho_g \frac{1}{x} + n_g = 0. \quad (3.11)$$

Here, $n_l^{f,g} \equiv N_l^{f,g}/A_l$, $\Delta R = R_l - R_l^0$, $R_l^0 \delta\rho_{l,g}$ are given by Eq. (3.6), $n_g = n^A(\rho_g(T), T)$, and the ratio x is defined in the lever-rule expression (3.7).

In order to make use of Eq. (3.11), we note that only the interface location shift (i.e., ΔR) and the ratio x depend on the average density ρ . Other quantities in (3.11) depend on temperature alone. If we differentiate Eq. (3.11) with respect to density and solve the resulting differential equation for ΔR , we can determine the density dependence of ΔR . Such an equation requires one boundary condition in density. Since $\rho_l^0(T) \geq \rho \geq \rho_g^0(T)$, we take the boundary density to be the critical density ρ_c . ρ_c is the one density which always satisfies $\rho_l^0(T) \geq \rho \geq \rho_g^0(T)$ for all $T \leq T_c$. If we define the parameter $x_c = x(\rho_c)$ [see Eq. (3.7)], the solution for $\Delta R(\rho, T)$ can be written as

$$\Delta R(\rho, T) = \left[\frac{x_c}{x} \right]^2 \left\{ \Delta R(\rho_c, T) + \frac{1-x/x_c}{\rho_l^0 - \rho_g^0} \left[\left(1 + \frac{x}{x_c} \right) [(n_f^0 - n_l^0) + \frac{1}{3}(R_l^0 \delta \rho_l - R_l^0 \delta \rho_g)] + \frac{1}{3} \frac{R_l^0 \delta \rho_g}{x_c^3} \left[\frac{x_c}{x} \right] \right] \right\}, \quad (3.12)$$

and the substitution of this expression into Eq. (3.11) then gives

$$\frac{1}{3} R_l^0 \delta \rho_g + (\rho_l^0 - \rho_g^0) \Delta R(\rho_c, T) x_c^3 = -x_c n_g, \quad (3.13)$$

or, from Eq. (3.6) and the definition of x_c , we have

$$\frac{2}{3} \rho_g^2 K_{Tg} \frac{\gamma(T)}{\rho_l(T) - \rho_g(T)} + \Delta R(\rho_c, T) [\rho_c - \rho_g(T)] = -n(\rho_g(T), T) \left[\frac{\rho_c - \rho_g(T)}{\rho_l(T) - \rho_g(T)} \right]^{1/3}, \quad (3.14)$$

where the densities $\rho_{l,g}$ refer now to the usual bulk values $\rho_{l,g}^0$.

The presence of the hard wall has produced two effects. First, the density in each phase has increased, and there is a compensating wall depletion $n(\rho_g(T), T)$ in the gas phase. Second, there is a shift $\Delta R = R_l - R_l^0$ from the lever-rule position of the liquid-gas interface, which depends explicitly on the average density $\rho = N/V$. The density dependence of ΔR is determined by the requirement that the interfacial densities n_f^0 and n_l^0 are independent of ΔR ; that is, independent of the average density.

There is a conventional approach to the treatment of $n_f^0 - n_l^0$. In this approach, no mention is made of the hard wall or its depletion effect, and $n_f^0 - n_l^0$ is taken to be zero. The argument is made that the division into gas and liquid parts (location of R_l) is not unique, and that the number of particles in each phase is uncertain, the indeterminacy being of the same order of magnitude as the surface effects under consideration.¹⁸ The location of a Gibbs dividing surface such that the surface excess density $n_f^0 - n_l^0$ is zero then simplifies the thermodynamics when no wall terms are considered; for example, the entropy associated with the interface is just $-A^I [d\gamma(T)/dT]$. We do not mean to imply that this is incorrect; $\gamma(T)$ still determines all the thermodynamic interfacial properties of interest, when the wall terms have been properly subtracted. Although it would seem that our specific location of R_l precludes an assignment of zero to the "surface excess" density $n_f^0 - n_l^0$, this appears to have no effect on the familiar thermodynamics. Thus, the interfacial expressions

$$\begin{aligned} S^I &= -A^I \frac{d\gamma(T)}{dT}, \\ F^I &= A^I \gamma(T) \quad (\text{Helmholtz free energy}), \\ E^I &= F^I + TS^I = A^I \left[\gamma(T) - T \frac{d\gamma(T)}{dT} \right], \end{aligned} \quad (3.15)$$

still apply. The interface excess density $n_f^0 - n_l^0$ appears explicitly only in the density dependence of ΔR exhibited by Eq. (3.12). We argue that Eq. (3.12) is perhaps an interesting curiosity, but is not very useful in view of the

fact that a detailed theory of the local-density profile is needed to calculate $n_f^0 - n_l^0$. Furthermore, the manner in which the interface location shifts with changes in average density is not of great significance or interest. It is, instead, Eq. (3.14) which is most interesting.

Recall that n and γ are both determined by α . The microscopic calculation in Sec. IV will give α . Consequently, Eq. (3.14) determines $\Delta R(\rho_c, T)$ when α is known. $\Delta R(\rho_c, T)$ is the shift in interface position (at critical density) from the lever-rule position (at critical density), and is known fully if α is known. Conversely, we can connect the behavior of $\Delta R(\rho_c, T)$ as $T \rightarrow T_c$ from below with the corresponding critical behavior of γ . Therefore, we consider Eq. (3.14) when T is close to T_c .

First, it is difficult to imagine that $n(\rho_g, T)$ goes to either zero or infinity as $T \rightarrow T_c^-$. The wall depletion is caused by the fact that the wave function goes to zero at the hard wall, and this effect should be independent of the nature of the transition in the medium. Since $\Delta R(\rho_c, T)$ and $n(\rho_g(T), T)$ are not familiar objects, we may suppose the following notation for their critical behavior as $\delta = 1 - T/T_c \rightarrow 0^+$. Here

$$\begin{aligned} n_g &\sim \delta^\zeta, \\ \Delta R &\sim \delta^{-\bar{\nu}}, \end{aligned} \quad (3.16)$$

where we expect $\zeta = 0$ in general, and we will show that this is definitely true in mean-field theory. The other quantities in Eq. (3.14) all have traditional critical-index notations:²¹

$$\begin{aligned} (\rho^2 K_T)_{l,g} &\sim \delta^{-\gamma}, \\ \rho_l - \rho_g &\sim \rho_c - \rho_g \sim \delta^\beta, \\ \gamma &\sim \delta^\mu, \end{aligned} \quad (3.17)$$

(the indices γ , β , and μ should not be confused with the surface tension, the inverse temperature, and chemical potential). These critical-index assignments, together with Eq. (3.14), then imply

$$c_1 \delta^{\mu - \beta - \gamma} + c_2 \delta^{\beta - \bar{\nu}} = \delta^\zeta. \quad (3.18)$$

Now, if $\beta - \bar{\nu} \geq \zeta$, then $\mu = \beta + \gamma + \zeta$. If $\beta - \bar{\nu} \leq \zeta$, then $\mu = 2\beta + \gamma - \bar{\nu}$. We expect $\zeta = 0$. In that case, the first supposition gives the mean-field expression $\mu = \beta + \gamma$, and the second supposition gives $\mu = 2\beta + \gamma - \bar{\nu}$ when $\beta < \bar{\nu}$. This latter expression would also apply if our argument that $\zeta = 0$ is incorrect and instead $\zeta \geq \beta - \bar{\nu}$. But what is $\bar{\nu}$? We recall that Widom's expression⁷ for the critical index μ is

$$\mu = 2\beta + \gamma - \nu, \quad (3.19)$$

where ν is the index associated with the correlation length. The argument leading to (3.19) is usually formulated in terms of the thickness associated with the interfa-

cial region;⁷ i.e., $t_s \sim \delta^{-\nu}$. Indeed, the argument that the correlation length is the only relevant length associated with interfacial thickness can be applied with equal validity (or perhaps we should say with equal uncertainty) to the surface location shift $\Delta R(\rho_c, T)$. Conceptually, of course, the surface thickness and the shift in surface location from the lever-rule position are different quantities, and the statement

$$\mu = 2\beta + \gamma - \bar{\nu}, \quad \beta < \bar{\nu} + \zeta \quad (3.20)$$

may be different from the Widom result in (3.19). In any case, we can say that the conjecture that $|\Delta R|$ and t_s have equivalent critical behavior leads to Widom's result, but that $\bar{\nu} < \nu$ if $|\Delta R|$ is less divergent than t_s , while $\bar{\nu} > \nu$ applies if $|\Delta R|$ is more divergent. There is some

$$\begin{aligned} -T^2 \frac{d}{dT} \frac{\gamma(T)}{T} = & -T^2 \left[\frac{\partial}{\partial T} \frac{\alpha(\rho, T)}{T} \Big|_{\rho=\rho_l(T)} - \frac{\partial}{\partial T} \frac{\alpha(\rho, T)}{T} \Big|_{\rho=\rho_g(T)} \right] \\ & - \frac{1}{2}(n_l + n_g)(G_l - G_g) + (n_l - n_g) \left\{ \frac{1}{2}(G_l + G_g) - \frac{\epsilon_l^v - \epsilon_g^v}{\rho_l - \rho_g} \right\}, \end{aligned} \quad (3.22)$$

where

$$G \equiv \frac{\epsilon^v + P}{\rho} - T \frac{\alpha_p^v}{\rho K_T} \quad (3.23)$$

is given in terms of the volume parameters (α_p^v is the bulk thermal expansion coefficient and K_T the isothermal compressibility). The subscripts l and g in (3.22) mean that one sets $\rho = \rho_{l,g}$ in the corresponding volume thermodynamic expression. ϵ^v is the bulk energy per unit volume.

This thermodynamic expression is simplest to apply in the case of the van der Waals bulk model, and we will make such an analysis after investigation of the general microscopic form for α . In the van der Waals case, the $\{ \}$ term in Eq. (3.22) is zero since

$$G^{\text{vdW}} = \frac{3}{2} k_B T - 2a\rho, \quad (3.24)$$

where a is the van der Waals a parameter. If we suppose that $\alpha(\rho, T)$ can be Taylor expanded in $\rho - \rho_c$ and $T - T_c$, and that

$$\lim_{T \rightarrow T_c^-} n(\rho_l(T), T) = \lim_{T \rightarrow T_c^-} n(\rho_g(T), T) = n_c,$$

we have (mean field only)

$$\begin{aligned} \frac{d}{dT} \left[\frac{\gamma(T)}{T} \right]_{T \rightarrow T_c} \Rightarrow & \left\{ \left[\frac{\partial}{\partial \rho} \frac{\partial}{\partial T} \left[\frac{\alpha(\rho, T)}{T} \right] \right]_{\rho=\rho_c} \right\}_{T=T_c} \\ & + \frac{2an_c}{T_c^2} [\rho_l(T) - \rho_g(T)]. \end{aligned} \quad (3.25)$$

This form is not restricted to van der Waals theory. It requires

indication that $\bar{\nu}$ should be slightly larger²² than ν for ^3He and ^4He [i.e., that the μ given by Eq. (3.19) is slightly too large].

We can establish another connection between γ and n , by purely thermodynamic analysis. Beginning with the areal Gibbs-Duhem relation [see Eqs. (2.7) and (2.9)], we find

$$-T^2 \frac{d}{dT} \frac{\gamma(T)}{T} = (\epsilon_l^A - \epsilon_g^A) - (n_l^A - n_g^A) \frac{\epsilon_l^v - \epsilon_g^v}{\rho_l - \rho_g}, \quad (3.21)$$

where we have used the Clausius-Clapeyron relation for the temperature derivative of the chemical potential in two-phase equilibrium. A bit of rearrangement, together with the help of the areal thermodynamics in Sec. II, gives

$$G_l - G_g \sim -2a(\rho_l - \rho_g),$$

where a is some constant, and since $\{ \}$ in Eq. (3.22) will not be identically zero except in the van der Waals (vdW) case, we suppose that n_l and $n_g \sim n_c + O(<(\rho_l - \rho_g))$. The assumption of a Taylor expansion for α is, of course, a mean-field assumption.

The function $\alpha(\rho, T)$ is analogous to the pressure P , in that its first and second density derivatives are zero at the critical point:

$$\frac{\partial \alpha(\rho, T)}{\partial \rho} \Big|_{\rho_c, T_c} = 0, \quad (3.26)$$

$$\frac{\partial^2 \alpha(\rho, T)}{\partial \rho^2} \Big|_{\rho_c, T_c} = 0. \quad (3.27)$$

However, unlike the pressure, $\alpha(\rho_l(T), T)$ and $\alpha(\rho_g(T), T)$ are *not* equal; their difference gives the surface tension γ . Since the first derivative of α with respect to ρ is zero at ρ_c, T_c , Eq. (3.25) becomes

$$\frac{d}{dT} \frac{\gamma(T)}{T} \approx \left[\frac{1}{T_c} \frac{\partial^2 \alpha(\rho, T)}{\partial \rho \partial T} \Big|_{\rho_c, T_c} + \frac{2an_c}{T_c^2} \right] (\rho_l - \rho_g),$$

and since $\rho_l - \rho_g \approx 4\rho_c \delta^{1/2}$ in vdW theory, we have, with $T = T_c(1 - \delta)$,

$$-\frac{1}{T_c^2} \frac{d\gamma^{\text{vdW}}(\delta)}{d\delta} \approx 4\rho_c \left[\frac{1}{T_c} \frac{\partial^2 \alpha}{\partial \rho \partial T} \Big|_{\rho_c, T_c} + \frac{2an_c^{\text{vdW}}}{T_c^2} \right] \delta^{1/2},$$

or, using $a = \frac{9}{8} [(k_B T_c)/\rho_c]$ from vdW theory, we have, solving this equation for γ ,

$$\gamma^{\text{vdW}}(\delta) \Big|_{\delta \rightarrow 0} \approx \left[-\frac{8}{3} \rho_c T_c \frac{\partial^2 \alpha^{\text{vdW}}}{\partial \rho \partial T} \Big|_{\rho_c, T_c} - 6n_c^{\text{vdW}} k_B T_c \right] \delta^{3/2}. \quad (3.28)$$

The $\delta^{3/2}$ behavior for van der Waals theory is expected. The three equations (3.26)–(3.28) allow a phenomenological construction of a van der Waals model for $\alpha(\rho, T)$ from the microscopic low-density classical expansion, in much the same way that the vdW a and b parameters can be constructed from the low-density classical virial expansion. We will return to this construction of a “van der Waals α ” in Sec. V.

First, however, we must show that the general hard wall α can be related exactly to the bulk pair correlation function and the single-particle momentum distribution. We therefore proceed to the microscopic calculation of the hard wall α via an examination of the integrated stress tensor average for hard-wall boundary conditions.

IV. SURFACE CONTRIBUTIONS AND THE INTEGRATED STRESS TENSOR AVERAGE

The important stress tensor operator difference is

$$\begin{aligned} (\bar{T}_{ii} - \bar{T}_{jj}) &= \int d^3 r_1 \psi^\dagger(r_1) \left[\frac{-\hbar^2 \nabla_{i1}^2}{2m} + \frac{\hbar^2 \nabla_{j1}^2}{2m} \right] \psi(r_1) \\ &\quad - \frac{1}{2} \int \int d^3 r_1 d^3 r_2 \frac{(r_{12})_i^2 - (r_{12})_j^2}{r_{12}} \\ &\quad \times \frac{dV(r_{12})}{dr_{12}} \psi^\dagger(r_1) \rho(r_2) \psi(r_1), \end{aligned} \quad (4.1)$$

where the region of integration, when the fields are confined to a finite box, is given by

$$\begin{aligned} -\frac{L_x}{2} &\leq x_1, \quad x_2 \leq \frac{L_x}{2}, \\ -\frac{L_y}{2} &\leq y_1, \quad y_2 \leq \frac{L_y}{2}, \quad \mathbf{r}_{12} = (\mathbf{r}_1 - \mathbf{r}_2), \\ -\frac{L_z}{2} &\leq z_1, \quad z_2 \leq \frac{L_z}{2}. \end{aligned} \quad (4.2)$$

The fields can be expanded in “box” eigenstates, in each coordinate variable, which vanish on the surface. That is,

$$\begin{aligned} u_{q_x}(x) &\equiv \left[\frac{2}{L_x} \right]^{1/2} \sin q_x \left[x + \frac{L_x}{2} \right], \\ q_x &= \frac{n_x \pi}{L_x}, \quad n_x = 1, 2, 3, \dots, \end{aligned} \quad (4.3)$$

$$u_{\mathbf{q}}(\mathbf{r}) \equiv u_{q_x}(x) u_{q_y}(y) u_{q_z}(z),$$

$$\begin{aligned} \psi(\mathbf{r}) &= \sum_{\mathbf{q}} u_{\mathbf{q}}(\mathbf{r}) a_{\mathbf{q}}, \\ a_{\mathbf{q}} &= \int d^3 r u_{\mathbf{q}}^*(\mathbf{r}) \psi(\mathbf{r}). \end{aligned} \quad (4.4)$$

It is convenient to use Eq. (4.4) to define $a_{\mathbf{q}}$ for negative $q_x, q_y,$ and q_z , so that $a_{\mathbf{q}}$ is odd in each q_i . Averages using this quantization scheme are box averages, and the corresponding Hamiltonian in the density matrix contains the wall potential explicitly.

In the true infinite-volume limit, many times it is convenient to suppose a translationally invariant Hamiltonian (without the wall), and to quantize in the familiar periodic states

$$\begin{aligned} \phi_{k_x}(x) &\equiv \frac{1}{(L_x)^{1/2}} e^{ik_x x}, \quad k_x = \frac{2\pi}{L_x} n_x, \quad n_x = 0, \pm 1, \pm 2, \dots, \\ \phi_{\mathbf{k}}(\mathbf{r}) &= \phi_{k_x}(x) \phi_{k_y}(y) \phi_{k_z}(z), \\ \psi(\mathbf{r}) &= \sum_{\mathbf{k}} \phi_{\mathbf{k}}(\mathbf{r}) c_{\mathbf{k}}, \\ c_{\mathbf{k}} &= \int d^3 r \phi_{\mathbf{k}}^*(\mathbf{r}) \psi(\mathbf{r}). \end{aligned} \quad (4.5)$$

Averages taken with respect to the translationally invariant density matrix, using this quantization scheme, involve no physical surface and no wall potential. They may be called “plane-wave” averages. For macroscopic system quantities, like total energy, particle number, and integrated stress tensor, the box and plane-wave averages must be the same, in the large-volume limit, both being proportional to the volume of the system. That is,

$$\langle A \rangle_{\text{box}} = \langle A \rangle_{\text{PW}} \quad \text{as } V \rightarrow \infty, \quad \text{each proportional to } V. \quad (4.6)$$

To calculate the macroscopic quantities of interest, one must investigate the averages $\langle a_{\mathbf{q}}^\dagger a_{\mathbf{q}} \rangle$ and $\langle a_{q_1}^\dagger a_{q_2}^\dagger a_{q_3} a_{q_4} \rangle$. That is, we need both one-particle and pair correlation functions. In carrying out the sums over the \mathbf{q} eigenstates needed for the large-volume limit and its leading correction, there will be a sum-to-integral conversion correction which depends explicitly on the density of states in \mathbf{q} space. This process is not difficult, but there are other possible corrections which can be eliminated *only* for certain operator averages. One of these, fortunately, is the stress tensor difference in Eq. (4.1).

Consider $\langle a_{\mathbf{q}}^\dagger a_{\mathbf{q}} \rangle_{\text{box}}$. This is some function of \mathbf{q} and of L_x, L_y, L_z also. The plane-wave average $\langle c_{\mathbf{k}}^\dagger c_{\mathbf{k}} \rangle_{\text{PW}}$ is some other function of \mathbf{k} . Call that function $n(k)$. It does not depend on the L 's explicitly, only the k 's. Now, in the limit of large L 's, the function $\langle a_{\mathbf{q}}^\dagger a_{\mathbf{q}} \rangle$ must equal $n(q)$. [For free particles in a box, the exact $\langle a_{\mathbf{q}}^\dagger a_{\mathbf{q}} \rangle$ equals $n(q)$, and is a Fermi or Bose function—but we cannot make this statement in general.] One can show, from (4.6) and comparison for the box-defined and plane-wave-defined single-particle thermal Green's function, that

$$\langle a_{\mathbf{q}}^\dagger a_{\mathbf{q}} \rangle_{\text{box}} = n(q) + \frac{1}{L_x} f_x(q) + \frac{1}{L_y} f_y(q) + \frac{1}{L_z} f_z(q) \quad (4.7)$$

as $L_x, L_y,$ and $L_z \rightarrow \infty$. The functions $f_i(q)$ are unknown, but are seen to be even in $q_x, q_y,$ and q_z . The function $n(q)$ is also unknown, of course, but is presumably to be determined by the usual plane-wave analysis. For an arbitrary thermodynamic average of the form $\sum_{\mathbf{q}} G(q) \langle a_{\mathbf{q}}^\dagger a_{\mathbf{q}} \rangle$, there are two kinds of corrections to the large-volume limit

$$V \int \frac{d^3q}{(2\pi)^3} G(q)n(q).$$

One such correction arises from the sum-to-integral conversion (density of states) and the other from the additional term in Eq. (4.7). If $G(q)$ is odd under interchange of two q components q_i and q_j , then the second correction is zero. In this circumstance, *all* the leading corrections come from the sum-to-integral conversion.

For purposes of this conversion, we need the following Euler-Maclaurin summation formula:

$$\begin{aligned} \sum_{q \neq 0} F(q) &= L_x L_y L_z \int \frac{d^3q}{(2\pi)^3} F(q) \\ &\quad - \pi \int \frac{d^3q}{(2\pi)^3} [L_x L_y \delta(q_z) + L_x L_z \delta(q_y) \\ &\quad + L_y L_z \delta(q_x)] F(q). \end{aligned} \quad (4.8)$$

Consider then the first term in the average of the integrat-

$$\langle N \rangle = L_x L_y L_z \int \frac{d^3q}{(2\pi)^3} n(q) + [2(L_x L_y + L_y L_z + L_x L_z)] \frac{1}{2} \int \frac{d^3q}{(2\pi)^3} [f_i(q) - \pi \delta(q_z) n(q)]. \quad (4.10)$$

The surface contribution $N_A/A = n_A$ is explicitly

$$-\frac{\pi}{2} \int \frac{d^3q}{(2\pi)^3} \delta(q_z) n(q)$$

for free particles, where $n(q)$ is in this case a Bose or Fermi function. That is, for free particles, $f_i(q) = 0$. However, we have no proof that $f_i(q)$ is generally zero, and so the form of n_A cannot be determined in general from the bulk single-particle momentum distribution. On the other hand, the integrated stress tensor difference in (4.9), or at least its kinetic part, is completely determined by the bulk $n(q)$.

The potential contribution to the average of Eq. (4.1) (the second term) is more difficult. The potential piece of the operator in Eq. (4.1) can be written as

$$\begin{aligned} (\bar{T}_{ii} - \bar{T}_{jj})_{PE} &= -\frac{1}{2} \int \int_{\Omega} d^3R d^3r \frac{r_i^2 - r_j^2}{r} V'(r) \\ &\quad \times \psi^\dagger \left[R + \frac{r}{2} \right] \rho \left[R - \frac{r}{2} \right] \\ &\quad \times \psi \left[R + \frac{r}{2} \right], \end{aligned} \quad (4.11)$$

with the restricted region of integration Ω for these relative and center-of-mass pair coordinates given by

$$\langle \bar{T}_{xx} - \bar{T}_{yy} \rangle_{PE} = -4 \int_0^{L_x} dx \int_0^{L_y} dy \int_0^{L_z} dz (L_x - x)(L_y - y)(L_z - z) \frac{x^2 - y^2}{r} V'(r) \rho^2 g(r), \quad (4.15)$$

where we use the xx and yy components for clarity. We must investigate terms proportional to products of three L 's and two L 's (i.e., volume and area terms) in the large L_k limit. Retaining only such terms in the integrand, we have

ed stress-tensor-operator difference of Eq. (4.1). Call this term $\langle \bar{T}_{ii} - \bar{T}_{jj} \rangle_{KE}$. This kinetic-energy piece is clearly odd under $i \leftrightarrow j$ interchange, and we find

$$\langle \bar{T}_{ii} - \bar{T}_{jj} \rangle_{KE} = L_k (L_j - L_i) \pi \int \frac{d^3q}{(2\pi)^3} \frac{\hbar^2 q^2}{2m} \delta(q_z) n(q), \quad (4.9)$$

where explicit use has been made of the even property of $f_i(q)$ in Eq. (4.7). The indices (i, j, k) are cyclic, and $\delta(q_z)$ is the one-dimensional Dirac δ function. It should be noted that the leading term in the average $\langle \bar{T}_{ii} \rangle_{KE}$ is

$$L_x L_y L_z \frac{2}{3} \int \frac{d^3q}{(2\pi)^3} \frac{\hbar^2 q^2}{2m} n(q),$$

or $\frac{2}{3}$ of the kinetic energy in the large-volume limit.

Note that the surface contribution to $\langle N \rangle$ can be extracted from $\sum_{q \neq 0} \langle a_q^\dagger a_q \rangle$, making use of Eqs. (4.7) and (4.8), and the assumption that the functions $f_i(q)$ have the same integral over all q . The result, including both volume and area terms, is

$$L_k \geq r_k \geq -L_k$$

and

$$\frac{1}{2}(L_k - |r_k|) \geq R_k \geq -\frac{1}{2}(L_k - |r_k|). \quad (4.12)$$

The integral on each component of these center-of-mass and relative variables therefore has the form

$$\begin{aligned} \int_{-L_k/2}^{L_k/2} dr_{1k} \int_{-L_k/2}^{L_k/2} dr_{2k} \\ = \int_{-L_k}^{L_k} dr_k \int_{-(1/2)(L_k - |r_k|)}^{(1/2)(L_k - |r_k|)} dR_k. \end{aligned} \quad (4.13)$$

In order to simplify the calculation, we add and subtract the translationally invariant limit. That is,

$$\langle \psi^\dagger \rho \psi \rangle_{\text{box}} = \rho^2 g(r) + [\langle \psi^\dagger \rho \psi \rangle_{\text{box}} - \rho^2 g(r)], \quad (4.14)$$

where $\rho^2 g(r)$ is the value of $\langle \psi^\dagger \rho \psi \rangle$ in the infinite, translationally invariant system. $g(r)$ is thus the bulk radial distribution function. The remainder is a correction, to be investigated later. The purpose of this separation is to obtain the important contributions to the average of (4.11) without involving explicitly the complications of the "box" quantization in Eq. (4.3)–(4.4).

Since $\rho^2 g(r)$ is independent of R , we may perform the R_k integration indicated in Eq. (4.13). The right-hand side of (4.3) then becomes $\int_{-L_k}^{L_k} dr_k (L_k - |r_k|)$. Recognizing that the integrand is an even function of each relative coordinate r_k separately, we have

$$\begin{aligned} \langle \bar{T}_{xx} - \bar{T}_{yy} \rangle_{PE} = & -4L_x L_y L_z \int_0^{L_x} dx \int_0^{L_y} dy \int_0^{L_z} dz \frac{x^2 - y^2}{r} V'(r) \rho^2 g(r) \\ & + 4 \int_0^{L_x} dx \int_0^{L_y} dy \int_0^{L_z} dz \{xL_y L_z + yL_x L_z + zL_y L_x\} \frac{x^2 - y^2}{r} V'(r) \rho^2 g(r). \end{aligned} \quad (4.16)$$

Consider now the second term in (4.16). Because the integrand is already of order $L_i L_j$, we can extend the limits of integration to infinity. Then, for the $zL_x L_y$ term in $\{ \}$, the entire integrand is odd under interchange of x and y , and this term is thus zero. For the term $yL_x L_z$ in $\{ \}$, now interchange x and y . The entire second term in (4.16) then becomes

$$L_z(L_y - L_x) 4 \int_0^\infty \int_0^\infty \int_0^\infty dx dy dz \frac{x(x^2 - y^2)}{r} V'(r) \rho^2 g(r),$$

so that, returning to spherical coordinates and integrating only over the appropriate region $\pi/2 \geq \theta, \phi \geq 0$, the result is

$$[\text{Second term in (4.16)}] = L_z(L_y - L_x) \frac{\pi}{4} \int_0^\infty dr r^4 V'(r) \rho^2 g(r). \quad (4.17)$$

The first term in (4.16) can be written (using the odd property of the integrand under $x \leftrightarrow y$ interchange)

$$[\text{First term in (4.16)}] = -4L_x L_y L_z \int_{L_x}^{L_y} dy \left[\int_0^{L_x} dx \int_0^{L_z} dz \frac{x^2 - y^2}{r} V'(r) \rho^2 g(r) \right]. \quad (4.18)$$

The function $[(x^2 - y^2)/r]V'(r)\rho^2 g(r)$ is even in x, y , and z . If we extend the x integral to ∞ , and calculate the leading term in (4.18) for all L 's large, and if that leading term has the correct proportionality to $L_z(L_y - L_x)$, then further contributions ignored by the extension of the x integral can be dropped. Define the function

$$G(y) = \int_0^{L_z} dz \int_0^\infty dx \frac{x^2 - y^2}{r} V'(r) \rho^2 g(r).$$

This function has a well-defined Fourier transform, and since it is even in y ,

$$G(y) = \int_{-\infty}^\infty \frac{dq}{2\pi} \cos(qy) \tilde{G}(q)$$

while \tilde{G} is even in q . Equation (4.18) can then be written as

$$\begin{aligned} [\text{First term in (4.16)}] & = -8L_x L_y L_z \int_0^\infty \frac{dq}{2\pi} [\sin(qL_y) - \sin(qL_x)] \frac{\tilde{G}(q)}{q}. \end{aligned} \quad (4.19)$$

Finally, we make use of the asymptotic expansion²³ for large L :

$$\begin{aligned} \int_0^\infty dq \sin(qL) F(q) & = \frac{F(0)}{L} - \frac{F''(0)}{L^3} + \dots, \\ \int_0^\infty dq \cos(qL) F(q) & = -\frac{F'(0)}{L^2} + \frac{F'''(0)}{L^4} - \dots, \end{aligned} \quad (4.20)$$

to obtain

$$[\text{First term in (4.16)}] = \frac{4}{\pi} L_z(L_y - L_x) \lim_{q \rightarrow 0} \left[\frac{\tilde{G}(q)}{q} \right]. \quad (4.21)$$

This expression is precisely the areal form expected for the integrated stress-tensor-difference average, and if the above limit is nonzero, this term will contribute. However, consider the function

$$\begin{aligned} \tilde{G}(q) & = \int_0^{L_z} dz \int_0^\infty dx \int_{-\infty}^\infty dy \cos(qy) \frac{x^2 - y^2}{r} \\ & \quad \times V'(r) \rho^2 g(r). \end{aligned}$$

The integral on x can be extended to $-\infty$, whereupon the entire integral is clearly zero at $q=0$. Therefore, $\tilde{G}(q) \sim q^2$ as $q \rightarrow 0$, and does not contribute anything to the limit in (4.21). Hence, the first term in (4.16) is zero, up to and including all area corrections, and we have therefore concluded, using Eq. (4.17), that

$$\begin{aligned} \langle (\bar{T}_{xx} - \bar{T}_{yy})_{PE} \rangle_{\text{box}} & = L_z(L_y - L_x) \frac{\pi}{4} \\ & \quad \times \int_0^\infty dr r^4 V'(r) \rho^2 g(r). \end{aligned} \quad (4.22)$$

This result shows that the simplest potential piece of the integrated stress tensor difference comes from the bulk part of the correlation function in the integrand. Only the nature of the integration region restrictions in the large box play a role in this term. There now remains the question of possible corrections from the second term in Eq. (4.14).

Since we have seen how the integration region restrictions affect the calculation, and have obtained a final expression (4.22) for the first term in (4.14), it is now simpler to return to the general form. We will then use the previous discussion to guide the necessary grouping of terms in a full box calculation. In general, the potential piece of the integrated stress tensor average is

$$\langle (\bar{T}_{ii} - \bar{T}_{jj})_{PE} \rangle_{\text{box}} = -\frac{1}{2} \int \int_v d^3 r_1 d^3 r_2 \frac{(r_{12})_i^2 - (r_{12})_j^2}{r_{12}} V'(r_{12}) F(\mathbf{r}_1, \mathbf{r}_2), \quad (4.23)$$

where $F(\mathbf{r}_1, \mathbf{r}_2)$ is $\langle \psi^\dagger(r_1) \rho(r_2) \psi(r_1) \rangle$, and the integrals \int_v are confined to the region $-L_i/2 \leq x_{i1}, x_{i2} \leq L_i/2$. We first expand F in the box eigenstates

$$F(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\substack{\mathbf{q}_1, \mathbf{q}_2 \\ q_{1i}, q_{2i} > 0}} u_{\mathbf{q}_1}(\mathbf{r}_1) u_{\mathbf{q}_2}(\mathbf{r}_2) \tilde{F}_{\text{box}}(\mathbf{q}_1, \mathbf{q}_2), \quad (4.24)$$

and therefore have

$$\tilde{F}_{\text{box}}(\mathbf{q}_1, \mathbf{q}_2) = \int_v d^3 r_1 \int_v d^3 r_2 u_{\mathbf{q}_1}^*(r_1) u_{\mathbf{q}_2}^*(r_2) F(\mathbf{r}_1, \mathbf{r}_2). \quad (4.25)$$

It is convenient to extend the definition of \tilde{F} to negative values for each q_i . From the form (4.3) for u , we see that $\tilde{F}_{\text{box}}(\mathbf{q}_1, \mathbf{q}_2)$ is odd in each component of \mathbf{q}_1 and \mathbf{q}_2

separately. Equation (4.24) can then be rewritten in the form

$$F(\mathbf{r}_1, \mathbf{r}_2) = \sum'_{\mathbf{q}_1, \mathbf{q}_2} \phi_{\mathbf{q}_1} \left[\mathbf{r}_1 + \frac{\mathbf{L}}{2} \right] \phi_{\mathbf{q}_2} \left[\mathbf{r}_2 + \frac{\mathbf{L}}{2} \right] \hat{F}(\mathbf{q}_1, \mathbf{q}_2), \quad (4.26)$$

where $\hat{F}(\mathbf{q}_1, \mathbf{q}_2) = -\frac{1}{8} \tilde{F}_{\text{box}}(\mathbf{q}_1, \mathbf{q}_2)$ and the \sum' means that no component of \mathbf{q}_1 or \mathbf{q}_2 is zero. ϕ is the product function defined in Eq. (4.5), and \mathbf{L} is the vector whose components are L_x, L_y , and L_z .

We now substitute Eq. (4.26) into Eq. (4.23) and convert the sums on \mathbf{q}_1 and \mathbf{q}_2 to integrals, making use of Eq. (4.8). The result is

$$\begin{aligned} \langle (\bar{T}_{ii} - \bar{T}_{jj})_{PE} \rangle_{\text{box}} = & -\frac{1}{2} \int \frac{d^3 q_1}{(2\pi)^3} \frac{d^3 q_2}{(2\pi)^3} \int_v d^3 r_1 \int_v d^3 r_2 \frac{(r_{12})_i^2 - (r_{12})_j^2}{r_{12}} V'(r_{12}) \exp i \left[\mathbf{q}_1 \cdot \left[\mathbf{r}_1 + \frac{\mathbf{L}}{2} \right] + \mathbf{q}_2 \cdot \left[\mathbf{r}_2 + \frac{\mathbf{L}}{2} \right] \right] \\ & \times L_x L_y L_z \hat{F}(\mathbf{q}_1, \mathbf{q}_2) \left\{ 1 - \pi \sum_{k=1}^3 \frac{1}{L_k} [\delta(q_{1k}) + \delta(q_{2k})] + \dots \right\}. \end{aligned} \quad (4.27)$$

This expression then includes all area corrections. If we take

$$\begin{aligned} \hat{F}(\mathbf{q}_1, \mathbf{q}_2) \Rightarrow \hat{F}_\infty(\mathbf{q}_1, \mathbf{q}_2) & \equiv \int \int d^3 r_1 d^3 r_2 \phi_{\mathbf{q}_1}^\dagger(r_1) \phi_{\mathbf{q}_2}^*(r_2) \rho^2 g(\mathbf{r}_1 - \mathbf{r}_2) \\ & = \frac{1}{L_x L_y L_z} \int d^3 r \exp \left[\frac{i(\mathbf{q}_1 - \mathbf{q}_2) \cdot \mathbf{r}}{2} \right] \rho^2 g(r) (2\pi)^3 \delta(\mathbf{q}_1 + \mathbf{q}_2), \end{aligned} \quad (4.28)$$

then the correct leading term (proportional to volume) is obtained in the equivalent of (4.27) for any component $\langle (T_{ii})_{PE} \rangle$ (or, for any function of r_{12} in the integrand). To include area corrections to this term, we have

$$\begin{aligned} L_x L_y L_z \hat{F}(\mathbf{q}_1, \mathbf{q}_2) & = L_x L_y L_z \hat{F}_\infty(\mathbf{q}_1, \mathbf{q}_2) \\ & + \sum_{k=1}^3 \frac{1}{L_k} \tilde{H}_k(\mathbf{q}_1, \mathbf{q}_2), \end{aligned} \quad (4.29)$$

where \tilde{H}_k is independent of the L 's.

Now, the $\hat{F}_\infty(\mathbf{q}_1, \mathbf{q}_2)$ piece, together with the first term

in the $\{ \}$ appearing in Eq. (4.27), gives the full result (4.22) of the previous analysis. As we have seen, the volume restrictions on the r_1 and r_2 integrals must be retained to obtain these areal terms. Further possible corrections, coming from the second term in (4.29) and the second term in the $\{ \}$ of Eq. (4.27) represent those terms arising from the correction expressed in Eq. (4.14). We may write the result in the form

$$\langle (\bar{T}_{xx} - \bar{T}_{yy})_{PE} \rangle_{\text{box}} = (\text{I}) + (\text{II}) + (\text{III}), \quad (4.30)$$

where (I) is given in Eq. (4.22). (II) is given by

$$(\text{II}) = \frac{\pi}{2} \sum_{i=1}^3 \frac{1}{L_i} \int \int \frac{d^3 q_1}{(2\pi)^3} \frac{d^3 q_2}{(2\pi)^3} [\delta(q_{1i}) + \delta(q_{2i})] \left\{ \int \int_v d^3 r_1 d^3 r_2 \left[\frac{x_{12}^2 - y_{12}^2}{r_{12}} \right] V'(r_{12}) e^{i\mathbf{q}_1 \cdot \mathbf{r}_{12}} \right\} L_x L_y L_z \hat{F}_\infty(\mathbf{q}_1, \mathbf{q}_2), \quad (4.31)$$

where the delta function $\delta(\mathbf{q}_1 + \mathbf{q}_2)$ appearing in (4.28) has been used to simplify the expression. The quantity (III) is given by

$$(\text{III}) = -\frac{1}{2} \sum_{i=1}^3 \frac{1}{L_i} \int \int_v d^3 r_1 d^3 r_2 \left[\frac{x_{12}^2 - y_{12}^2}{r_{12}} \right] V'(r_{12}) \int \frac{d^3 q_1}{(2\pi)^3} \frac{d^3 q_2}{(2\pi)^3} \exp \{ i [\mathbf{q}_1 \cdot (\mathbf{r}_1 + \mathbf{L}/2) + \mathbf{q}_2 \cdot (\mathbf{r}_2 + \mathbf{L}/2)] \} \tilde{H}_i(\mathbf{q}_1, \mathbf{q}_2). \quad (4.32)$$

We now wish to show that both (II) and (III) are smaller than order "area," and that hence (I) gives the full result for the average integrated stress tensor difference.

Consider the integrals appearing in the $\{ \}$ term of Eq. (4.31), denoted as \mathcal{S} . The center of mass integration can be performed immediately to obtain

$$\mathcal{S} = \prod_{i=1}^3 \int_{-L_i}^{L_i} dx_i (L_i - x_i) \frac{x^2 - y^2}{r} V'(r) e^{i\mathbf{q}_1 \cdot \mathbf{r}} \quad (4.33)$$

and we need only the volume contribution here, because of the $1/L_i$ coefficient appearing in Eq. (4.31). This contribution is

$$\mathcal{S}(\text{leading term}) = L_x L_y L_z \int d^3 r \frac{x^2 - y^2}{r} V'(r) e^{i\mathbf{q}_1 \cdot \mathbf{r}}. \quad (4.34)$$

If we take \mathbf{q}_1 along the z axis, we see that the full integral is zero for all \mathbf{q}_1 . Thus, II produces at most a length, not an area, correction.

We may write Eq. (4.32) in the form

$$\langle (\bar{T}_{xx} - \bar{T}_{yy}) \rangle_{\text{box}} = L_z (L_y - L_x) \left[\pi \int \frac{d^3 q}{(2\pi)^3} \frac{\hbar^2 q^2}{2m} \delta(q_z) n(q) + \frac{\pi}{4} \int_0^\infty dr r^4 V'(r) \rho^2 g(r) \right]. \quad (4.37)$$

Therefore, Eqs. (4.37) and (2.13) together imply

$$\alpha = \frac{\pi}{2} \int \frac{d^3 q}{(2\pi)^3} \frac{\hbar^2 q^2}{2m} \delta(q_z) n(q) + \frac{\pi}{8} \int_0^\infty dr r^4 V'(r) \rho^2 g(r). \quad (4.38)$$

Finally, making use of Eq. (3.2), we find the interfacial surface tension

$$\gamma = \frac{\pi}{2} \int \frac{d^3 q}{(2\pi)^3} \frac{\hbar^2 q^2}{2m} \delta(q_z) [n_l(q) - n_g(q)] + \frac{\pi}{8} \int_0^\infty dr r^4 V'(r) [\rho_l^2 g_l(r) - \rho_g^2 g_g(r)]. \quad (4.39)$$

Equation (4.38) is an exact expression for the single phase α , quite analogous to the virial theorem for the pressure. Equation (4.39) is likewise exact, and involves only bulk correlation functions, explicitly for each phase. Note that γ is a function of T only, since the density ρ is explicitly set equal to the liquid or vapor coexistence densities $\rho_l(T)$ and $\rho_g(T)$ in the two parts shown in (4.39).

We were able to obtain α by a subtraction of stress-tensor-operator averages, where symmetry properties conspired to eliminate several unknown quantities. It should be noted again that a similar attempt to calculate, for example, $\langle N \rangle$ will not yield a simple expression for the area correction. In fact, α appears to be the *only* surface quantity which can be isolated in this manner, and the other surface variables can be then obtained only by using the thermodynamic relations (2.6) through (2.10). It is not difficult to show that for free particles, the surface depletion n_A is given by

$$\text{(III)} = -\frac{1}{2} \sum_{i=1}^3 \frac{1}{L_i} \int \int \frac{d^3 q_1}{(2\pi)^3} \frac{d^3 q_2}{(2\pi)^3} B(\mathbf{q}_1, \mathbf{q}_2) \tilde{H}_i(\mathbf{q}_1, \mathbf{q}_2) \times \exp[i(\mathbf{q}_1 + \mathbf{q}_2) \cdot \mathbf{L} / 2], \quad (4.35)$$

where

$$B(\mathbf{q}_1, \mathbf{q}_2) = \int \int_v d^3 r_1 d^3 r_2 \left[\frac{x_{12}^2 - y_{12}^2}{r_{12}} \right] V'(r_{12}) \times \exp[i(\mathbf{q}_1 \cdot \mathbf{r}_1 + \mathbf{q}_2 \cdot \mathbf{r}_2)]. \quad (4.36)$$

The leading term of III for large L , independent of the nature of $B(\mathbf{q}_1, \mathbf{q}_2)$, requires $\mathbf{q}_1 = -\mathbf{q}_2$. [See the asymptotic expansion in Eq. (4.20).] Consequently, the leading contribution from B in Eq. (4.36) involves the expression displayed on the right-hand side of Eq. (4.34). Thus, the leading term in III, as in II, is of order length, not area.

Consequently, we have demonstrated that Eq. (4.22) is the full "potential" contribution to the integrated stress tensor difference. Combination with the "kinetic" part in Eq. (4.9) then gives the full result:

$$n_A = -\frac{\pi}{2} \int \frac{d^3 q}{(2\pi)^3} \delta(q_z) n(q), \quad (4.40)$$

where in this case $n(q)$ is explicitly a Bose or Fermi function. However, we were unable to prove that (4.40) is in any way a general result for the interacting case. Along the same line, it is tempting to suppose that the surface energy per unit area is given by

$$\epsilon_A = -\frac{\pi}{2} \int \frac{d^3 q}{(2\pi)^3} \delta(q_z) \frac{\hbar^2 q^2}{2m} n(q) - \frac{\pi}{2} \int_0^\infty dr r^3 V(r) \rho^2 g(r), \quad (4.41)$$

a result suggested by several approximation schemes.⁵ However, we should emphasize that we do not believe (4.41) to be generally true.

Our general result for α in Eq. (4.38) is quite analogous to the virial theorem expression for the pressure. We can complete the angular integral in the kinetic part, and display the familiar virial theorem result for comparison. The result is

$$\alpha = \frac{1}{8\pi} \int_0^\infty k \epsilon(k) n(k) dk + \frac{\pi}{8} \int_0^\infty r^4 V'(r) \rho^2 g(r) dr, \quad (4.42)$$

$$P = \frac{1}{3\pi^2} \int_0^\infty k^2 \epsilon(k) n(k) dk - \frac{2\pi}{3} \int_0^\infty r^3 V'(r) \rho^2 g(r) dr, \quad (4.43)$$

with $\epsilon(k) = \hbar^2 k^2 / 2m$. The first term in (4.43) is just two-thirds of the kinetic-energy density, but the first term of

(4.42) has no such simple physical interpretation. Both expressions are simplified in the classical limit, where $n(k)$ is replaced by the Boltzmann distribution. The first term in (4.42) becomes $\frac{1}{4}\lambda(T)\rho k_B T$, with $\lambda(T)$ the thermal de Broglie wavelength, while the first term in (4.43) becomes $\rho k_B T$. The two equations together allow us to simplify the classical result further. If we divide the interparticle potential $V(r)$ into hard-core and long-range parts,

$$V(r) = \begin{cases} \infty, & r \leq r_c \\ V_{\text{LR}}(r), & r > r_c \end{cases} \quad (4.44)$$

and eliminate the short-range part of the integral in (4.42) by making use of (4.43), we can put the classical result in the form

$$\alpha^{\text{cl}}(\rho, T) = \frac{1}{4}\lambda(T)\rho k_B T + \frac{3}{16}r_c[\rho k_B T - P(\rho, T)] + a_s(\rho, T)\rho^2, \quad (4.45)$$

with

$$a_s(\rho, T) = \frac{\pi}{8} \int_{r_c}^{\infty} dr r^3 (r - r_c) V'_{\text{LR}}(r) g(r). \quad (4.46)$$

Therefore, classical models for α can be based on approximations for the function $a_s(\rho, T)$. In the extreme low-density limit, for example, we can replace $g(r)$ by its classical zero-density value $e^{-\beta V_{\text{LR}}(r)}$, and if the temperature is such that $|\beta V_{\text{LR}}(r)| \ll 1$, then the microscopic parameter

$$a_0 \equiv \frac{\pi}{8} \int_{r_c}^{\infty} dr r^3 (r - r_c) V'_{\text{LR}}(r) \quad (4.47)$$

should play a role similar to the van der Waals “ a ” parameter of the corresponding pressure analysis.

V. A SIMPLE CLASSICAL MODEL

In order to use the classical form for α in Eqs. (4.45) and (4.46), so that $\gamma(T)$ can be calculated from Eq. (3.2), we must first consider the bulk properties; in particular, we need both an equation of state and the liquid-gas densities in equilibrium. For this purpose, we may use the van der Waals model (vdW) equation of state. Although the inadequacies of this model are well known, its simplicity and familiarity are quite helpful in exploring the surface-tension analysis. We should again emphasize the close connection between pressure and surface tension exhibited in the general expressions (4.42) and (4.43).

The vdW model pressure

$$P = \rho k_B T / (1 - \rho b) - \rho^2 a$$

can be derived from the low-density expansion

$$P \sim \rho k_B T + \rho^2 (b k_B T - a) + \dots,$$

using the classical form of (4.43), a hard-core part to the potential as in (4.44), the low-density classical form $g(r) \sim e^{-\beta V_{\text{LR}}(r)}$ for $r > r_c$, and the further assumption that $|\beta V_{\text{LR}}(r)| \ll 1$ for $r > r_c$ [the true $g(r)$ must also vanish sufficiently rapidly inside the core]. Thus, one identifies the vdW parameters

$$b = (2\pi/3)r_c^3$$

and

$$a = -2\pi \int_{r_c}^{\infty} r^2 V_{\text{LR}}(r) dr.$$

Analysis of the equation of state then gives the familiar relations for critical parameters

$$\rho_c = 1/3b, \quad k_B T_c = \frac{8}{27} \frac{a}{b}, \quad \text{and } P_c^{\text{vdW}} = \frac{3}{8} \rho_c k_B T_c,$$

with the reduced equation of state

$$\tilde{P} = \frac{8\tilde{\rho}s^2}{3-\tilde{\rho}} - 3\tilde{\rho}^2, \quad \tilde{P} \equiv \frac{P}{P_c^{\text{vdW}}}, \quad \tilde{\rho} \equiv \frac{\rho}{\rho_c}, \quad s^2 \equiv \frac{T}{T_c}. \quad (5.1)$$

Near T_c , in two phase equilibrium, the vdW model has a quite simple (mean-field) behavior. This behavior, summarized below, is needed for a subsequent analysis of the surface tension. [That is, we need to know such information about the bulk properties in order to construct a corresponding phenomenological model for $\gamma(T)$.] The familiar results are

$$\begin{aligned} \tilde{\rho}_{l,g}(T) &= 1 \pm 2\delta^{1/2} + \frac{2}{5}\delta \mp \frac{13}{25}\delta^{3/2} + \frac{128}{875}\delta^2 \\ &\quad \mp \frac{1359}{17500}\delta^{5/2} + \frac{136}{3125}\delta^3 + \dots, \\ \mu/k_B T &= -(c + \frac{3}{4}) + c\delta - \frac{6}{5}\delta^2 - \frac{446}{875}\delta^3 + \dots, \\ \tilde{P}(T) &= 1 - 4\delta + \frac{24}{5}\delta^2 - \frac{816}{875}\delta^3 + \dots, \\ (\rho^2 K_T)_{l,g} &= \frac{2}{9}\delta^{-1} \pm \frac{4}{45}\delta^{-1/2} - \frac{76}{225} \\ &\quad \mp \frac{2}{2625}\delta^{1/2} + \frac{2008}{39395}\delta + \dots, \end{aligned} \quad (5.2)$$

with $\delta = (1 - T/T_c)$ and $c = 1 - \ln[\frac{3}{2}\rho_c \lambda^3(T_c)]$. In this case, the equilibrium densities and corresponding isothermal compressibility K_T contain half-integral powers of δ , while the chemical potential and pressure contain only integral powers.

Now, consider our classical expression for α in Eqs. (4.45) and (4.46). We first define reduced variables $\tilde{\alpha}$ and \tilde{n} according to

$$\begin{aligned} \alpha &\equiv \frac{1}{(2\pi)^{1/3}} \rho_c^{2/3} k_B T_c \tilde{\alpha} \quad (\text{same for } \gamma, \tilde{\gamma}), \\ n^A &\equiv -\frac{1}{(2\pi)^{1/3}} \rho_c^{2/3} \tilde{n} \quad [\text{see Eq. (2.10)}], \end{aligned} \quad (5.3)$$

so that

$$\tilde{n} = \frac{8}{3} \tilde{\rho} \left. \frac{\partial \tilde{\alpha}}{\partial \tilde{\rho}} \right|_T \bigg/ \left. \frac{\partial \tilde{P}}{\partial \tilde{\rho}} \right|_T, \quad (5.4)$$

and Eq. (4.45) becomes

$$\tilde{\alpha} = g_0 \tilde{\rho} s + \frac{3}{16} g_1 (\tilde{\rho} s^2 - \frac{3}{8} \tilde{P}) + \tilde{a}_s(\tilde{\rho}, s) \tilde{\rho}^2, \quad (5.5)$$

with

$$\begin{aligned} g_0 &\equiv \frac{1}{4} [2\pi \rho_c \lambda^3(T_c)]^{1/3}, \\ g_1 &\equiv (2\pi \rho_c)^{1/3} r_c, \\ \tilde{a}_s &\equiv (2\pi)^{1/3} \frac{\rho_c^{4/3}}{k_B T_c} a_s. \end{aligned} \quad (5.6)$$

The limit of a_s , as $\rho \rightarrow 0$, is given by Eq. (4.47), so that the dimensionless quantity \tilde{a}_s in this limit can be obtained directly from the potential.

In the vdW model, \tilde{P} is the reduced pressure and $g_1 = 1$. If we take, for concrete example, the traditional Lennard-Jones 6-12 potential (plus hard core below r_c), the three parameters ϵ_0 (strength of 6-12), r_c (core radius), and σ (range or zero position of 6-12) then fix both the vdW a and b (or ρ_c and T_c), and the limit

$$a_0 = \lim_{\tilde{\rho} \rightarrow 0} \tilde{a}_s(\tilde{\rho}, s) = \frac{27}{128} \left[\frac{1 - \frac{1}{6}(\sigma/r_c)^6}{1 - \frac{1}{3}(\sigma/r_c)^6} \right]. \quad (5.7)$$

Thus, the low-density limit of Eq. (5.5) for the classical α is completely determined from the potential, in the same way that the vdW a and b parameters are fixed. [In the above example, the core radius is frequently taken to equal σ , but this is not necessary. r_c should be slightly smaller than or equal to σ , and $|\beta V_{LR}(r_c)|$ should still be small to allow the traditional expansion described above.]

Now, we must construct a phenomenological form for \tilde{a}_s in Eq. (5.5), consistent with both the limit observed in Eq. (5.7) and the general thermodynamic analysis at the end of Sec. III. Consider first the lowest order (in density) term $\frac{1}{4}\lambda(T)\rho k_B T$ in α [or the $g_0\tilde{\rho}s$ term in Eq. (5.5)]. This term, and any terms containing g_0 which appear in \tilde{a}_s , are "nonuniversal"; that is, they depend on the specific ρ_c and T_c [see Eq. (5.6)]. g_0 is, however, a small parameter for classical systems (the formal $\hbar \rightarrow 0$ limit would give $g_0 = 0$). For Ne, Ar, Kr, and Xe, for example, g_0 is 0.08, 0.03, 0.01, and 0.009, respectively. To the extent that the "reduced equation of state for α " (i.e., 5.5) is a simple function of the reduced density and temperature for different substances, the g_0 terms must be negligible. However, the $\frac{1}{4}\lambda(T)\rho k_B T$ term is the full classical result for free particles, and we cannot retain it while deleting all g_0 terms in a_s , because then the thermodynamic conditions (3.26) and (3.27) cannot be satisfied. There must be g_0 terms in \tilde{a}_s to provide thermodynamic consistency. On the other hand, whatever phenomenology we adopt for such terms cannot have much effect on the behavior of the classical surface tension (other than the achievement of thermodynamic consistency for the model, which is of course necessary for expansions close to T_c). We already know that the surface tensions for Ne, Ar, Kr, and Xe, for example, are experimentally close to being functions of reduced temperature only, when divided⁵ by the factor $\rho_c^{2/3}k_B T_c$.

In order to construct a thermodynamically consistent phenomenology, we adopt the simplest treatment of the g_0 terms. Note first that, for free particles, $\frac{1}{4}\lambda\rho k_B T$ and $\frac{1}{4}\lambda P$ are indistinguishable. Thus, one might imagine higher-order terms $\sim \lambda(T)(P - \rho kT)$, or of the form $\lambda(T)[c_1 k_B T / (1 - \rho b) + c_2] \rho^2$. However, such low-order density corrections cannot be present in the classical theory, because all the ρ^2 terms at low density are "potential-like"—they come from replacing a_s by its zero density limit in Eq. (4.45). Any correction terms with this suggested temperature dependence must be at least third

order in density. Hence, such terms will be of order ρ in \tilde{a}_s . We take the simplest choice;

$$\tilde{a}_s \rightarrow a_0 + g_0 \tilde{\rho} \left[\frac{c_1 s}{1 - \frac{1}{3}\tilde{\rho}} + \frac{c_2}{s} \right],$$

where the $g_0 s$ term corresponds to $\lambda(T)k_B T [g_0/s$ to $\lambda(T)]$ temperature dependence. Since all the g_0 terms, including the first term in Eq. (5.5), must satisfy (3.26) and (3.27), we see that c_1 and c_2 are fixed. Thus,

$$\tilde{a}_s \rightarrow a_0 + \frac{g_0 \tilde{\rho}}{15} \left[\frac{8s}{1 - \frac{1}{3}\tilde{\rho}} - \frac{19}{s} \right]$$

represents a thermodynamically consistent phenomenological correction to a_0 for the construction of \tilde{a}_s .

Now, there must be other density corrections to \tilde{a}_s with no g_0 dependence. These must vanish as $\tilde{\rho} \rightarrow 0$, and must be such that (3.26) and (3.27) are satisfied. The simplest two-parameter choice (phenomenologically guided by the vdW loop form for the pressure) is $a_1 \tilde{\rho} / (1 - a_2 \tilde{\rho})$. Thus, a simple phenomenological form for the full \tilde{a}_s , generated from the microscopic theory, the van der Waals structure of the equation of state, and the thermodynamic consistency requirements is

$$\tilde{a}_s = a_0 + \frac{a_1 \tilde{\rho}}{1 - a_2 \tilde{\rho}} + \frac{g_0 \tilde{\rho}}{15} \left[\frac{8s}{1 - \frac{1}{3}\tilde{\rho}} - \frac{19}{s} \right], \quad (5.8)$$

where the constants a_1 and a_2 are determined by the conditions (3.26) and (3.27). These requirements yield immediately a value first for

$$a_1 = \frac{3(1 - a_2)^2(3 - 5a_2 + 2a_2^2)}{16(3 - 2a_2)(3 - a_2)}$$

and an expression for \tilde{a}_s in the form

$$\tilde{a}_s = \frac{3}{16} \left[a_2 + \frac{3 - \tilde{\rho}}{a_2 - 3} \right] \frac{1}{(1 - a_2 \tilde{\rho})} + \frac{g_0 \tilde{\rho}}{15} \left[\frac{8s}{1 - \frac{1}{3}\tilde{\rho}} - \frac{19}{s} \right] \quad (5.9)$$

with

$$a_2 = \frac{3}{2} + \frac{8}{3} \left\{ a_0 - \left[a_0^2 - \frac{9}{8} \left(a_0 + \frac{3}{32} \right) \right]^{1/2} \right\}.$$

Only a_0 remains as the "adjustable" microscopic parameter [see Eq. (5.7)]. Note that the simplest fully classical result would merely drop the g_0 terms in both (5.5) and (5.9), and the resulting form for \tilde{a} can then be thought of as a true van der Waals model, with the single parameter a_0 . a_0 is related to potential parameters, [Eq. (5.7)], in a manner similar to the connection between potential and the original vdW parameters a and b . The g_0 terms are an added complication, brought about by the demands of the free particle limit and thermodynamic consistency, but g_0 is small for classical systems.

The calculated surface tension, using (5.9), (5.5), (3.2), and the vdW phase boundary properties (5.2) becomes

$$\gamma(\delta) = f_1 \delta^{3/2} + f_2 \delta^{5/2} + \dots \quad (5.10)$$

with

$$f_1 = \frac{116}{15} g_0 - \frac{3}{4} + \frac{3}{x(x-2)},$$

$$f_2 = \frac{5656}{375} g_0 + \frac{39}{200} + \frac{3}{50x^2} \left[87 + \frac{2}{x} \left[247 + \frac{594}{x-2} \right] \right],$$

and

$$x \equiv (a_2 - 1) = \frac{1}{2} + \frac{8}{3} \left\{ a_0 - \left[a_0^2 - \frac{9}{8} \left(a_0 + \frac{3}{32} \right) \right]^{1/2} \right\}. \quad (5.11)$$

The leading $\delta^{3/2}$ behavior is expected, of course, and from Eq. (3.28) we see that the coefficient f_1 should equal

$$-\frac{4}{3} \frac{\partial^2 \bar{\alpha}}{\partial \bar{\rho} \partial s} \Big|_{\bar{\rho}=s=1} + 6\bar{n}_c,$$

where

$$\bar{n}_c = \lim_{\bar{\rho}=s=1} \bar{n}(\rho_{l,g}(T), T)$$

[see Eq. (5.4)]. The fact that this relation is correctly satisfied is merely a further verification of thermodynamic consistency. The calculated value of \bar{n}_c becomes

$$\bar{n}_c = \frac{134}{45} g_0 - \frac{11}{48} + \frac{1}{2x(x-2)}. \quad (5.12)$$

The shift in interface location $\Delta R(\rho_c, T)$ can be obtained directly from the expansion of Eq. (3.14) about T_c . We find

$$(2\pi\rho_c)^{1/3} \Delta R(\rho_c, T) = \left[2^{-4/3} \bar{n}_c - \frac{f_1}{54} \right] \delta^{-1/2} + \dots \quad (5.13)$$

The critical index $\bar{\nu}$ discussed in Sec. III is therefore $\frac{1}{2}$ for the vdW model, as expected. The sign of the coefficient in Eq. (5.13) can, in principle, be either positive or negative. That is, a large particle depletion at the wall (large \bar{n}_c) forces the interface to shift to larger R_l , giving a positive $\Delta R(\rho_c, T)$. A large coefficient in the surface tension (large f_1) has the opposite effect. It is physically reasonable that a large gas depletion at the hard wall forces more particles into the liquid phase when the total number of particles is fixed. The numerical values below, appropriate for this vdW approximation, suggest that $\Delta R(\rho_c, T)$ is positive.

We know that the $\mu = \frac{3}{2}$ behavior predicted by this vdW model for α is incorrect. The early data⁵ shows that $\mu \approx 1.28$ for simple classical fluids. More recent experiments give the same result.²⁴ A numerical two-parameter rms numerical fit for argon, giving the form $\gamma = 8.42\delta^{1.28}$ produces only a 0.25% average relative error over a fairly wide range of temperature. The corresponding one-parameter fit to the $\mu = \frac{3}{2}$ version given by vdW theory, $6.16\delta^{3/2}$, produces a much less accurate fit to the same data (20% average relative error over the same temperature range, with even higher error very close to T_c). The value of σ/r_c required by this latter fit [from Eq. (5.7)] is quite reasonable ($\sigma/r_c = 1.19$), but the major error lies in the direct use of the vdW equation of state, with the subsequent mean-field value for μ .

Our construction of α , starting with Eq. (5.5), used both the vdW form for P and a phenomenological structure of $\bar{\alpha}_s$ based on that form. The method was conceptually

straightforward, except for the severe phenomenology of the g_0 terms, which resulted in very small corrections since g_0 is itself small. Before attempting to make a major improvement with a more realistic equation of state, our analysis then suggests that the form

$$\bar{\gamma} \sim (A + Bg_0)\delta^\mu \quad (5.14)$$

should be investigated in detail for simple fluids to see if the small g_0 component can be extracted from experimental data. That is, we know how the incorrect μ arises from the vdW equation of state, but we do not know if a g_0 dependence in the coefficient is required by experimental evidence. (As noted above, the phenomenology of the g_0 term is not unique—we *could* have required all g_0 parts to vanish in the leading γ terms by introducing additional constraints in the construction of $\bar{\alpha}_s$. This would have required more parameters, and there is no compelling reason for such complication unless experiment demands a particular g_0 dependence.) The g_0 term in Eq. (5.14) is interesting, because its presence implies that the coefficient of the critical-region temperature dependence is nonuniversal. A preliminary examination of argon and xenon data^{5,24} together, which includes surface tension close to T_c in both cases, suggests values $A = 8.50$ and $B = -3.05$, using $\mu = 1.28$. For this choice, the average relative error, over all data points, is less than 0.4%. The value of B appears to be negative, but it should be noted that there is a large uncertainty in its determination.

VI. CONCLUSION

We have approached the calculation of interfacial surface tension by a "global thermodynamic" rather than a local formulation. Thus, we are able to define a single-phase surface tension $\alpha(\rho, T)$ in terms of the bulk correlation functions $n(k)$ and $g(r)$, by an examination of integrated stress tensor averages in a large box. The general result [Eq. (4.38)] is quite analogous to the virial theorem for the pressure. Physically, this represents a surface tension associated with the introduction of a hard wall into a uniform, single-phase system. Nevertheless, by an examination of the equilibrium between the hard wall and two phases of the same substance, we are able to show (Sec. III) that the interfacial surface tension for the two phases can be calculated from α , given the bulk phase correlation functions [Eq. (4.39)]. In the single phase, there is an area correction to the overall particle number, brought about by the hard-wall boundary conditions, which force the system wave function to zero at the walls. This single-phase depletion n_A is related thermodynamically to α .

On the local level, we are able to avoid details of the interfacial density profile, and to connect the wall depletion and interfacial tension with the shift in interface position (caused by surface corrections) from the bulk "lever rule" location. This shift is a function of both average density and temperature [see Eq. (3.12)]. At critical density, there is a relation between interfacial tension, interfacial shift, and wall number depletion in the gas phase [Eq. (3.14)]. The latter relation is used to explore some critical index properties [Eq. (3.20)], in which the conceptual distinction between surface thickness and interfacial shift plays a role.

Finally, we have simplified the treatment for classical systems [Eqs. (4.45) and (4.46)] and have applied the surface-tension formulation to a simple classical model, using a van der Waals form for bulk properties, primarily to explore the close connection between the bulk equation of state and the surface tension, even though the vdW

form has well-known deficiencies. This analysis leads to the speculation that, in the critical region, the reduced surface tension for classical systems depends in a simple manner on the small parameter $g_0 = \frac{1}{4}[2\pi\rho_c\lambda^3(T_c^*)]^{1/3}$, and is not of universal form.

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- ¹R. Brout and M. Nauenberg, *Phys. Rev.* **112**, 1451 (1958).
²R. H. Fowler, *Proc. R. Soc. London, Ser. A* **159**, 229 (1937).
³A. Harasima and Y. Shimura, *J. Phys. Soc. Jpn.* **11**, 14 (1956).
⁴J. Hirschfelder, C. Curtiss, and R. Bird, *The Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), pp. 336–356.
⁵J. Kirkwood and F. P. Buff, *The Theory of Liquids, Collected Works of J. G. Kirkwood* (Gordon and Breach, New York, 1968), p. 127. See, also, F. P. Buff and R. A. Lovett, in *Simple Dense Fluids*, edited by H. L. Frisch and Z. W. Salsbury (Academic, New York, 1968).
⁶M. Toda, *J. Phys. Soc. Jpn.* **10**, 512 (1955).
⁷B. Widom, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1972), Vol. 2.
⁸P. Tavan and B. Widom, *Phys. Rev. B* **27**, 180 (1983).
⁹R. Bragado and G. Navascués, *Phys. Rev. A* **29**, 2134 (1984).
¹⁰M. Saarela, P. Pietiläinen, and A. Kallio, *Phys. Rev. B* **27**, 231 (1983).
¹¹G. Navascués, *Rep. Prog. Phys.* **42**, 1131 (1979).
¹²R. Evans, *Adv. Phys.* **28**, 143 (1979).
¹³D. O. Edwards, J. R. Eckardt, and F. M. Gasparini, *Phys. Rev. A* **9**, 2070 (1974).
¹⁴P. M. Lam, *Z. Phys. B* **53**, 245 (1983).
¹⁵L. J. Campbell, *Phys. Rev. B* **27**, 1913 (1983).
¹⁶R. D. Puff and N. S. Gillis, *Ann. Phys.* **46**, 363 (1968).
¹⁷The more general local stress tensor operator $T_{ij}(r)$, and the discussion of the scale transformation G can be found in Ref. 16. Here, we will need only the integrated diagonal element of $T_{ij}(r)$.
¹⁸L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1982), Part I.
¹⁹R. Defay and I. Prigogine, *Surface Tension and Adsorption* (Longmans, Green, New York, 1966).
²⁰L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, New York, 1959).
²¹M. E. Fisher, *J. Math. Phys.* **5**, 944 (1964).
²²D. O. Edwards and W. F. Saam, in *Progress in Low Temperature Physics*, edited by D. F. Brewer (North Holland, Amsterdam, 1978), Vol. VIIA, p. 284.
²³M. J. Lighthill, *Fourier Analysis and Generalized Functions* (Cambridge University Press, Cambridge, New York, 1960).
²⁴H. L. Gielen, O. B. Verbeke, and J. Thoen, *J. Chem. Phys.* **81**, 6154 (1984).