$$R—C \overset{O}{\underset{O\cdot}{\diagdown}} \rightarrow R\cdot + CO_2. \qquad (12)$$

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Free Energy in the Presence of Constraint Surfaces

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We have examined the influence of rigid boundaries on the free energy and distribution functions for classical single-component molecular assemblies. By means of boundary position variation, new formulas are derived for the flat boundary tension in both two and three dimensions. In the case of circular or spherical internal boundaries that are relevant to "scaled particle" theory, we prove that the associated cavity work is free of contributions varying logarithmically with the radius, in the large size limit. A similar result has been obtained for a "droplet" constrained to circular or spherical shape by an impenetrable boundary. The scaling theory of critical correlations has been used to analyze the behavior of the boundary tension in the critical region.

I. INTRODUCTION

For the most part, equilibrium statistical mechanics has been directed to the study of homogeneous matter in bulk. The perturbing influence of container walls has thus been relegated to a minor role, with associated effects that have normally been neglected. Similarly, interfaces between coexisting phases have usually been disregarded in study of the bulk statistical thermodynamics of phase change.

There are notable exceptions to this convention, though. The theories of interface structure[1-3] and of capillarity[4] have produced important insights into the phenomena of surface chemistry and physics. In addition, there has been substantial recent emphasis on the inhomogeneous distribution of matter among "clusters" or "droplets" in fluids to aid in understanding nucleation[5-7] and critical phenomena.[8-10]

The present paper also provides an exception. It is directed exclusively to the effects of "hard" walls (i.e., those for which the potential is either zero or infinite) upon matter distribution and free energy, within the domain of classical statistical mechanics. For reasons that will be stressed at the appropriate points below, we believe our results to be relevant both to nucleation theory and to the analysis of critical phenomena.

The most direct application of the present work, however, lies in the so-called "scaled particle theory,"[11,12] which since its original development for rigid spheres and disks has been applied to a wide variety of isotropic liquids,[13] and to nematic liquid crystals.[14] A central quantity in the scaled-particle theory is the work $W(\lambda)$ required reversibly and isothermally to create an empty cavity in the system with linear dimension proportional to λ. Since the formation of such a cavity is equivalent to interposition of a suitable constraint surface in the system, our results can be utilized directly in scaled-particle theory. In particular, it follows that an asymptotic development of $W(\lambda)$ in
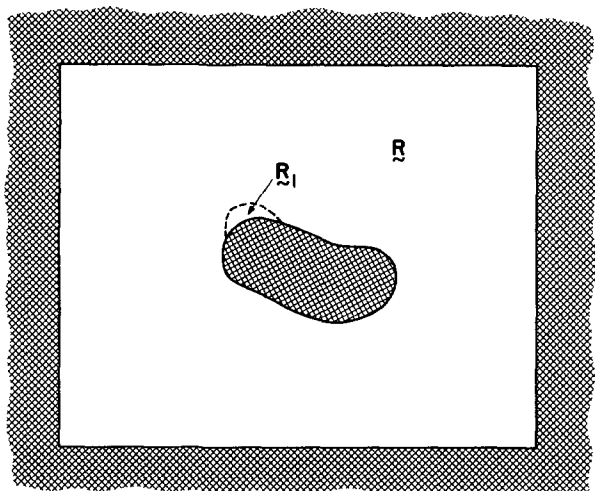
FIG. 1. Inward boundary displacement, confined to an interior surface. The original region available to the particles, $\mathbf{R}$, is the space between shaded (impenetrable) regions.

descending orders of λ can have no contribution proportional to $\ln\lambda$.

Section II considers the effect of a small variation in constraint surface shape upon the distribution of molecular density. The resulting formalism is applied in Sec. III to the special cases of circular and spherical constraint surfaces, for two- and three-dimensional systems, respectively. As a consequence, one finds a new type of surface or boundary tension formula which is not obtainable from the standard stress-tensor expression[15] specialized to the present circumstances.

A useful identity for Γ, the excess amount of matter located near an impenetrable body, is derived in Sec. IV. This identity is then used in Sec. V, for circular and spherical bodies, to establish the above-cited vanishing of logarithmic terms in the associated W's. Section VI subsequently provides the conjugate results for matter contained *within* a large circular or spherical boundary.

Section VII contains discussion of several topics arising from our main theme.

II. DENSITY CHANGES DUE TO BOUNDARY VARIATION

Our first requirement is introduction of the molecular distribution functions $\rho^{(n)}$ (for $n=1,2,3,\cdots$) to describe the density of n-tuples in the system of

interest.[16] For present purposes the grand ensemble provides the greatest convenience. If we assume for simplicity that internal molecular degrees of freedom (if any) are separable, then we have

$$\rho^{(n)}(\mathbf{r}_1\cdots\mathbf{r}_n) = \exp(\beta\Omega)\sum_{N=n}^{\infty}\frac{y^N}{(N-n)!}$$

$$\times\int d\mathbf{r}_{n+1}\cdots\int d\mathbf{r}_N\exp[-\beta V_N(\mathbf{r}_1\cdots\mathbf{r}_N)],$$

$$\beta=(k_BT)^{-1}. \quad (2.1)$$

The absolute activity has been denoted by y, and the grand partition function, which acts as a normalizing factor in expression (2.1), has the form

$$\exp(-\beta\Omega) = 1 + \sum_{N=1}^{\infty}\frac{y^N}{N!}$$

$$\times\int d\mathbf{r}_1\cdots\int d\mathbf{r}_N\exp[-\beta V_N(\mathbf{r}_1\cdots\mathbf{r}_N)]. \quad (2.2)$$

We shall place no restrictions on the set of potential functions V_N beyond the requirement that they lead to thermodynamically stable systems, with extensive mean energies, in the conventional macroscopic limit. Hence the V_N are not required to be pairwise additive.

The integrals in Eqs. (2.1) and (2.2) are confined to a region $\mathbf{R}$, which need not be singly connected. This particle confinement is equivalent to treating the boundary of $\mathbf{R}$ as a perfectly impenetrable barrier against which particles impulsively collide.

We now examine the effect of a small inward displacement of the boundary of $\mathbf{R}$. Let $\mathbf{R}_1$ denote the portion of $\mathbf{R}$ excised by this displacement, so that the new region of integration for Eqs. (2.1) and (2.2) becomes $\mathbf{R}-\mathbf{R}_1$. In anticipation of our later applications, Fig. 1 illustrates a specific boundary displacement that is confined to a portion of an interior surface in a system with a multiply connected $\mathbf{R}$.

The characteristic function for $\mathbf{R}_1$ will be denoted by $E(\mathbf{r})$:

$$E(\mathbf{r}) = 1, \quad (\mathbf{r}\text{ in }\mathbf{R}_1),$$

$$= 0, \quad (\mathbf{r}\text{ not in }\mathbf{R}_1). \quad (2.3)$$

By using this characteristic function, we can formally write the grand partition function and the molecular distribution functions, after boundary displacement, still as multiple integrals over the original region $\mathbf{R}$:

$$\exp[-\beta(\Omega+\delta\Omega)] = 1+\sum_{N=1}^{\infty}\frac{y^N}{N!}\int_{\mathbf{R}}d\mathbf{r}_1\cdots\int_{\mathbf{R}}d\mathbf{r}_N\exp(-\beta V_N)\prod_{i=1}^{N}[1-E(\mathbf{r}_i)], \quad (2.4)$$

$$\rho^{(n)}(\mathbf{r}_1\cdots\mathbf{r}_n)+\delta\rho^{(n)}(\mathbf{r}_1\cdots\mathbf{r}_n) = \exp[\beta(\Omega+\delta\Omega)]\sum_{N=1}^{\infty}\frac{y^N}{(N-n)!}\int_{\mathbf{R}}d\mathbf{r}_{n+1}\cdots\int_{\mathbf{R}}d\mathbf{r}_N\exp(-\beta V_N)\prod_{i=1}^{N}[1-E(\mathbf{r}_i)]. \quad (2.5)$$

The N-fold product of factors $1-E$ obviously vanishes unless all N particles lie in $\mathbf{R}-\mathbf{R}_1$.

If the displacement region $\mathbf{R}_1$ is small, occurrence of particles within its interior before the boundary displacement would have been a rare event. By developing the $1-E$ product in Eqs. (2.4) and (2.5) in ascending E

orders:

$$\prod_{i=1}^{N} [1-E(\mathbf{r}_i)] = 1 - \sum_{i=1}^{N} E(\mathbf{r}_i) + \sum_{i<j=1}^{N} E(\mathbf{r}_i)E(\mathbf{r}_j) - \sum_{i<j<k=1}^{N} E(\mathbf{r}_i)E(\mathbf{r}_j)E(\mathbf{r}_k) + \cdots, \qquad (2.6)$$

we therefore gather together contributions of ascending order in the displacement magnitude.

Our primary interest lies in the effect of boundary variation on $\rho^{(1)}(\mathbf{r}_1)$, i.e., in the nature of $\delta\rho^{(1)}$. To obtain $\delta\rho^{(1)}$, expansion (2.6) must be inserted into Eqs. (2.4) and (2.5); then terms of comparable $\mathbf{R}_1$ order must be collected and simplified using definitions (2.1) and (2.2). When carried through third order, the tedious manipulations show that for $\mathbf{r}_1$ in $\mathbf{R} - \mathbf{R}_1$,

$$\delta\rho^{(1)}(\mathbf{r}_1) = -\int_{R_1} d\mathbf{r}_2 [\rho^{(2)}(12) - \rho^{(1)}(1)\rho^{(1)}(2)] + \frac{1}{2} \int_{R_1} d\mathbf{r}_2 \int_{R_1} d\mathbf{r}_3 [\rho^{(3)}(123) - \rho^{(2)}(12)\rho^{(1)}(3) - \rho^{(2)}(13)\rho^{(1)}(2)$$

$$-\rho^{(2)}(23)\rho^{(1)}(1) + 2\rho^{(1)}(1)\rho^{(1)}(2)\rho^{(1)}(3)] - \frac{1}{6} \int_{R_1} d\mathbf{r}_2 \int_{R_1} d\mathbf{r}_3 \int_{R_1} d\mathbf{r}_4 [\rho^{(4)}(1234) - \rho^{(3)}(123)\rho^{(1)}(4)$$

$$-\rho^{(3)}(124)\rho^{(1)}(3) - \rho^{(3)}(134)\rho^{(1)}(2) - \rho^{(3)}(234)\rho^{(1)}(1) - \rho^{(2)}(12)\rho^{(2)}(34) - \rho^{(2)}(13)\rho^{(2)}(24)$$

$$-\rho^{(2)}(14)\rho^{(2)}(23) + 2\rho^{(2)}(12)\rho^{(1)}(3)\rho^{(1)}(4) + 2\rho^{(2)}(13)\rho^{(1)}(2)\rho^{(1)}(4) + 2\rho^{(2)}(14)\rho^{(1)}(2)\rho^{(1)}(3)$$

$$+2\rho^{(2)}(23)\rho^{(1)}(1)\rho^{(1)}(4) + 2\rho^{(2)}(24)\rho^{(1)}(1)\rho^{(1)}(3) + 2\rho^{(2)}(34)\rho^{(1)}(1)\rho^{(1)}(2)$$

$$-6\rho^{(1)}(1)\rho^{(1)}(2)\rho^{(1)}(3)\rho^{(1)}(4)]. \qquad (2.7)$$

The distribution function combinations which occur as integrands here have the following cluster property: They vanish whenever the particles involved fall into widely separated subsets. General expressions for these special combinations of all orders have long been known.[17]

III. BOUNDARY TENSION FORMULA

The first application to which general expression (2.7) for $\delta\rho^{(1)}$ will be put is the derivation of a new type of boundary tension formula. For simplicity, we shall initially confine attention to two dimensions, then briefly indicate the corresponding three-dimensional argument.

We employ a specific internal system boundary with circular shape, far removed from the external boundary. Let the radius of this exclusion circle be some arbitrary multiple λ of a fundamental length a.[18] The boundary displacement to be used will increase the radius of this region of exclusion to $(\lambda + \delta\lambda)a$,
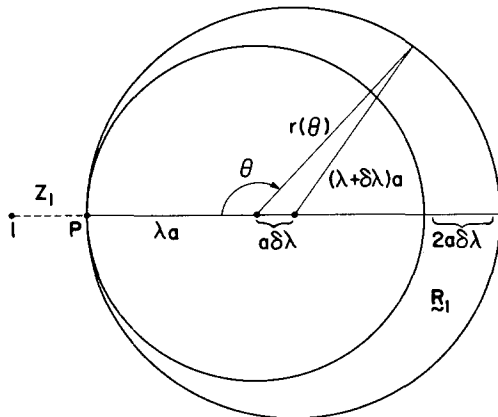

FIG. 2. Uniform dilation of a circular exclusion region. The circle center shifts during the dilation so as to keep boundary point P fixed.

without destroying circularity. As Fig. 2 shows, this expansion will be carried out in such a way that one point P of the internal boundary remains fixed. Relative to the center of the *original* circle, the polar coordinate expression for the displaced boundary is

$$r(\theta) = a\{-\delta\lambda\cos\theta + [\lambda^2 + 2\lambda\delta\lambda + (\delta\lambda)^2\cos^2\theta]^{1/2}\}$$

$$= a\{\lambda + \delta\lambda(1-\cos\theta) - [(\delta\lambda)^2/2\lambda]\sin^2\theta + O[(\delta\lambda)^3]\}, \qquad (3.1)$$

where $\theta = 0$ corresponds to invariant point P.

For sufficiently small $\delta\lambda$, nonlinear terms in Eq. (3.1) in this dilation parameter can be dropped. Furthermore, only the leading-order integral in $\delta\rho^{(1)}$ expression (2.7) then needs to be considered. One therefore finds

$$\delta\rho^{(1)}(\mathbf{r}_1) = -\int_{-\pi}^{+\pi} d\theta_2 \int_{\lambda a}^{[\lambda + \delta\lambda(1-\cos\theta_2)]a} dr_2 r_2 [\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$$

$$-\rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)]. \qquad (3.2)$$

Here the position $\mathbf{r}_2$ of particle 2 has been expressed in the polar coordinates used in Fig. 2.

It would entail no loss in generality to suppose that position $\mathbf{r}_1$ is along the common circle normal emanating from point P. In fact for present purposes we set this normal distance z_1 (see Fig. 2) equal to zero, and specifically consider the rate of change with $\delta\lambda$ of particle density at contact with the circular exclusion region. Since $\delta\lambda$ is infinitesimal, it is proper to evaluate the integrand when particles 1 and 2 are both precisely in contact with the undisplaced circle. The r_2 integral in Eq. (3.2) may then trivially be

carried out to yield

$$\delta\rho^{(1)}(\lambda a) = -a^2\lambda\delta\lambda \int_{-\pi}^{+\pi} d\theta_2 (1-\cos\theta_2)\{\rho^{(2)}(\lambda a, \lambda a, \theta_2) - [\rho^{(1)}(\lambda a)]^2\}. \quad (3.3)$$

Far from any boundary surfaces of the system, internal or external, $\rho^{(1)}(\mathbf{r})$ will equal a constant particle density ρ.[19] Therefore, set[18]

$$\rho^{(1)}(\lambda a) = \rho G_2(\lambda) \quad (3.4)$$

for arbitrary λ, thereby introducing a contact correlation function $G_2(\lambda)$ for two-dimensional systems. Subsequently set

$$\rho^{(2)}(\lambda a, \lambda a, \theta) = \rho^2 G_2^{(2)}(\lambda, \lambda, \theta), \quad (3.5)$$

where $G_2^{(2)}$ is a double-contact pair correlation function which satisfies

$$\lim_{\lambda\to\infty} \{G_2^{(2)}(\lambda, \lambda, \theta)/[G_2(\lambda)]^2\} = 1 \quad (\theta\neq 0). \quad (3.6)$$

Then Eq. (3.3) is equivalent to the following integrodifferential equation for G_2:

$$\frac{\partial G_2(\lambda)}{\partial\lambda} = -2\rho a^2\lambda \int_0^\pi d\theta(1-\cos\theta) \times \{G_2^{(2)}(\lambda, \lambda, \theta) - [G_2(\lambda)]^2\}. \quad (3.7)$$

One of the key ingredients in the scaled particle theory is the relation between the contact correlation function $G_2(\lambda)$, and the reversible work $W_2(\lambda)$ required to place the corresponding internal circular boundary in the system[11-13]:

$$\beta W_2(\lambda) = 2\pi\rho a^2 \int_0^\lambda \lambda' G_2(\lambda') d\lambda'. \quad (3.8)$$

When the impenetrable circle is very large (i.e., when λ is very large), $W_2(\lambda)$ will consist predominately of pressure–volume work, corrected by a boundary tension contribution. If we let p represent the isotropic pressure in the initially homogeneous bulk system, and let γ_2 represent the appropriate linear boundary tension (whose associated Gibbs dividing surface[20] is coincident with the repelling boundary), then

$$W_2(\lambda) \sim \pi p a^2\lambda^2 + 2\pi\gamma_2 a\lambda. \quad (3.9)$$

Equation (3.8) thereupon requires that

$$G_2(\lambda) \sim (\beta p/\rho) + (\beta\gamma_2/\rho a\lambda) \quad (3.10)$$

as $\lambda\to\infty$. In the same limit, therefore,

$$\partial G_2(\lambda)/\partial\lambda \sim -\beta\gamma_2/\rho a\lambda^2. \quad (3.11)$$

The boundary tension γ_2 may be related to contact correlation functions in another way by requiring (3.7) and (3.11) to agree for large λ. In the former of these equations, set

$$s = \lambda a\theta,$$
$$G_2^{(2, w)}(s) = \lim_{\lambda\to\infty} G_2^{(2)}[\lambda, \lambda, (s/a\lambda)], \quad (3.12)$$

so that $G_2^{(2, w)}$ stands for the flat boundary double-contact pair correlation function, whose variable s is the distance between centers of the two boundary-contacting particles. Since

$$G_2^{(2, w)}(s) - [G_2(\infty)]^2 \quad (3.13)$$

should vanish rapidly with increasing distance s, it is easy to see that Eq. (3.7) must lead to

$$\frac{\partial G_2(\lambda)}{\partial\lambda} \sim -\frac{\rho}{a\lambda^2} \int_0^\infty ds\, s^2\{G_2^{(2, w)}(s) - [G_2(\infty)]^2\}. \quad (3.14)$$

Therefore, we must have

$$\beta\gamma_2 = \rho^2 \int_0^\infty ds\, s^2\{G_2^{(2, w)}(s) - [G_2(\infty)]^2\}. \quad (3.15)$$

In order to derive the three-dimensional analog of result (3.15), it will be necessary to consider dilation of an impenetrable sphere with initial radius λa. Figure 2 may be interpreted as a planar section for this process which again will involve an invariant point P. Polar representation (3.1) for the displaced surface is still valid for the sphere. The first-order expression for $\delta\rho^{(1)}(\mathbf{r}_1)$ is directly analogous to Eq. (3.2):

$$\delta\rho^{(1)}(\mathbf{r}_1) = -\int_0^{2\pi} d\varphi_2 \int_0^\pi d\theta_2 \int_{\lambda a}^{[\lambda+\delta\lambda(1-\cos\theta_2)]a} dr_2 \times r_2^2 \sin\theta_2[\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)]. \quad (3.16)$$

After introducing surface correlation functions G_3 and $G_3^{(2)}$ for this three-dimensional case:

$$\rho^{(1)}(\lambda a) = \rho G_3(\lambda),$$
$$\rho^{(2)}(\lambda a, \lambda a, \theta) = \rho^2 G_3^{(2)}(\lambda, \lambda, \theta), \quad (3.17)$$

one can deduce as before an integrodifferential equation for G_3:

$$\frac{\partial G_3(\lambda)}{\partial\lambda} = -2\pi\rho a^3\lambda^2 \int_0^\pi d\theta_2 \sin\theta_2(1-\cos\theta_2) \times \{G_3^{(2)}(\lambda, \lambda, \theta) - [G_3(\lambda)]^2\}. \quad (3.18)$$

This may be compared to the previous Eq. (3.7).

The reversible work $W_3(\lambda)$ required for insertion of a spherical exclusion region in three dimensions satisfies

$$\beta W_3(\lambda) = 4\pi\rho a^3 \int_0^\lambda (\lambda')^2 G_3(\lambda') d\lambda' \sim (\tfrac{4}{3}\pi\beta p a^3)\lambda^3 + 4\pi\beta\gamma_3 a^2\lambda^2. \quad (3.19)$$

Here γ_3 is the flat boundary tension, again referred to a Gibbs dividing surface that is coincident with a planar repelling boundary. Hence

$$G_3(\lambda) \sim (\beta p/\rho) + (2\beta\gamma_3/\rho a\lambda), \quad (3.20)$$

$$\partial G_3(\lambda)/\partial\lambda \sim -2\beta\gamma_3/\rho a\lambda^2. \quad (3.21)$$

The requirement that expressions (3.18) and (3.21)

agree as $\lambda \to \infty$ leads to the desired γ_3 formula:

$$\beta\gamma_3 = \tfrac{1}{2}\pi\rho^2 \int_0^\infty ds\, s^3 \{G_3^{(2,w)}(s) - [G_3(\infty)]^2\}, \quad (3.22)$$

in which we have introduced

$$G_3^{(2,w)}(s) = \lim_{\lambda\to\infty} G_3^{(2)}[\lambda, \lambda, (s/a\lambda)]. \quad (3.23)$$

IV. IDENTITY FOR Γ

The presence of a repelling circular or spherical boundary within the system of course creates a density distribution $\rho^{(1)}(\mathbf{r})$ which locally deviates from ρ. The total excess number of molecules adsorbed at the boundary will be given the symbol Γ:

$$\Gamma(\lambda) = \int_{\lambda a}^\infty \binom{2\pi r}{4\pi r^2} [\rho^{(1)}(\mathbf{r}) - \rho]\, dr. \quad (4.1)$$

The notation used here comprises both two- and three-dimensional results (upper and lower entries, respectively). In this section we shall derive a formula for Γ in terms of the corresponding G_2 or G_3 function.

The local density distribution surrounding the infinitely repulsive region would be unchanged if this region were free to move about. For present purposes it is convenient to treat this region as a large colloidal particle with radius λa that does in fact move about under the action of Brownian motion. We have then the freedom to apply the results of general solution theory to the colloidal suspension.

The Kirkwood–Buff[21] version of general solution theory provides an expression for the partial molar volume $\bar{v}(\lambda)$ of the colloidal solute (in the low concentration limit for this component):

$$\bar{v}(\lambda) = \rho^{-1} + \int d\mathbf{r}[g^{(2)}(r) - 1] - \int d\mathbf{r}[\rho^{-1}\rho^{(1)}(\mathbf{r}) - 1]. \quad (4.2)$$

In this equation, $g^{(2)}(r)$ stands for the pair correlation function in the pure solvent. By using the well-known compressibility theorem for the pure bulk solvent:

$$k_B T \rho^{-1}(\partial\rho/\partial p)_T = \rho^{-1} + \int d\mathbf{r}[g^{(2)}(r) - 1], \quad (4.3)$$

as well as definition (4.1), the colloid partial molar volume may be put into the following form:

$$\bar{v}(\lambda) = k_B T \rho^{-1}(\partial\rho/\partial p)_T + \tau(\lambda) - \rho^{-1}\Gamma(\lambda). \quad (4.4)$$

The area, or volume, of the interior of the colloidal particle has been denoted here by $\tau(\lambda)$:

$$\tau(\lambda) = \int_{|\mathbf{r}|\le\lambda} d\mathbf{r} = \binom{\pi\lambda^2 a^2}{\tfrac{4}{3}\pi\lambda^3 a^3}. \quad (4.5)$$

The partial molar volume $\bar{v}(\lambda)$ satisfies the general thermodynamic identity

$$\bar{v}(\lambda) = (\partial\mu_\lambda/\partial p)_{T,N,N\lambda}, \quad (4.6)$$

where the subscript λ indicates the colloidal solute. Scaled particle theory provides an expression for the colloid chemical potential μ_λ in terms of the contact correlation function[11,12]:

$$\mu_\lambda = \mu_\lambda^{(0)}(T) + k_B T \ln\rho_\lambda$$
$$+ k_B T\rho \int_0^\lambda \binom{2\pi a^2\lambda' G_2(\lambda')}{4\pi a^3(\lambda')^2 G_3(\lambda')} d\lambda', \quad (4.7)$$

which is valid as the colloid number density ρ_λ approaches zero. By placing (4.7) into identity (4.6), and carrying out the indicated derivative by the chain rule with solvent density as an intermediary, we find

$$\bar{v}(\lambda) = k_B T\rho^{-1}(\partial\rho/\partial p)_T + k_B T(\partial\rho/\partial p)_T$$
$$\times \int_0^\lambda \binom{2\pi a^2\lambda'(\partial/\partial\rho)\rho G_2(\lambda')}{4\pi a^3(\lambda')^2(\partial/\partial\rho)\rho G_3(\lambda')} d\lambda'. \quad (4.8)$$

It is generally true that for pure "solvent"

$$p = k_B T\rho \binom{G_2(\infty)}{G_3(\infty)}, \quad (4.9)$$

so that

$$(k_B T)^{-1}\left(\frac{\partial p}{\partial\rho}\right)_T = \binom{(\partial/\partial\rho)\rho G_2(\infty)}{(\partial/\partial\rho)\rho G_3(\infty)}. \quad (4.10)$$

One may therefore add and subtract $\tau(\lambda)$ in Eq. (4.8) in such a way as to yield

$$\bar{v}(\lambda) = k_B T\rho^{-1}(\partial\rho/\partial p) + \tau(\lambda) + k_B T(\partial\rho/\partial p)_T$$
$$\times \int_0^\lambda \binom{2\pi a^2\lambda'(\partial/\partial\rho)\rho[G_2(\lambda') - G_2(\infty)]}{4\pi a^3(\lambda')^2(\partial/\partial\rho)\rho[G_3(\lambda') - G_3(\infty)]} d\lambda'. \quad (4.11)$$

When this form for $\bar{v}(\lambda)$ is compared with the earlier form displayed in Eq. (4.4), we see that the following expression for Γ must hold in two dimensions:

$$\Gamma(\lambda) = 2\pi a^2\rho\left(\frac{\partial\rho}{\partial\beta p}\right)_T \int_0^\lambda \lambda'\, \frac{\partial\{\rho[G_2(\infty) - G_2(\lambda')]\}}{\partial\rho}\, d\lambda', \quad (4.12)$$

while in three dimensions the analogous result is

$$\Gamma(\lambda) = 4\pi a^3\rho\left(\frac{\partial\rho}{\partial\beta p}\right)_T \int_0^\lambda (\lambda')^2\, \frac{\partial\{\rho[G_3(\infty) - G_3(\lambda')]\}}{\partial\rho}\, d\lambda'. \quad (4.13)$$

With the normalization used, $\Gamma(\lambda)$ will be proportional to the colloid particle boundary area (or length) in the large λ limit. Equations (3.10) and (3.20) show that in this limit our general Γ expressions (4.12) and (4.13) reduce to statements of the Gibbs adsorption equation[22] for flat boundaries.

V. LOGARITHMIC FREE ENERGY TERMS

The formalism presented in Sec. II will now be used to develop the density function $\rho^{(1)}(\mathbf{r})$ in an asymptotic

series in λ, valid for large λ. When this asymptotic series is inserted into the two distinct Γ expressions [(4.1), and (4.12) or (4.13)], the results force one to conclude that the reversible works $W_2(\lambda)$ and $W_3(\lambda)$ must be devoid of contributions proportional to $\ln\lambda$ as $\lambda\rightarrow\infty$.

The full integral series for $\delta\rho^{(1)}$, the first three orders of which were exhibited in Eq. (2.7), has the form

$$\delta\rho^{(1)}(\mathbf{r}_1)= \sum_{n=2}^{\infty} \frac{(-1)^{n-1}}{(n-1)!} \int_{R_1} d\mathbf{r}_2 \cdots \int_{R_1} d\mathbf{r}_n F^{(n)}(\mathbf{r}_1\cdots\mathbf{r}_n).$$
(5.1)

The function $F^{(n)}$ represents the characteristic cluster-property combination of distribution functions for n molecules. We shall restrict attention for the moment to two dimensions, and the geometry shown in Fig. 2 again becomes relevant. As before, we can restrict $\mathbf{r}_1$ to the outward normal direction emanating from invariant point P. All of the integrals in (5.1) are confined to the space between the two circles shown in Fig. 2; thus

$$\delta\rho^{(1)}(z_1)= \sum_{n=2}^{\infty} \frac{(-1)^{n-1}}{(n-1)!}$$

$$\times \int_{-\pi}^{+\pi} d\theta_2 \int_{\lambda a}^{r(\theta_2)} dr_2 \cdots \int_{-\pi}^{+\pi} d\theta_n \int_{\lambda a}^{r(\theta_n)} dr_n$$

$$\times r_2 \cdots r_n F^{(n)}(\mathbf{r}_1\cdots\mathbf{r}_n).$$
(5.2)

The small variable

$$\chi = 1/\lambda$$
(5.3)

is somewhat more natural than λ itself for discussing the problem in hand. Therefore, since

$$\chi + \delta\chi = (\lambda + \delta\lambda)^{-1},$$

$$\delta\lambda = (\chi + \delta\chi)^{-1} - \chi^{-1},$$
(5.4)

when λ is finite, the polar coordinate expression (3.1) for the displaced circle transforms to

$$\frac{r(\theta)}{a} = \chi^{-1} \left(\frac{[1+(\delta\chi/\chi)^2(\cos^2\theta-1)]^{1/2}+(\delta\chi/\chi)\cos\theta}{1+\delta\chi/\chi} \right)$$

$$= \chi^{-1} \left\{ 1 + (\cos\theta-1)\frac{\delta\chi}{\chi} + \frac{1}{2}(\cos\theta-1)^2 \right.$$

$$\left. \times \left(\frac{\delta\chi}{\chi}\right)^2 + O\left[\left(\frac{\delta\chi}{\chi}\right)^3\right]\right\}.$$
(5.5)

After setting

$$r_j = (a/\chi) + t_j,$$

$$r(\theta) = (a/\chi) + t(\theta),$$
(5.6)

the integral series (5.2) adopts the form

$$\delta\rho^{(1)}(z_1)= \sum_{n=2}^{\infty} \frac{(-a/\chi)^{n-1}}{(n-1)!}$$

$$\times \int_{-\pi}^{+\pi} d\theta_2 \int_0^{t(\theta_2)} dt_2 \cdots \int_{-\pi}^{+\pi} d\theta_n \int_0^{t(\theta_n)} dt_n$$

$$\times [1+(\chi t_2/a)]\cdots[1+(\chi t_n/a)]F^{(n)}(\mathbf{r}_1\cdots\mathbf{r}_n).$$
(5.7)

On account of their cluster property, the functions $F^{(n)}$ will be negligible unless each of $\mathbf{r}_2\cdots\mathbf{r}_n$ is close to the invariant point P. But for small χ (large λ) this implies that these $n-1$ particle positions are never very far from the boundary of the smaller circle in Fig. 2. As a leading-order estimate (analogous to the one required in Sec. III) for each integral in Eq. (5.7) it would suffice to evaluate $F^{(n)}(\mathbf{r}_1\cdots\mathbf{r}_n)$ with $\mathbf{r}_2\cdots\mathbf{r}_n$ precisely on this undisplaced boundary. More accurately, one would utilize a multiple Taylor series for $F^{(n)}$ in the radial displacements $t_2\cdots t_n$ normal to that boundary:

$$F^{(n)}(\mathbf{r}_1, \theta_2, t_2\cdots\theta_n, t_n) = \sum_{m_2\cdots m_n=0}^{\infty} \frac{t_2^{m_2}}{m_2!}\cdots\frac{t_n^{m_n}}{m_n!}\left[\left(\frac{\partial}{\partial t_2}\right)^{m_2}\cdots\left(\frac{\partial}{\partial t_n}\right)^{m_n} F^{(n)}(\mathbf{r}_1, \theta_2, t_2\cdots\theta_n, t_n)\right]_{t_2\cdots t_n=0}.$$
(5.8)

With Eqs. (5.5), (5.7), and (5.8) as ingredients, we are now in a position to obtain $\delta\rho^{(1)}(z_1)$ as an expansion in $\delta\chi$. Since $t(\theta_j)$ is $O(\delta\chi)$, it is clear that the multiple integral with index n in Eq. (5.7) contributes in order $(\delta\chi)^{n-1}$, and in all higher orders of $\delta\chi$. Furthermore, each factor t_j, whether arising from expansion of the integrand product

$$[1+(\chi t_2/a)]\cdots[1+(\chi t_n/a)],$$
(5.9)

or from terms beyond the first in Taylor's series (5.8), increases the order of the resulting contribution by one power of $\delta\chi$. Thus we will have

$$\delta\rho^{(1)}(z_1)= \sum_{l=1}^{\infty} (\delta\chi)^l \delta\rho^{(1,l)}(z_1),$$
(5.10)

where the first coefficient function $\delta\rho^{(1,1)}$ comes entirely from the $n=2$ term in Eq. (5.7), the second coefficient

function $\delta\rho^{(1,2)}$ from the $n=2$ and $n=3$ terms, and so forth. Explicit calculation shows

$$\delta\rho^{(1,1)}(z_1) = -\frac{a^2}{\chi^3}\int_{-\pi}^{+\pi} d\theta_2(\cos\theta_2-1) F^{(2)}\left(z_1+\frac{a}{\chi}, 0, \theta_2, 0\right),$$

$$\delta\rho^{(1,2)}(z_1) = -\frac{a^2}{\chi^4}\int_{-\pi}^{+\pi} d\theta_2(\cos\theta_2-1)^2\left\{\left[1+\left(\frac{a}{2\chi}\right)\frac{\partial}{\partial t_2}\right] F^{(2)}\left(z_1+\frac{a}{\chi},0,\theta_2, t_2\right)\right\}_{t_2=0} \qquad (5.11)$$

$$+\frac{a^4}{2\chi^6}\int_{-\pi}^{+\pi} d\theta_2(\cos\theta_2-1)\int_{-\pi}^{+\pi} d\theta_3(\cos\theta_3-1) F^{(3)}\left(z_1+\frac{a}{\chi}, 0, \theta_2, 0, \theta_3, 0\right).$$

The higher-order coefficient functions become increasingly complicated, but nothing as a matter of principle stands in the way of deducing explicit integral expressions for them of the type (5.11).

Owing to the nature of our derivations, $\delta\lambda$ has been nonnegative, i.e., $\delta\chi$ has been nonpositive. However, it is clear that $\delta\rho^{(1)}(z_1)$ in Eq. (5.10) must be a smooth function of $\delta\chi$ defined for both signs of this variable. Hence Eq. (5.10) provides the correct continuation of $\delta\rho^{(1)}(z_1)$ from negative to positive $\delta\chi$. One can in fact devise a more cumbersome derivation which accommodates both signs of $\delta\lambda$ and $\delta\chi$ from the outset to verify the universality of Eq. (5.10), but at unwarranted cost in clarity.

In the limit $\chi\rightarrow0$, and with $\delta\chi>0$, the series (5.10) shows how $\rho^{(1)}$ varies upon changing from a straight boundary to a circular boundary (with a radius which we shall henceforth call $a/\delta\chi=a\lambda$), in terms of distribution functions for the straight boundary case alone. In this limit, we have precisely

$$\delta\chi=1/\lambda,$$

$$\delta\rho^{(1)}(z_1,\lambda) = \sum_{l=1}^{\infty}\lambda^{-l}\delta\rho^{(1,l)}(z_1, \lambda=\infty). \qquad (5.12)$$

The coefficient functions shown in Eq. (5.11) simplify somewhat when $\chi=0$; as will be the case for *all* coefficient functions when $\chi=0$, they will involve distribution functions for sets of particles all at the straight boundary, as well as normal derivatives (direction z) of these distribution functions. In particular one finds

$$\delta\rho^{(1,1)}(z_1, \lambda=\infty) = \int_0^{\infty} s_{12}^2[\rho^{(2)}(12)-\rho^{(1)}(1)\rho^{(1)}(2)]ds_{12},$$

$$\delta\rho^{(1,2)}(z_1, \lambda=\infty) = \left(\frac{1}{4a^2}\right)\int_0^{\infty}s_{12}^4\left(\frac{\partial}{\partial z_2}[\rho^{(2)}(12)-\rho^{(1)}(1)\rho^{(1)}(2)]\right)_{z_2=0}ds_{12}+\left(\frac{1}{4a^2}\right)\int_0^{\infty}ds_{12}\int_{-\infty}^{+\infty}ds_{13}s_{12}^2s_{13}^2[\rho^{(3)}(123)$$

$$-\rho^{(2)}(12)\rho^{(1)}(3)-\rho^{(2)}(13)\rho^{(1)}(2)-\rho^{(2)}(23)\rho^{(1)}(1)+2\rho^{(1)}(1)\rho^{(1)}(2)\rho^{(1)}(3)]. \quad (5.13)$$

The variables s_{12} and s_{13} employed here measure distance along the flat boundary from the point P (directly under particle 1).

Now that we have shown $\rho^{(1)}(\mathbf{r})$ in the vicinity of a large circular boundary to have an expansion (5.12) in powers of $1/\lambda$, we can obtain a corresponding development of $\Gamma(\lambda)$ in descending orders of λ. Starting with the basic definition (4.1), one obtains, in two dimensions,

$$\Gamma(\lambda) = \sum_{i=0}^{\infty}\Gamma^{(1-i)}\lambda^{(1-i)}, \qquad (5.14)$$

$$\Gamma^{(1)} = 2\pi a\int_0^{\infty}[\rho^{(1)}(z, \lambda=\infty)-\rho]dz, \qquad (5.15)$$

$$\Gamma^{(0)} = 2\pi\int_0^{\infty}\{a\delta\rho^{(1,1)}(z, \lambda=\infty)+z[\rho^{(1)}(z, \lambda=\infty)-\rho]\}dz, \qquad (5.16)$$

and for $1\leq j<\infty$ one has

$$\Gamma^{(-j)} = 2\pi\int_0^{\infty}[a\delta\rho^{(1,j+1)}(z, \lambda=\infty)+z\delta\rho^{(1,j)}(z, \lambda=\infty)]dz. \qquad (5.17)$$

The alternative two-dimensional expression for $\Gamma(\lambda)$ [Eq. (4.12)] yields somewhat different results. Now that λ' is the integration variable, a contribution proportional to $\ln\lambda$ seems to arise:

$$\Gamma(\lambda) \sim -2\pi a^2\rho\left(\frac{\partial\rho}{\partial\beta p}\right)_T\left[\left(\frac{\partial\delta\rho^{(1,1)}(z=0, \lambda=\infty)}{\partial\rho}\right)_T\lambda\right.$$

$$\left.+\left(\frac{\partial\delta\rho^{(1,2)}(z=0, \lambda=\infty)}{\partial\rho}\right)_T\ln\lambda+O(\lambda^0)\right]. \qquad (5.18)$$

In order that this be consistent with Eq. (5.14), we

must first require equality of the coefficients of λ:

$$\int_0^\infty [\rho^{(1)}(z, \lambda = \infty) - \rho]dz$$

$$= -a\rho \left(\frac{\partial \rho}{\partial \beta p}\right)_T \left(\frac{\partial \delta\rho^{(1,1)}(z=0, \lambda = \infty)}{\partial \rho}\right)_T. \quad (5.19)$$

In addition it is necessary that the coefficient of $\ln\lambda$ in Eq. (5.18) vanish, since no corresponding logarithmic term appears in Eq. (5.14). Since $(\partial \rho/\partial \beta p)_T$ never vanishes, we can infer that

$$[\partial \delta\rho^{(1,2)}(z=0, \lambda = \infty)/\partial \rho]_T = 0. \quad (5.20)$$

This may immediately be integrated to give

$$\delta\rho^{(1,2)}(z=0, \lambda = \infty) = 0 \quad (5.21)$$

for all ρ, because it is obviously true when $\rho = 0$.

The identical vanishing of $\delta\rho^{(1,2)}(z=0)$ in two dimensions is hardly a transparent property of the complicated $\delta\rho^{(1,2)}(z)$ expression (5.13). But once this property has been established, the clear implication is that the reversible work $W_2(\lambda)$ [like $\Gamma(\lambda)$] must be free of contributions proportional to $\ln\lambda$ as $\lambda \to \infty$. Such contributions can only arise from integrand terms in Eq. (3.8) varying as $1/\lambda'$ in the large-λ' limit, but Eq. (5.21) ensures the absence of these terms. The asymptotic series for $W_2(\lambda)$, the first two orders of which were displayed in Eq. (3.9), will therefore contain only integral powers of λ.

The format of a corresponding analysis for three-dimensional systems is almost obvious from the two-dimensional argument. An expansion for $\delta\rho^{(1)}(z_1)$ in powers of $\delta\chi$ follows the earlier pattern, and Eq. (5.10) will apply to the three-dimensional case as well. Of course the explicit integral forms for $\delta\rho^{(1,1)}$, $\delta\rho^{(1,2)}$, etc., will differ somewhat from those shown in (5.11), mainly by inclusion of the modified polar coordinates for each particle. But, as before, the flat-wall limits for each $\delta\rho^{(1,i)}$ [see Eq. (5.13)] will involve distribution functions for simultaneous particle contact, and normal derivatives of those distribution functions.

The Γ definition (4.1) for three dimensions will lead to an expansion in descending integral powers of λ, starting now with λ^2:

$$\Gamma(\lambda) = \sum_{i=0}^\infty \Gamma^{(2-i)}\lambda^{(2-i)}. \quad (5.22)$$

The alternative Γ expression (5.13), however, formally generates a $\ln\lambda$ term, associated with $\delta\rho^{(1,3)}(z=0, \lambda = \infty)$. Consequently, we must have

$$\delta\rho^{(1,3)}(z=0, \lambda = \infty) = 0 \quad (5.23)$$

as the three-dimensional analog of Eq. (5.21). In view of Eq. (3.19) for W_3, we can finally conclude once again that $\ln\lambda$ contributions are absent from the reversible work as $\lambda \to \infty$.

It should be stressed that although $\delta\rho^{(1,d)}(z=0,$

$\lambda = \infty$) vanishes in d dimensions, we have no evidence that the same is true when $z > 0$.

VI. CONSTRAINED DROPLET

To complement the results obtained thus far, we shall now consider the free energy associated with a circular or spherical boundary which encloses the molecular system as a container. The geometry specified in Fig. 2 is still applicable, except for the fact that negative values of the normal distance z_1 in that figure are now those which are available to the molecular centers. If ρ corresponds to a liquid phase at the given temperature, the enclosed system amounts to a constrained droplet.

Once again we shall require an expansion for $\delta\rho^{(1)}$ in powers of reduced boundary curvature χ, in terms of the flat boundary distribution functions. Previously χ was reckoned to be positive when the boundary curved *away* from the molecular point of observation, and $\delta\chi > 0$ would decrease the radius of curvature. It is natural to regard the droplet case now under consideration as the negative χ extension of the preceding case, for which $\delta\chi < 0$ decreases the radius of curvature, and for which the boundary bends *toward* the molecular point of observation. Since it is conventional always to regard the geometric radius of curvature (λa) as a positive number, we are obliged for the droplet case to replace Eqs. (5.3) and (5.4) by

$$\chi = -1/\lambda,$$
$$\chi + \delta\chi = -1/(\lambda + \delta\lambda),$$
$$\delta\lambda = \chi^{-1} - (\chi + \delta\chi)^{-1}, \quad (6.1)$$

when the boundary before variation has a finite radius of curvature.

Our earlier result (5.10) for the dependence of $\delta\rho^{(1)}$ upon $\delta\chi$ is valid for negative curvatures as it stands, and in particular may now be used as a general expansion about zero curvature. However, if we subsequently express $\delta\rho^{(1)}$ for the droplet in terms of λ, the result is an alternating sign analog of the earlier key result (5.12):

$$\delta\rho^{(1)}(z_1, \lambda) = \sum_{l=1}^\infty (-\lambda)^{-l}\delta\rho^{(1,l)}(z_1, \lambda = \infty) \quad (6.2)$$

for both two- and three-dimensional cases, while the explicit coefficient function integrals shown in (5.13) for two dimensions still apply.

For the enclosed "droplet", the excess number of molecules adsorbed at the boundary must be defined by

$$\Gamma(\lambda) = \int_0^{\lambda a} \binom{2\pi r}{4\pi r^2} [\rho^{(1)}(\mathbf{r}) - \rho]dr. \quad (6.3)$$

The curvature expansion (6.2) when inserted here will yield

$$\Gamma(\lambda) = -\sum_{i=0}^\infty \Gamma^{(1-i)}(-\lambda)^{(1-i)} \quad (6.4)$$

in two dimensions, with the same coefficients (5.15)–(5.17) as before, while in three dimensions it will yield

$$\Gamma(\lambda) = \sum_{i=0}^{\infty} \Gamma^{(2-i)}(-\lambda)^{(2-i)}. \tag{6.5}$$

The alternative $\Gamma(\lambda)$ expressions (4.12) and (4.13) played a key role in the preceding elimination of logarithmic contributions, and we require their analogs for enclosure. These analogs may easily be established through the artifice of "hollow colloids", i.e., large circular or spherical bodies containing, respectively, single circular or spherical holes (see Fig. 3). The partial molar volume at infinite dilution, $\bar{v}$, and the chemical potential expression generalizing (4.7) will contain new terms referring only to the inner region. Then by applying the "hollow colloid" version of thermodynamic identity (4.6), one can proceed ultimately to show that

$$\Gamma(\lambda) = 2\pi a^2 \rho \left(\frac{\partial \rho}{\partial \beta p}\right)_T \int_0^\lambda \lambda' \left(\frac{\partial \delta\rho^{(1)}(z=0, \lambda')}{\partial \rho}\right)_T d\lambda', \tag{6.6}$$

$$\Gamma(\lambda) = 4\pi a^3 \rho \left(\frac{\partial \rho}{\partial \beta p}\right)_T \int_0^\lambda (\lambda')^2 \left(\frac{\partial \delta\rho^{(1)}(z=0, \lambda')}{\partial \rho}\right)_T d\lambda', \tag{6.7}$$

in two and three dimensions, respectively.

Following the earlier theme, we must reconcile Eqs. (6.4) and (6.6), as well as Eqs. (6.5) and (6.7). Since the curvature expansion (6.2) will tend to produce $\ln\lambda$ terms in the latter equation in each of these pairs, the reconciliation is possible only if

$$\delta\rho^{(1,d)}(z=0, \lambda=\infty) = 0 \tag{6.8}$$

in d dimensions, thereby totally annihilating the $\ln\lambda$ terms. But the requirement (6.8) has already been established in Sec. V [Eqs. (5.21) and (5.23)].

The Gibbs free energy for the enclosed and constrained droplet is $\bar{N}\mu$, where μ is the chemical potential and $\bar{N}$ is the average number of molecules in the open

FIG. 3. "Hollow colloid" body. Molecules of "solvent" surround the body, and are permitted to fill the interior cavity of radius λa.

droplet system:

$$\bar{N}(\lambda) = \begin{pmatrix} \pi\lambda^2 a^2 \\ \frac{4}{3}\pi\lambda^3 a^3 \end{pmatrix} \rho + \Gamma(\lambda). \tag{6.9}$$

For fixed μ, the Gibbs free energy will have a large-λ asymptotic expansion in descending integral orders of λ. The same property also obtains for the open droplet Helmholtz free energy $F(\lambda)$:

$$F(\lambda) = \bar{N}(\lambda)\mu - \int_0^\lambda \begin{pmatrix} 2\pi\lambda' a^2 \delta\rho^{(1)}(z=0, \lambda') \\ 4\pi(\lambda')^2 a^3 \delta\rho^{(1)}(z=0, \lambda') \end{pmatrix} d\lambda', \tag{6.10}$$

since result (6.8) eliminates the possibility that logarithmic terms in λ can arise from the λ' integral.

VII. DISCUSSION

Some of the elements of scaled particle theory have been useful ingredients to borrow for our preceding analysis. It is therefore appropriate that we repay the debt by stressing the implication of our results for the further development of scaled particle theory. For application of that theory to spherically symmetric molecules, it has been traditional[11–13,23] to represent the contact correlation functions $G_2(\lambda)$ and $G_3(\lambda)$, for large λ, solely in terms of integral powers of λ. We can now unambiguously assert that $G_d(\lambda)$ will have no term in λ^{-d}. Although the physical desirability of this result had previously been suggested,[23] a strict proof was apparently not available.

There seems to be nothing standing in the way of an extension to solvent particles and exclusion regions with nonspherical (or noncircular) shapes. The complications posed by these generalizations for the results obtained in this paper are largely notational, rather than conceptual. For an exclusion cavity or enclosing boundary with constant shape, but with size scaled by λ, one surely can show that the associated free energy must be devoid of $\ln\lambda$ contributions. This observation should be useful in extending the recent applications of scaled-particle theory to liquid crystals composed of rigid spherocylinders.[14,24]

In considering the homogeneous nucleation of liquid droplets from supersaturated vapor, it is necessary to know the concentration of droplets, or nuclei, of various sizes. This requires the partition function for the droplet to be computed. In the course of calculating droplet partition functions, it has been suggested[7] that knowledge of the partition function for a droplet constrained by an impenetrable spherical boundary would be an important ingredient in the theory. In this respect the results of Sec. VI become relevant.

The droplets considered in Sec. VI were open systems, with only the average number of molecules $\bar{N}$ fixed by the chemical potential. Nucleation theory, however, requires the free energy for *fixed* number of molecules N. The conversion of open droplet free energies (6.8)
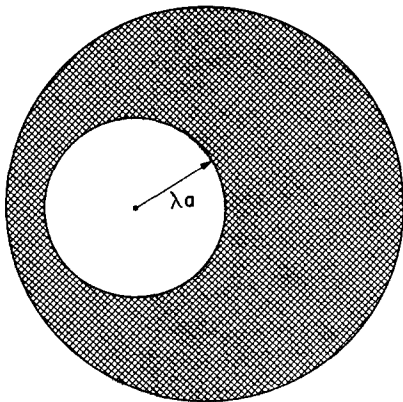
and (6.9) to those for fixed N though is a relatively straightforward matter using fluctuation theory. The result for open (F) and closed (F_N) droplet Helmholtz free energies is the following:

$$\beta F_N = \beta F(\bar{N} = N) + \tfrac{1}{2} \ln[(2\pi N/\beta)(\partial\rho/\partial p)_T]. \quad (7.1)$$

For large droplets with fixed interior density equal to that of bulk liquid, N will vary as λ^d in leading order. Equation (7.1) shows therefore that the closed droplet *does* give rise to logarithmic free energy terms: βF_N contains $(d/2)\ln\lambda$ as $\lambda \to \infty$. In view of the protracted discussion in nucleation theory over the "translation-rotation paradox,"[6,7] it seems significant that this exact result in logarithmic order has been obtained without explicit consideration of droplet translational and rotational degrees of freedom.

The validity of the curvature expansions derived in earlier sections, both for distribution functions and for free energies, rests upon the smallness of the ratio of molecular correlation length to λa. At the liquid-vapor critical point, the correlation length diverges, so our expansions without question become inapplicable there. It is possible, for example, that precisely at the critical point quantities like $\Gamma(\lambda)$, $W_d(\lambda)$, and $F(\lambda)$ do indeed exhibit terms in $\ln\lambda$ in the relevant critical asymptotic λ expansions.[25] The coefficient of $\ln\lambda$ in βF_N would thereupon change discontinuously at the critical point.

The boundary tension formulas derived above for γ_2 and γ_3 will certainly reflect the increasing range of molecular correlation as the critical point is approached. One would expect on intuitive grounds that a depletion region with width equal to the bulk fluid correlation length $1/\kappa$ would exist next to the nonwettable repelling boundary. Along the critical isotherm, the Gibbs adsorption equation[22] then requires that

$$d\gamma_d/d\mu \propto 1/\kappa. \quad (7.2)$$

The scaling laws for critical-region molecular correlation functions specify that $\kappa(\rho, T_c)$ shall vanish at the critical point ($T = T_c$, $\rho = \rho_c$) in the following way[26]:

$$\kappa(\rho, T_c) \sim \kappa_0 \mid \rho_c - \rho \mid^{(\delta+1)/d}, \quad (7.3)$$

where δ is the degree of the critical isotherm. Subsequently, differential relation (7.2) may be integrated to show

$$\gamma^d \sim \text{const} \times \mid \rho_c - \rho \mid^{\zeta}, \quad \zeta = \delta - (\delta+1)/d. \quad (7.4)$$

The boundary tension exponent should be 7 in two dimensions, and about 3 in three dimensions. The scaling arguments finally may be extended to our general boundary-tension formulas (3.15) and (3.22)

to show that at the critical point, and for large lateral distance s,

$$G_d^{(2,w)}(s) - [G_d(\infty)]^2 \sim \text{const}/s^q,$$

$$q = d(2\delta+1)/(\delta+1). \quad (7.5)$$

The droplet conditions that must ultimately be considered both for nucleation theory, and for the droplet model of critical phenomena, involve free surfaces rather than constraining boundaries. Effort should therefore be directed in the future to calculating the additional liquid droplet free energy attendant upon reversible removal of a constraint boundary. It would be particularly valuable to establish without ambiguity whether logarithmic contributions arising from this removal can be entirely attributed to the freeing of capillary wave motions of the droplet surface.[10,27]

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