an adequate portrait of the diffusion process. Correspondingly, it seems clear the the use of a classical diffusive description of the electronic motion with a phenomenological diffusion constant is faithful down to quite small distances and time scales.

A new challenge for analytical theory is thus presented. The prevalent theory of ionic dynamics in solution derives from the hydrodynamic approach due to Zwanzig[21] that evaluates the additional dielectric friction term arising in a polar solvent. In its sophisticated extended formulation by Hubbard and co-workers,[22,23] this theory is relatively successful compared to experimental data. Analytical treatments along these lines for the classical diffusion of a particle that responds instantaneously to polarization fluctuations, *but* lacks any classical inertial behavior, are clearly of great interest in light of the picture presented here for the electronic motion. It is an interesting question whether

the deformability of the electronic distribution from a spherical shape plays any important role.

Computer simulation investigations of such alternative pseudoclassical models are accessible in any case, and it appears likely that our understanding of the transport properties of electrons in complicated dense polar fluids will make further strides in the near future.

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Implications of the Triezenberg–Zwanzig Surface Tension Formula for Models of Interface Structure

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While the Triezenberg–Zwanzig (TZ) formula and a modified version introduced by Wertheim both relate the surface tension of a liquid–vapor interface to interfacial correlation functions, they appear to support very different models of interface structure. We resolve this paradox by showing that although the Wertheim and the TZ formulas are equivalent in the thermodynamic limit, their underlying physics as well as their range of validity is different. The former is valid only on very long length scales (requiring system sizes much larger than the capillary length), while the latter continues to be relatively accurate down to scales of the order of the bulk correlation length. Thus the TZ formula is consistent both with the capillary wave model, which gives correlation functions affected by the long-wavelength interface fluctuations that occur in a large system, and with the classical van der Waals picture, which holds for small system sizes. We also discuss some more general issues involved in the use of the density functional formalism for a two-phase system.

I. Introduction

The derivation of the Triezenberg–Zwanzig (TZ) formula for the surface tension[1] represented a major conceptual advance in the modern theory of interfacial phenomena. This was one of the first, and certainly one of the most elegant and instructive, applications of density functional theory to a two-phase system, and today it remains the starting point for almost all theoretical work in interfaces.[2]

In this paper we reexamine some of the results and implications of the density functional methods pioneered by TZ and their connection to the qualitative pictures of interface structure suggested by the capillary wave model[3–5] and the van der Waals theory.[6,7] That some subtle issues arise can be seen from an examination of the original TZ formula (generalized to d-dimensions[5]) for the surface tension σ of a planar liquid–vapor interface whose normal vector is along the z axis:

$$\beta\sigma = -\frac{1}{2(d-1)} \int dz_1 \int dz_2 \int d\mathbf{r}_2\, r_{12}^2 C(z_1,z_2,r_{12})\, \rho'_0(z_1)\, \rho'_0(z_2)$$

$$(1.1)$$

Here β is the inverse temperature $(k_B T)^{-1}$, C the (generalized) direct correlation function, $\mathbf{r}$ a $(d-1)$ dimensional vector in the interface plane, $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, and $d\rho_0(z)/dz \equiv \rho'_0(z)$ the derivative of the density profile $\rho_0(z)$ (see section III for precise definitions). Implicit in (1.1) is the existence of a weak external field $\phi_0(z)$ that produces macroscopic phase separation.

According to capillary wave theory, in dimensions $d \leq 3$, $\rho'_0(z)$ has a sensitive dependence on the strength of that external (gravitational) field and vanishes as the field strength g tends to zero.[3–5] If this prediction is correct, then implicitly C must also have a strong field dependence so that the surface tension σ has a finite limit, becoming essentially independent of g as $g \to 0^+$. This is physically required and is predicted by the exact Kirkwood–Buff formula[8] for σ. For $d = 2$, Bedeaux and Weeks[5] explicitly showed that the capillary wave model satisfied (1.1) as an identity, with a C that indeed had a strong field dependence. Along with the strong field dependence, the capillary wave model also predicts a strong dependence on system size for C and $\rho'_0(z)$ in (1.1). One of the main goals of this paper will be to examine the approximate validity of (1.1) and (1.2) below for finite systems as well as in the thermodynamic limit.

This predicted strong field and size dependence of the correlation functions in (1.1) is quite different from what is suggested by the classical van der Waals picture. Here one envisions an "intrinsic" profile of finite width and correlation functions resembling those of the bulk phases, which are essentially independent of system size or the strength of a weak external field.[6]

Perhaps this point can be seen even more clearly from the formally equivalent expression for σ involving the (generalized)

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pair correlation function $H(z_1, z_2, r_{12})$, first derived by Wertheim[9]

$$\beta\sigma = \frac{1}{2(d-1)} \int dz_1 \int dz_2 \int dr_{12}\ r_{12}^2 H(z_1, z_2, r_{12})\ \beta\phi'_0(z_1) \times \beta\phi'_0(z_2) \quad (1.2)$$

where the external field, $\phi_0(z)$, now appears explicitly. For the gravitational field $\phi_0 = mgz$, we see that the right-hand side of (1.2) is formally proportional to g^2. Hence only for a "nonclassical" H that has long-ranged correlations diverging as $g \to 0^+$ could (1.2) possibly be correct.[9]

This is consistent with capillary wave theory,[3-5] which predicts an exponential decay of correlations in H only for distances of the order of the *capillary length* L_c, where

$$L_c \equiv [\sigma/(mg(\rho_l - \rho_v))]^{1/2} \quad (1.3)$$

Here $(\rho_l - \rho_v) \equiv \Delta\rho$ is the difference in number density of the bulk phases. Indeed for $d < 3$, H is of order unity[5] until r_{12} is of order L_c. It is easy to show from the results of Bedeaux and Weeks[5] that (1.2) is satisfied exactly in all dimensions in capillary wave theory.

On the other hand, one of the attractive features of the original TZ formula (1.1) was that it appeared to give a more rigorous justification for the classical van der Waals square-gradient expression for the surface tension.[1,6,7] As noted by TZ, if one makes a local Ornstein–Zernicke (OZ) approximation for C in (1.1), appropriate for the bulk phases, then it immediately reduces to the classical van der Waals formula. This is known to give at least a qualitatively correct value for σ for a Lennard-Jones fluid near the triple point, provided an "intrinsic" $\rho'_0(z)$ whose width is of the order of the bulk correlation length ξ_B is used.[2]

Thus the question arises, how can the TZ formula continue to give sensible results when two such widely different assumptions about the behavior of interface correlation functions are made? Since this is certainly not the case for the formally equivalent result (1.2), is the apparent consistency with the classical picture just a misleading coincidence? What is the TZ formula telling us about interface structure?

The answers to these questions turn out to touch on some general criticisms that several workers[10-12] have raised about the logical foundations of the derivations based on functional methods that lead to (1.1) and (1.2), and indeed about the validity of the TZ formula itself. As will be discussed in more detail below, we believe all these concerns can be met, provided proper attention is paid to the external field when taking the thermodynamic limit.

A general discussion of this point and definition of our model system is found in section II. We believe it is advisable to thoroughly understand this simple system before attempting a more general treatment. In sections III and IV, we carefully review the derivations of (1.1) and (1.2). While our treatment is certainly not rigorous or the most general possible, we have tried to focus on the important conceptual issues that we believe must be dealt with in any more formal approach. In section V our results are compared to the predictions of capillary wave theory, and some final remarks are found in section VI.

II. Importance of External Field in Description of a Two-Phase System

There are several qualitatively new issues that arise in the description of a two-phase system using the grand ensemble, where the number of particles can vary. Bulk-phase correlation functions and thermodynamic properties are *completely specified in terms of the inverse temperature β and the chemical potential μ*. As the system size tends to infinity, a one-phase system acquires a well-defined average number density independent of any local

effects from short-ranged wall potentials or from an arbitrarily small but nonzero external field.

In contrast, if $\mu = \mu_{eq}$ appropriate for two-phase coexistence, then both the location of the two bulk phases and their relative volume fractions are sensitive functions of the wall potentials and external field strength. As a result, the thermodynamic limit must be taken with care, with explicit consideration of external field effects. This basic point has been ignored in some recent discussions in the literature, including some that purport to be rigorous treatments.

It was recognized long ago[13] that in the complete absence of any external field the distribution functions in a two-phase system simply become appropriately weighted linear combinations of those for the two bulk phases. In this degenerate case, the correlation function H in (1.2) does not decay to zero at large r_{12}, and the results like (1.2), or that involving its inverse C in (1.1), make no sense.

A nonzero field regularizes these ambiguities, just as an arbitrarily weak magnetic field allows us to realize that there is a finite magnetization in the Ising model below T_c. In a system where two-phase coexistence is possible, an appropriately chosen external field will induce macroscopic phase separation and, in the grand ensemble, can also determine the relative volume fractions of the two bulk phases. In the presence of a nonzero field there is an invertible relation between the potential $\phi_0(z)$ and the density $\rho_0(z)$, and we can use density functional methods in much the same way we do for a one-phase system. The resulting equations [e.g., (1.2)] will themselves give indications of the subtle effects of interface wandering[3-5] that can arise as $g \to 0^+$, and these can be treated in a controlled way.

Our analysis is carried out in the simplest possible system, so that we can focus on conceptual issues. We assume the interparticle interactions are of strictly finite range (e.g., a truncated Lennard-Jones potential) and will later briefly discuss some of the complications that arise from longer ranged (power law) interactions. The particles are contained within a large vertical "column" with volume $L^{d-1}L_z$, where the height in the z direction L_z is much larger than the transverse dimensions L. To avoid extraneous effects arising from wall potentials (and resulting questions of wetting, etc.), we take periodic boundary conditions along all transverse faces. In the presence of an appropriately chosen external field, by taking the limit $L_z \to \infty$ before $L \to \infty$, we can clearly find results independent of boundary conditions in the z directions.

If liquid–vapor coexistence is possible ($\mu = \mu_{eq}$), then as $L_z \to \infty$ an arbitrarily weak gravitational field $\phi_0(z) = mgz$ will induce macroscopic phase separation with the denser (liquid) phase favored for $z < 0$. By proper choice of constants in μ and ϕ_0 we can arrange for the Gibbs dividing surface at $z = 0$ to be in the center of the column. To minimize the effects of the field on the bulk phases, we truncate[14] it at some distance $0 \ll z_w \ll L_z/2$ so that

$$\phi_0(z) = mgz \qquad |z| \le z_w$$
$$= \text{sgn}\,(z)mgz_w \qquad |z| > z_w \quad (2.1)$$

with z_w chosen so that $\lim_{g \to 0^+} gz_w = 0^+$. With this truncated field, for small g the chemical potential in both bulk phases approaches μ_{eq}. According to capillary wave theory,[5,14] we can make such a choice for z_w and still have z_w of $O(W)$, where W is the interface width in the weak field. Thus we can arrange to have a field gradient only in the interfacial region.

Let us now return to the derivation of the TZ formula (1.1) and the Wertheim variant (1.2), which we refer to as the TZW formula. Although (1.2) was originally derived[9] as a consequence of (1.1) and the inverse relation between H and C (see (4.4) below), it is quite instructive to derive it directly using functional methods in the grand ensemble. This is the subject of the next section.

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III. Derivation of the TZW Formula (1.2)

We consider a large system, as always at finite g. In the grand canonical ensemble, the free energy Ω is a functional of the external potential $\phi(\mathbf{R})$. Here

$$-\beta\Omega = \ln \Xi \tag{3.1}$$

with Ξ the grand partition function, $\mathbf{R} = (\mathbf{r}, z)$ is a d-dimensional vector, and we take a general potential $\phi(\mathbf{R})$ not necessarily equal to $\phi_0(z)$ in (2.1). The singlet distribution function (density profile) consistent with this potential is given by the functional derivative[2,15,16]

$$\rho(\mathbf{R}) = \frac{\delta[-\beta\Omega]}{\delta[\beta\mu - \beta\phi(\mathbf{R})]} \tag{3.2}$$

and the average number of particles in the open system is

$$\langle N \rangle = \int d\mathbf{R}\, \rho(\mathbf{R}) \tag{3.3}$$

Finally the generalized *pair correlation function* is given by a second functional derivative[2,15,16]

$$\begin{aligned}
H(\mathbf{R}_1, \mathbf{R}_2) &= \frac{\delta\rho(\mathbf{R}_1)}{\delta[\beta\mu - \beta\phi(\mathbf{R}_2)]} \\
&= \frac{\delta^2[-\beta\Omega]}{\delta[\beta\mu - \beta\phi(\mathbf{R}_1)]\, \delta[\beta\mu - \beta\phi(\mathbf{R}_2)]}
\end{aligned} \tag{3.4}$$

When we perturb about the potential $\phi_0(z)$ in (2.1), then (3.2) and (3.4) give the functions $\rho_0(z)$ and $H(z_1, z_2, r_{12})$ used in (1.1) and (1.2).

Consider now imposing a small-amplitude and long-wavelength variation of the external potential $\phi_0(z)$:

$$\begin{aligned}
\delta\phi(\mathbf{R}) &\equiv \phi_0(z - h(\mathbf{r})) - \phi_0(z) \\
&= -\phi_0'(z)\, h(\mathbf{r})
\end{aligned} \tag{3.5}$$

where we imagine $h(\mathbf{r})$ arbitrarily small so that we need keep only the lowest order terms. Note that the small parameter is the distortion $h(\mathbf{r})$ rather than the magnitude of the potential $\phi(\mathbf{R})$. Thus this formalism can also be used when there are regions where $\phi(\mathbf{R})$ is large, e.g., when considering a finite system with a hard wall. To indicate explicitly the scale of variation of $h(\mathbf{r})$, we take

$$h(\mathbf{r}) \equiv h_s(\mathbf{r}/\lambda) \tag{3.6}$$

where the parameter λ will be chosen later. By definition of the functional derivative we then have from (3.4)

$$\delta\rho(\mathbf{R}_1) = \int d\mathbf{r}_2\, dz_2\, H(z_1, z_2, r_{12})\, \beta\phi_0'(z_2)\, h_s(\mathbf{r}_2/\lambda) \tag{3.7}$$

In particular, a simple displacement of the external field, with $h(\mathbf{r}) = \delta h = $ constant, must produce a similar displacement in $\rho_0(z)$, since in the grand ensemble only the field induces inhomogeneities in the fluid. Thus $\delta\rho(\mathbf{R}) = -\rho_0'(z)\, \delta h$, and (3.7) becomes[9,17]

$$\rho_0'(z_1) = -\int d\mathbf{r}_2\, dz_2\, H(z_1, z_2, r_{12})\, \beta\phi_0'(z_2) \tag{3.8}$$

Equation (3.8) is exact and applies to one- as well as two-phase systems.

According to capillary wave theory,[5] in the presence of a finite field there is a scale L_c [see (1.3)] such that, for $r_{12} \gtrsim L_c$, the interface correlation function H decays exponentially to zero. As far as we know, this important result has not been proven rig-

orously, but it is certainly very plausible that for finite g and finite-ranged particle interactions there is *some* scale $L_c'(g)$ (which itself will diverge as $g \to 0^+$) where H decays exponentially to zero.[18] While we have every reason to believe the capillary wave prediction $L_c' = L_c$ is correct, in order to make the fewest assumptions in this paper, we admit the possibility $L_c' \neq L_c$ for the moment.

We now consider a long-wavelength distortion of the external field, i.e., a scale of variation $\lambda \gg L_c'$ in $h_s(\mathbf{r}/\lambda)$. Expanding $h_s(\mathbf{r}_2/\lambda)$ about $h_s(\mathbf{r}_1/\lambda)$ in a Taylor series, we have from (3.7) to first order

$$\delta\rho(\mathbf{R}_1) = h_s(\mathbf{r}_1/\lambda) \int d\mathbf{r}_2\, dz_2\, H(z_1, z_2, r_{12})\, \beta\phi_0'(z_2) \tag{3.9}$$

Provided that the deformations in h occur on a length scale long compared to the decay length L_c' of H, i.e., $\lambda \gg L_c'$, the contributions from the higher order terms in the Taylor series expansion can be made arbitrarily small.[19] Using (3.8), (3.9) can then be rewritten as $\delta\rho(\mathbf{R}_1) = -\rho_0'(z_1)\, h(\mathbf{r}_1)$. Thus, as an obvious generalization of the idea leading to (3.8), for sufficiently small-amplitude and long-wavelength variations in the external field, the density variations follow those of the field:

$$\phi_0(z - h(\mathbf{r})) \Rightarrow \rho_0(z - h(\mathbf{r})) \tag{3.10}$$

We are now in a position to derive (1.2). We require that the distortion of the potential satisfies

$$\int d\mathbf{r}\, h(\mathbf{r}) = 0 \tag{3.11}$$

At long wavelengths, where (3.10) holds, (3.11) implies that $\langle \delta N \rangle = \int d\mathbf{R}\, \delta\rho(\mathbf{R}) = 0$. To second order, the change in free energy Ω from the modified external field is then[20]

$$\begin{aligned}
\beta\delta\Omega &= -\frac{1}{2}\int d\mathbf{R}_1\, d\mathbf{R}_2\, \beta\delta\phi(\mathbf{R}_1)\, H(\mathbf{R}_1, \mathbf{R}_2)\, \beta\delta\phi(\mathbf{R}_2) \\
&= -\frac{1}{2}\int d\mathbf{R}_1\, d\mathbf{R}_2\, \beta\phi_0'(z_1)\, h(\mathbf{r}_1)\, H(z_1, z_2, r_{12})\, \beta\phi_0'(z_2)\, h(\mathbf{r}_2)
\end{aligned} \tag{3.12}$$

since the first-order term vanishes upon using (3.11) and (3.2). With the aid of (3.8), (3.12) can be rewritten exactly as

$$\begin{aligned}
\beta\delta\Omega = -\frac{1}{2}\int d\mathbf{R}\, \beta\phi_0'(z)\, h^2(\mathbf{r})\, \rho_0'(z) \,+ \\
\frac{1}{4}\int d\mathbf{R}_1\, d\mathbf{R}_2\, [h(\mathbf{r}_1) - h(\mathbf{r}_2)]^2\beta\phi_0'(z_1)\, H(z_1, z_2, r_{12})\, \beta\phi_0'(z_2)
\end{aligned} \tag{3.13}$$

Expanding $f(\mathbf{r}_1, \mathbf{r}_2) \equiv [h(\mathbf{r}_1) - h(\mathbf{r}_2)]^2$ in a Taylor series about $\mathbf{r}_2 = \mathbf{r}_1$, we see that the first nonzero term is $[\mathbf{r}_{12} \cdot \nabla h(\mathbf{r}_1)]^2 = x_{12}^2 |\nabla h(\mathbf{r}_1)|^2$, where we take the x axis of $\mathbf{r}_{12}$ along $\nabla h(\mathbf{r}_1)$. Noting that H is a function of $|\mathbf{r}_{12}|$ only, (3.13) to lowest order can then be written

$$\beta\delta\Omega = $$
$$-\frac{1}{2}\int d\mathbf{R}\, \beta\phi_0'(z)\, h^2(\mathbf{r})\, \rho_0'(z) + \frac{1}{2}\beta\Gamma_{\text{TZW}} \int d\mathbf{r}_1\, |\nabla h(\mathbf{r}_1)|^2 \ldots \tag{3.14}$$

(15) See, e.g.: Stell, G. In *The Equilibrium Theory of Classical Fluids*; Frisch, H. L., Lebowitz, J. L., Eds.; Benjamin: New York, 1965; p II-171. Percus, J. K. *Ibid.*, p II-33. An elementary introduction is given in section 7.5 of Balescu, R. *Equilibrium and Non-equilibrium Statistical Mechanics*; Wiley: New York, 1975.

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(18) Of course, when the particle interactions are not of finite range, but decay to zero as a power law of the distance [i.e., $r^{-\gamma}$], we expect H and C to finally cross over to a power law behavior for $r \to \infty$ and nonzero g. Though important in a careful mathematical treatment (see, e.g., ref 10), this crossover is physically not very relevant, since on length scales of $O(L_c)$, the capillary wave contributions to H are much larger than those from the direct power law interactions (For $d < 3$, the capillary wave contribution is $O(1)$ at L_c). Thus, in the limit $g \to 0^+$ the power law contribution becomes arbitrarily small. However, if the power γ is sufficiently small, capillary waves may be suppressed altogether. See, e.g., the anisotropic van der Waals model of ref 16, where the interface is "stiff". The situation is similar to the one in critical phenomena, where it has been shown that as $\xi_B \to \infty$, power law interactions do not affect the critical behavior, and in particular the exponent η, provided the power γ is large enough (see, e.g.: Sak, J. *Phys. Rev. B* **1973**, *88*, 281 and references therein).

(19) Note that if we have power law interactions as discussed in ref 18, the expansion (3.9) is only asymptotic.

(20) This same approach was taken by Weeks et al.[16] (see Appendix C) in deriving the TZ formula (1.1). See also ref 11.

where

$$\beta\Gamma_{TZW} \equiv$$

$$\frac{1}{2(d-1)} \int dz_1 \int dz_2 \; \beta\phi'_0(z_1) \; \beta\phi'_0(z_2) \int d\mathbf{r}_{12} \; r_{12}^2 H(z_1, z_2, r_{12})$$

(3.15)

Note that it is because we have a nonzero external field ($g > 0$) that the correlation function H vanishes at large $|\mathbf{r}_{12}|$ and (3.15) is well-defined. If the scale of variation of $h(\mathbf{r})$ satisfies $\lambda \gg L_c'$, then the higher order terms in the Taylor series in (3.14) (indicated by ...) again make negligible contributions, and (3.14) is an arbitrarily accurate approximation to (3.13). In precisely the same limit, we know from (3.10) that the field induces a long-wavelength density variation $\delta\rho(\mathbf{R}) = -\rho'_0(z) \, h(\mathbf{r})$; the accompanying change in area of the distorted Gibbs dividing surface is then

$$\delta A = \frac{1}{2} \int d\mathbf{r} \; |\nabla h(\mathbf{r})|^2$$

(3.16)

Hence for long-wavelength distortions the last term in (3.14) involves the change in area of the Gibbs dividing surface induced by the field, while the first term involves work against the external field (see (3.17) below).

Under these conditions, we can identify $\beta \, \delta\Omega$ in (3.14) with the *thermodynamic* prediction for the free energy change induced by a macroscopic distortion of the Gibbs dividing surface. This same idea forms the basis for capillary wave theory[3] and was a key step in the derivation of the original TZ formula.[1]

There are two terms in the thermodynamic approach: work given by the change in area of the distorted surface times the macroscopic surface tension σ and work against the external field. The latter term gives

$$\beta\delta V = \int d\mathbf{R} \; \beta\phi_0(z) \; \delta\rho(\mathbf{R})$$

$$= \frac{1}{2} \int dz \; \beta\phi_0(z) \; \rho''_0(z) \int d\mathbf{r} \; h^2(\mathbf{r})$$

$$= -\frac{1}{2} \int dz \; \beta\phi'_0(z) \; \rho'_0(z) \int d\mathbf{r} \; h^2(\mathbf{r})$$

(3.17)

where we have expanded $\delta\rho(z, h(\mathbf{r}))$ to second order, since the first-order correction to δV vanishes on using (3.11), and integrated by parts. Using (3.16) for the change in area, the total thermodynamic free energy change is then

$$\beta\delta W = -\frac{1}{2} \int d\mathbf{R} \; \beta\phi'_0(z) \; h^2(\mathbf{r}) \; \rho'_0(z) + \frac{1}{2}\beta\sigma \int d\mathbf{r} \; |\nabla h(\mathbf{r})|^2$$

(3.18)

where σ is the (macroscopic) surface tension (or surface stiffness in an anisotropic fluid[16]) in the presence of the field ϕ_0. The first term reduces to the usual capillary wave expression $(1/2)mg\Delta\rho \int d\mathbf{r} \; h^2(\mathbf{r})$ on using the explicit expression (2.1) for ϕ_0.[21]

Comparing the thermodynamic result (3.18) with (3.14), we have $\Gamma_{TZW} = \sigma$; thus (3.15) or (1.2) is our desired expression for the surface tension. We believe this derivation makes it clear that (3.15) is indeed an exact expression for the surface tension provided the following important points are kept in mind. (i) There must be a nonzero external field for these expressions to make sense, though the external field strength can be taken arbitrarily small. (ii) Thus, strictly speaking, Γ in (3.15) represents the surface tension in the presence of a weak external field, but the field dependence is that of the macroscopic σ in (3.18), which we know to be negligibly small as $g \to 0^+$. As recognized by Wertheim,[9] this implies that H must have long-ranged correlations as $g \to 0^+$, so that Γ indeed reaches a finite limit independent of g. (iii) Because of the long-ranged correlations, the system size L must be much greater than L_c', the range of correlations in H. (Strictly speaking, the thermodynamic result (1.2) applies only in the limit

$L \to \infty$, so we imagine taking the limit $L \to \infty$ before letting $g \to 0^+$. However, for $L \gg L_c'$ there should be essentially no difference in the two expressions.) Note that it is *only* for variations $h(\mathbf{r})$ whose scale of variation satisfies $\lambda \gg L_c'$ that we can (a) justify the truncation of the Taylor series expansion of $[h(\mathbf{r}_1) - h(\mathbf{r}_2)]^2$ in (3.13) to lowest order as in (3.14) and (b) identify the resulting $|\nabla h|^2$ term with the change in area of the distorted Gibbs surface on the basis of (3.10). Both these conditions are required to identify $\beta \, \delta\Omega$ in (3.13) with the thermodynamic result (3.18).

IV. Derivation of the TZ Formula (1.1)

In contrast, we argue that the TZ formula (1.1), while equivalent to (1.2) in the thermodynamic limit $L \to \infty$, also gives a good approximation to σ even in small systems with $O(\xi_B) \lesssim L \ll L_c'$. In such a small system, long-ranged horizontal correlations are not possible, and we expect that the classical ideas of van der Waals should hold approximately.[4] Thus the TZ formula can indeed provide some insight and justification for the classical approach. As the system size is increased, we enter the nonclassical regime dominated by long-wavelength fluctuations between distant parts of the interface. It is only in this latter regime that the TZW formula (1.2) is correct. Hence the TZ formula (1.1) can be thought of as a bridge taking us from classical to nonclassical behavior as the system size L is increased.

As we will see, the formal steps leading to our derivation of the TZ formula (1.1) closely follow those we have just taken to derive (3.15) and to identify Γ with σ in (3.18). However, a crucial new feature is that manipulations involving the direct correlation function are most naturally carried out in a *different ensemble* where the density $\rho(\mathbf{R})$, rather than the external field $\phi(\mathbf{R})$, is the independent variable.[2,15,16] Thus we can directly impose an arbitrary density variation on the system. The density functional formalism will, in effect, determine the (complicated) external field needed to produce a given density variation on smaller length scales where (3.10) no longer holds. Once the density variation is prescribed, we can immediately determine the change in area of the Gibbs dividing surface. Furthermore, as we argue below, the thermodynamic expression (3.18) remains approximately valid for finite L, even with $L_c \gg L \gtrsim O(\xi_B)$. Thus the identification of the density functional and thermodynamic expressions for the change of free energy with interface distortion can be made under less restrictive conditions, leading to a much greater range of validity of the TZ formula.

The appropriate free energy F for the density functional approach[2,15,16] is based on a Legendre transformation of the grand ensemble free energy Ω in (3.1):

$$\beta F = \beta\Omega + \int d\mathbf{R} \; \rho(\mathbf{R})[\beta\mu - \beta\phi(\mathbf{R})]$$

(4.1)

where F is a functional of the density $\rho(\mathbf{R})$. From the properties of the Legendre transformation, the external field $\phi(\mathbf{R})$ consistent with a given $\rho(\mathbf{R})$ satisfies a relation reciprocal to (3.2):

$$\frac{\delta\beta F}{\delta\rho(\mathbf{R})} = \beta\mu - \beta\phi(\mathbf{R})$$

(4.2)

A second functional derivative gives the (generalized) *direct correlation function*

$$C(\mathbf{R}_1, \mathbf{R}_2) = \frac{\delta[\beta\mu - \beta\phi(\mathbf{R}_1)]}{\delta\rho(\mathbf{R}_2)}$$

$$= \frac{\delta^2\beta F}{\delta\rho(\mathbf{R}_1) \; \delta\rho(\mathbf{R}_2)}$$

(4.3)

For $\rho(\mathbf{R}) = \rho_0(z)$, (4.2) and (4.3) give the functions $\phi_0(z)$ and $C(z_1, z_2, r_{12})$ appearing in the TZ formula (1.1). From (3.4), (4.3), and (4.1), we see that C is the inverse of H:

$$\int d\mathbf{R}_3 \; H(\mathbf{R}_1, \mathbf{R}_3) \; C(\mathbf{R}_3, \mathbf{R}_2) = \delta(\mathbf{R}_1 - \mathbf{R}_2)$$

(4.4)

To find the analogue of (3.8), rather than physically changing the density $\rho_0(z)$ and the associated field $\phi_0(z)$, we calculate the

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(21) Note that the potential energy term is positive for all (long-wavelength) density fluctuations satisfying (3.11), since we consider distortions relative to the equilibrium Gibbs dividing surface at $z = 0$, whose position is set by $\phi_0(z)$.

change formally induced by a small vertical shift δh in the entire system, including wall potentials, if present. Thus $\delta\rho(z) = \rho_0(z-\delta h) - \rho_0(z)$ and $\delta\phi(z) = \phi_0(z-\delta h) - \phi_0(z)$. As $\delta h \rightarrow 0$, we have from (4.3) the exact result

$$-\beta\phi'_0(z_1) = \int d\mathbf{r}_2 \, dz_2 \, C(z_1,z_2,r_{12}) \, \rho'_0(z_2) \qquad (4.5)$$

We can derive the TZ formula (1.1) directly from (3.15), using (4.5) and (4.4), but this would not indicate the greater utility of the TZ formula in systems with finite $L < L_c$, where (3.15) no longer holds. Further, there have been some questions raised about the validity of these formal manipulations and the nature of C as $L \rightarrow \infty$ for $d = 3$.[10-12] Thus it is quite useful to consider first a system with L some finite multiple of the bulk correlation length ξ_B, but much less than L_c. We see no reason to doubt the applicability of density functional methods to such a system (provided of course that $g > 0$!), and we can later examine whether the complications arise as $L \rightarrow \infty$.

For finite systems, as argued by Weeks,[4] the most natural description of interfacial properties arises in the *canonical* ensemble, where the number of particles, N, is fixed, and chosen so that the Gibbs dividing surface is at $z = 0$, consistent with the field $\phi_0(z)$. This suppresses the trivial zero wave vector vertical translation of the Gibbs dividing surface as a whole produced by fluctuations in particle number N; these cause the interface width as measured in the *grand* canonical ensemble to diverge in the limit $g \rightarrow 0^+$ with L fixed.[4,22] Clearly it is the "intrinsic" structure of the interface unbroadened by such translations that is envisioned in the classical picture and that is measured in computer simulations. (Strictly speaking, L_z should be taken finite as well in order to prevent even the canonical interface width from diverging as $g \rightarrow 0^+$. See the Appendix for a discussion of this and other related subtleties.)

We use the flexibility of the density functional formalism to choose canonical densities and correlation functions in the following. We note that the above derivation of (4.5) is valid in the canonical as well as in the grand ensemble,[23] and for our system with periodic boundary conditions, it holds also for finite L without any boundary corrections in the transverse directions. We argue in the Appendix that boundary corrections from the top and bottom walls in (4.5) are negligible for z_1 in the interface region, while for the analogous result, (3.8), such boundary corrections are essential in a finite system.

The surface tension σ_L in a finite system can be computed by molecular dynamics techniques using the Kirkwood–Buff formula; these calculations[2,24] have shown that it differs by only a relatively small amount from the infinite system limit σ. The differences between σ and σ_L mainly involve "unfreezing" longer wavelength capillary waves, which carry very little free energy provided L is at least of $O(\xi_B)$.[4,25]

In the same way, we expect that if we impose a small-amplitude density perturbation $\delta\rho(\mathbf{R}) = \rho_0(z-h(\mathbf{r})) - \rho_0(z)$ on this finite

system, the thermodynamic result (3.18) will still remain approximately valid, with some $\sigma_L \approx \sigma$. This idea forms the basis for Weeks' interpretation of capillary wave theory:[4] even down at scales of $O(\xi_B)$ one can approximately describe the free energy change for small distortions of the interface using the thermodynamic argument leading to (3.18). Note that since the density is now the independent variable, we can require tht $|\nabla h(\mathbf{r})|$ is small enough that the quadratic approximation to the change in area of the distorted surface, used in (3.18), is accurate. With this proviso, (3.18) should describe the free energy change for *arbitrary* small-amplitude distortions of the Gibbs dividing surface.

Our strategy now parallels that of section III. We evaluate the free energy change for such a small-amplitude distortion from the density functional formalism and equate this to (3.18). Again requiring that (3.11) holds, so the first-order term vanishes, we find immediately from (4.2), (4.3), and (4.5), the analogue of (3.13):

$$\beta\delta F = -\frac{1}{2}\int d\mathbf{R} \, \rho'_0(z) \, h^2(\mathbf{r}) \, \beta\phi'_0(z) - $$
$$\frac{1}{4}\int d\mathbf{R}_1 \, d\mathbf{R}_2 \, [h(\mathbf{r}_1) - h(\mathbf{r}_2)]^2 \rho'_0(z_1) \, C(z_1,z_2,r_{12}) \, \rho'_0(z_2) \quad (4.6)$$

Expanding $h(\mathbf{r}_2)$ about $h(\mathbf{r}_1)$ in a Taylor series we get the analogue of (3.14):

$$\beta\delta F = $$
$$-\frac{1}{2}\int d\mathbf{R} \, \rho'_0(z) \, h^2(r) \, \beta\phi'_0(z) + \frac{1}{2}\beta\Gamma_{TZ}\int d\mathbf{r} \, |\nabla h(\mathbf{r})|^2 + \dots \quad (4.7)$$

where

$$\beta\Gamma_{TZ} = $$
$$-\frac{1}{2(d-1)}\int dz_1 \int dz_2 \, \rho'_0(z_1) \, \rho'_0(z_2) \int d\mathbf{r}_{12} \, r_{12}{}^2 C(z_1,z_2,r_{12}) \quad (4.8)$$

and where ... stands for the contributions from higher order terms in the Taylor series.

In contrast to (3.14), the $|\nabla h(\mathbf{r})|^2$ term in (4.7) is now known to represent the change in area of the Gibbs surface, even for $L < L_c$, since this density variation was *imposed* from the outset. Moreover, since the form of the thermodynamic result (3.18) remains valid for *arbitrary* small-amplitude $h(\mathbf{r})$, (provided only that $|\nabla h(\mathbf{r})| \ll 1$), we conclude from comparison with (4.6) and (4.7) that the higher order terms in the Taylor series in (4.7) must be small, and that

$$\Gamma_{TZ} \approx \sigma_L \qquad (4.9)$$

where σ_L is the (finite system) surface tension appearing in (3.18) with L finite. In the limit $L \rightarrow \infty$, $\sigma_L \rightarrow \sigma$, and the neglect of higher order terms can be justified more rigorously as in section III. Then (4.9) reduces to the original TZ formula (1.1).

From the above analysis, we can draw the following conclusions. (i) The unimportance of the higher order terms in the expansion implies that the higher order moments along the interface of

$$\tilde{C}(r_{12}) \equiv \int dz_1 \int dz_2 \, \rho'_0(z_1) \, C(z_1,z_2,r_{12}) \, \rho'_0(z_2) \qquad (4.10)$$

must each be small. While one could imagine an accidental cancellation of higher order terms for some particular distortion, the equality of (3.18) and (4.6) for a variety of distortions is possible only if all higher order terms are small. Thus the projection $\tilde{C}$ of C onto ρ'_0 as in (4.10) *must be short-ranged* along the interface. As we discuss below in section V, this result is in agreement with the predictions of capillary wave theory. (ii) Since (4.10) suggests that C is short-ranged, a reasonable order of magnitude approximation in a small system with L of $O(\xi_B)$ is to replace C by its bulk phase value. This is the local OZ approximation of TZ, and (4.8) then reduces to the classical square gradient formula of van der Waals. In such a small system the density profile $\rho'_0(z)$ represents the "intrinsic" profile, unbroadened by capillary wave fluctuations, consistent with the OZ approximation and classical ideas. In our interpretation, this approach

(22) The difference between the two ensembles, discussed in great detail in ref 4 and 16, essentially concerns only the treatment of the $k = 0$ translation mode. These differences can be important, since in the grand ensemble only the external field prevents large fluctuations in N; indeed, for fixed system size and arbitrarily small g, these fluctuations can wash out the profile.[4] On the other hand,[4,16] for large systems with L_z and $L \gg L_c$, the field suppresses fluctuations in N and the density profiles in the two ensembles become the same, both being predominately determined by *nonzero* wave vector fluctuations between different parts of the interface. Note also that, in the canonical ensemble, the inverse C of H is defined for nonzero wave vectors only, because H is normalized such that $\int d\mathbf{R}_2 \, H(\mathbf{R}_1,\mathbf{R}_2) = 0$. See eq D.4 of ref 16.

(23) Thus (4.5) holds exactly for both the grand canonical profile and correlation functions, which for small system sizes are broadened by the $k = 0$ translation mode, as well as when the more "classical" canonical functions are used. This illustrates the flexibility of the density functional formalism, where we can choose the appropriate densities and ensembles to fit our purposes.

(24) See, e.g.: Sikkenk, J. H.; Indekeu, J. O.; van Leeuwen, J. M. J.; Vossnack, E. O. *Phys. Rev. Lett.* **1987**, *59*, 98.

(25) See also: Sengers, J. V.; van Leeuwen, J. M. J. *Phys. Rev. A* **1989**, *39*, 6346, and van Leeuwen, J. M. J.; Sengers, J. V. Capillary Waves of a Vapor-Liquid Interface in a Gravitational Field Very Close to the Critical Temperature (preprint) for an analysis of the wave vector dependence of σ_L on scales larger than $O(\xi_B)$.

is successful because σ_L for a small system is a good approximation to the thermodynamic quantity σ.

V. Relation to Capillary Wave Model

In the previous section, we have seen that the TZW formula (1.2) explicitly predicts that long-range correlations develop at an interface in the limit $g \rightarrow 0^+$. To our knowledge, the only possible source of such correlations are the long-wavelength capillary waves. However, doubts continue to be expressed about the applicability of the standard capillary wave model as well as the validity of the TZ formula,[10-12] particularly for $d = 3$.

We believe all these criticisms can be dealt with, provided one takes proper account of the external field. A detailed discussion of these issues and an analysis of the correlation functions H and C in the capillary wave model for $d = 3$ will be given elsewhere,[26] so we confine ourselves here to a few brief remarks. As stated earlier, it is easy to verify that the TZW formula (1.2) is satisfied identically in the capillary wave model. In this approach C is calculated through an explicit inversion of H with the aid of (4.4); in line with the remarks made in section II, this has to be done in finite field g, since only then does H decay at large distances $r \gg L_c$. We find[26] that if this is done carefully by taking the limit $g \rightarrow 0^+$ ($L_c \rightarrow \infty$) only at the final stage of the calculation, one properly recovers the expected behavior and obtains agreement with the general results of the earlier sections.

Another important finding of this paper is the fact that

$$\tilde{C}(r_{12}) = \int dz_1 \int dz_2 \, \rho'_0(z_1) \, C(z_1,z_2,r_{12}) \, \rho'_0(z_2) \quad (5.1)$$

should be short-ranged [cf. (4.10)]. More specifically, the fact that (4.6), (4.7), and (3.18) should be essentially equivalent for arbitrary $h(\mathbf{r})$ and all system sizes $L \gtrsim O(\xi_B)$ leads us to conclude that

$$\tilde{C}(r_{12}) \approx c_1 \delta(\mathbf{r}_{12}) + \beta\sigma\nabla^2\delta(\mathbf{r}_{12}) \quad (5.2)$$

Here $\delta(\mathbf{r})$ is understood to be a delta function on the scale $r \gtrsim O(\xi_B)$. Note that the first term proportional to $\delta(\mathbf{r}_{12})$ does not contribute to the surface tension[27] and that we have left out any higher derivatives of $\delta(\mathbf{r})$ on the basis of the earlier observation that these terms should be small on scales larger than ξ_B. It is straightforward to verify (5.2) explicitly for the capillary wave model in *all* dimensions,[5,26] so that both the TZ formula and the TZW formula are satisfied *identically* in capillary wave theory.

Although on the basis of the TZ formula alone one can only draw conclusions regarding $\tilde{C}$, we can use capillary wave theory to determine the essential structure of C for $d \leq 3$. We find[26,28] for fixed $z_1, z_2 \ll W$ and $r_{12} \ll L_c$

$$C(z_1,z_2,r_{12}) \approx \frac{\beta\sigma}{\Delta\rho\rho'_0(z_1)} \, \delta(z_1-z_2) \, \nabla^2\delta(\mathbf{r}_1-\mathbf{r}_2) \quad (5.3a)$$

$$= \frac{\beta\sigma}{\Delta\rho} \, \delta[\rho_0(z_1) - \rho_0(z_2)]\nabla^2\delta(\mathbf{r}_1-\mathbf{r}_2) \quad (5.3b)$$

For $d = 2$, (5.3) is exact on *all* length scales in the capillary wave model.[5] In retrospect, one could probably have guessed the form of (5.3a) for $d < 3$, since it is the simplest form that is short-ranged in both z and r and still obeys the scaling relations given by Bedeaux and Weeks.[5] However, note that we also obtain this form[26] for $d = 3$, even though here scaling only holds for $r \gtrsim L_c$. Above three dimensions, however, H and C develop power law behavior[14,5] on scales $\xi_B \ll r \ll L_c$; as a result C does not reduce to the form (5.3) for $d > 3$.

VI. Final Remarks

Capillary wave theory exploits the same fundamental idea that is used in the derivation of the TZ formula: the change in free energy for long-wavelength interface distortions is given by the surface tension times the change in area. It offers a physical picture that helps us understand the limiting processes that must be taken to properly treat the complex interplay between the long-wavelength interface fluctuations, the external field, and finite system size effects. Combining these insights with the powerful formal methods of density functional theory gives us a deeper understanding of interface structure than would be possible from either approach alone. We believe this is one of the main uses of the density functional formulas involving σ. They provide insight into the logical consistency of various descriptions of interface structure, and, given an appropriate theory, they can yield expressions useful in practical calculations. On the other hand, in molecular dynamics simulations, a determination of the net stresses as in the Kirkwood–Buff formula[2,24] will almost surely be a simpler and more accurate way of calculating the numerical value of σ. A similar situation is seen for the compressibility formula for the pressure, which is the bulk analogue of the TZ formula.[2] In simulations, the virial pressure is the preferred route, but the compressibility formula provides an important consistency check on theories for liquid structure. Indeed, several of the most accurate integral equation theories for liquid structure require consistency between the virial and compressibility pressures.[29]

We have seen the remarkable robustness of the TZ formula: its (approximate) validity for small "classical" systems as well as for large systems dominated by long-wavelength fluctuations. This is in large part a consequence of its derivation using an ensemble where the density is the external variable. This freedom can be exploited in other situations where density functional methods are used; e.g., the theory of freezing, where a "broken symmetry" periodic singlet density is assumed for the solid phase.[30]

Our work has more general implications. There have been several attempts to show directly the equivalence of the TZ and Kirkwood–Buff[8] formulas for the surface tension.[31] However, the first step in every attempt has been to transform the TZ formula (1.1) to the TZW formula (1.2). In this representation, one must explicitly deal with the long-ranged interface correlations, and the thermodynamic limit must be taken with great care, taking account of the external fields. This remark applies equally well to studies of the wetting transition that make use of the analogue of the TZW formula, where we believe some of the literature is misleading. We agree with Requardt and Wagner[10] that to date no demonstration of the equivalence of the TZ and TZW formulas can be considered completely satisfactory. Of course, given the sound thermodynamic basis of these formulas, we have no doubts that such a rigorous demonstration could be carried out, particularly if insights from the capillary wave picture are used to guide the formal analysis. The key idea that needs to be proven rigorously, and then exploited in the demonstration of the equivalence using the TZW formula, is the decay of correlations in H at sufficiently large distances in the presence of a finite external field.

Appendix: Finite Size Effects and Boundary Corrections

In section IV, we considered the interface in a canonical system of finite lateral size L in order to study the "intrinsic" structure of the interface, unbroadened by zero wave vector fluctuations. Strictly speaking, however, the vertical length L_z also should be finite to suppress these fluctuations. Otherwise, in the case L_z

(26) Weeks, J. D.; van Saarloos, W.; Bedeaux, D.; Blokhuis, E. Preprint. See ref 16 for a discussion of earlier objections to the capillary wave model.

(27) The value of c_1 can be determined by using (4.5).

(28) As was done for $\tilde{C}$, we omit a term proportional to $\delta(\mathbf{r})$ that may also arise. See ref 26 for further details.

(29) See, e.g.: Rogers, F. J.; Young, D. A. *Phys. Rev. A* **1984**, *24*, 999.

(30) See, e.g.: Haymet, A. D. J.; Oxtoby, D. W. *J. Chem. Phys.* **1986**, *84*, 1769.

(31) See ref 10 for a critical review of this work. The most straightforward attempt is found in: Waldor, M. H.; Wolf, D. E. *J. Chem. Phys.* **1986**, *85*, 6082. However, in addition to problems that arise in taking the thermodynamic limit, which the authors recognize, we believe their eq 17 is incorrect. The form $(-\beta^{-1}\partial_{i3} + F_{i3})(-\beta^{-1}\partial_{j3} + F_{j3})\exp(-\beta W)$ should read instead $\exp(\beta W)[(-\beta^{-1}\partial_{i3} + F_{i3})\exp(-\beta W)][(-\beta^{-1}\partial_{j3}) + F_{j3})\exp(-\beta W)]$. With this form of eq 17, we have not been able to prove the equivalence of the Kirkwood–Buff and the TZ formulas, using the type of analysis of Waldor and Wolf.

→ ∞ with L finite, in the limit $g \to 0^+$ the liquid phase could break up into multiple domains by the creation of more than one interface, in order to take advantage of the entropy gain associated with the increased wandering of the domains. (A similar argument explains the lack of long-ranged order in the one-dimensional Ising model.) Alternatively, consider a canonical system with a single liquid domain containing two interfaces in an infinitely long column with a symmetric potential $\phi_0(z) = \phi_0(-z)$ that tends to locate the center of the domain near $z = 0$. Clearly, this system also develops diverging zero wave vector fluctuations as the field strength tends to zero.

We now discuss some of the additional complications that one encounters in an analysis of a system with finite L and L_z. The classical picture is most naturally realized in a finite system with short-ranged wall potentials at $z = \pm L_z/2$ chosen to induce phase separation.[4] It suffices to impose a "hard wall" condition $\phi_0(z) = \infty$ for $|z| > L_z/2$ and to incorporate into $\phi_0(z)$ for z near the lower wall at $z = -L_z/2$ an additional short-ranged attractive term that favors wetting by the denser (liquid) phase. Otherwise, as before, we take $\phi_0(z) = mgz$ with g arbitrarily small.

For such a finite system with L_z and L of $O(\xi_b)$, a nearly classical picture holds provided we use a canonical ensemble description,[4] where the number of particles, N, is fixed and chosen so that the Gibbs dividing surface is at $z = 0$, consistent with the potential $\phi_0(z)$. With this setup, we expect to find an "intrinsic" interface whose properties are essentially unchanged as $g \to 0^+$,

i.e., as the potential becomes arbitrarily weak in the interfacial region.

In principle, with L_z finite there are contributions in (4.5) from the top and bottom boundaries of our system.[9] Since $\rho(z)$ vanishes for $|z| > L_z/2$, the following boundary terms are generated by (4.5): $C_0(-L_z/2, z_2)\rho_{lw} - C_0(L_z/2, z_2)\rho_{vw}$. Here $C_0(z_1,z_2)$ denotes the integral over $\mathbf{r}_2$ of $C(z_1,z_2,r_{12})$ and ρ_{lw} and ρ_{vw} are the densities at the bottom and top walls. Using the definition (4.3), we expect that a given density change near the wall should correspond to a potential essentially localized near the wall, since the wall damps out long-ranged correlations. Thus the boundary corrections should be negligible for z_2 near 0 in the interfacial region.

The same "shift" argument used to derive (4.5) can be repeated to give a more general derivation of (3.8), valid for finite systems and in the canonical as well as the grand ensemble. In the grand ensemble, with L_z infinite and L of $O(\xi_b)$, (3.8) holds true, not because of long-ranged "horizontal" correlations, but because of long-ranged "vertical" correlations caused by fluctuations in N as $g \to 0^+$. In the canonical ensemble, with L_z and L of $O(\xi_b)$, boundary corrections from the top and bottom walls, yielding terms like $H_0(\pm L_z/2, z_2)$, allow (3.8) to continue to hold as $g \to 0^+$. Note that because of conservation requirements in the canonical ensemble and the small system size, the density displacement induced by a change in potential near the wall could have substantial effects on the density profile in the interfacial region. Thus, boundary corrections are more important in (3.8) than in (4.5).

Measures of Effective Ergodic Convergence in Liquids

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The recently introduced measure for ergodic convergence is used to illustrate the time scales needed for effective ergodicity to be obtained in various liquids. The cases considered are binary mixtures of soft spheres, two-component Lennard-Jones systems, and liquid water. It is shown that various measures obey a dynamical scaling law which is characterized by a single parameter, namely, a novel diffusion constant. The time scales for ergodic behavior are found to be dependent on the particular observable being considered. For example, in water, the diffusion constants for the translational and rotational kinetic energies and for the laboratory frame dipole moments are very different. The implications of these results for the calculation of the dielectric constant of polar liquids by computer simulations are discussed.

I. Introduction

The ergodic hypothesis is one of the central concepts in the development of the statistical mechanical theory of thermodynamics.[1] This hypothesis states that time averages and ensemble averages are identical for a system in thermodynamic equilibrium. The ergodic hypothesis provides a connection between the results obtained from analyzing the trajectory of a many-particle system, generated in computer simulations of the dynamics of molecular motions, to the results calculated by using the more abstract notion of an ensemble. An ensemble characterizes the various equilibrium states of the system. In computer simulation studies, estimates of these observable properties are obtained as time averages of functions, called phase-space functions, of the coordinates and momenta of the particles making up the system. Let $f(t)$ be a phase-space function whose time average is a physically observable quantity. The ergodic hypothesis asserts that

$$\lim_{T \to \infty} \frac{1}{T} \int_0^T dt \, f(t) = \langle f \rangle \tag{1.1a}$$

where the $\langle \ \rangle$ indicate an ensemble average. The appropriate ensemble for constant-energy, constant-volume molecular dynamics simulations is the microcanonical ensemble. For a system with a given Hamiltonian $H(p,q)$ and total energy E_0, averages are expressed as

$$\langle f \rangle = \int d\Gamma \, \delta(H(p,q) - E_0) \, f(\Gamma) \Big/ \int d\Gamma \, \delta(H(p,q) - E_0) \tag{1.1b}$$

and the integration is over the phase space Γ of the system.

It should be emphasized that there does not appear to be any uniform definition of ergodicity in the literature.[2] As was ori-

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(1) A good discussion of ergodic theory in statistical mechanics is provided by: Wightman, A. S. In *Statistical Mechanics at the turn of the Decade*; Cohen, E. G. D., Ed.; Mercel Decker: New York, 1971; pp 1–32.