Capillary waves and the inherent density profile for the liquid-vapor interface

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The statistical mechanical theory of the density distribution through the liquid-vapor interface has been re-examined for single-component monatomic substances. Particles are covered by spheres with radii such that uncovered volume is globally connected throughout the vapor but disconnected throughout the liquid. This approach in turn allows: (1) identification of an "outermost layer" of particles on the liquid, (2) definition of capillary wave collective coordinates for the surface, and (3) recognition of an "inherent density profile" for the interface that for $T < T_c$ retains finite width even as the gravitational field strength vanishes. This latter profile is free of any arbitary parameters (such as capillary wave cutoffs), is a nonmonotonic function of normal distance through the interface, and is expected to reflect the diverging bulk-phase correlation lengths as $T \to T_c$.

I. INTRODUCTION

Over fifteen years have passed since capillary waves were proposed as collective coordinates basic to determination of the liquid-vapor interface profile.[1] Nevertheless, their precise role in the statistical mechanical theory of phase coexistence has remained controversial. To a large extent, the controversy stems from the prediction of the capillary wave approach that in the conventional large system limit the interfacial width should increase as $(-\ln g)^{1/2}$ when the gravitational constant g goes to zero. This seemingly contradicted the view, widely held even today, that an inherent density profile ought to exist independently of gravity. Such a profile is presumed to have a finite width dependent only on temperature, with divergence occurring only as the critical point is approached. The prototype for this latter point of view was supplied long ago by van der Waals,[2] and it has subsequently received many elaborations. Several review articles are available discussing both of these points of view, indicating their apparent merits and weaknesses.[3-5] However no fully satisfactory synthesis has emerged.

From the standpoint of fundamental statistical mechanics of phase coexistence, the central problem concerns precise definition of collective capillary wave coordinates, their separation from the remainder of the many-body problem, and examination of the interface structure when those capillary waves are constrained to zero amplitude (thus giving the "inherent density profile"). No artificial parameters should be introduced in the analysis (such as upper wave-vector cutoffs for capillary modes) which cannot naturally and uniquely be evaluated from molecular properties of the system itself. Even if such a theoretical program can be carried to completion, it is not a foregone conclusion that the resulting gravity-free inherent density profile will satisfy a functional equation of the van der Waals genre.

The point of this paper is to propose an approach to interfacial structure which satisfies the above criteria. The inherent density profile that emerges is a nonmonotonic function of normal distance through the interface, and for that reason the present method may be repugnant to adherents of the van der Waals tradition.

Our analysis begins in Sec. II with an examination of a special percolation process defined on the molecular distribution for the system in a state of liquid-vapor phase coexistence. This leads to identification of an outermost layer of molecules for the denser liquid phase. Section III introduces capillary waves using the coordinates of this outermost molecular layer. The areal density of the monolayer determines precisely the number of available capillary waves and thereby eliminates any ambiguity connected with an upper cutoff for these modes. Section IV discusses the inherent density profile that emerges from the analysis in the $g \to 0$ limit, stressing the necessity that it be nonmonotonic. Fluctuations in capillary wave coordinates and their relationship to "bare" and experimental surface tensions for the interface form the subject for Sec. V. The final section (Sec. VI) offers discussion of several relevant issues, including the role that computer simulation might play in quantifying the theoretical ideas presented here.

II. VOID PERCOLATION AND SURFACE PARTICLES

The grand ensemble provides a convenient representation for the coexisting liquid-vapor system. The corresponding grand partition function has the following form:

$$Z_G = \sum_{N=0}^{\infty} (y^N/N!) \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N \exp(-\beta \Phi_t) , \qquad (2.1)$$

where as usual β stands for $(k_B T)^{-1}$, and y is the absolute activity. The total potential energy Φ_t includes both intermolecular interactions Φ and external field interactions U.

$$\Phi_t(\mathbf{r}_1 \cdots \mathbf{r}_N) = \Phi(\mathbf{r}_1 \cdots \mathbf{r}_N) + \sum_{j=1}^{N} U(\mathbf{r}_j) . \qquad (2.2)$$

The external potential U in turn contains interaction with the container wall U_w as well as the gravitational interaction

$$U(\mathbf{r}) = U_w(\mathbf{r}) + mgz . \qquad (2.3)$$

Here m is the molecular mass, g is the gravitational constant, and the coordinate system has been aligned with its z axis along the gravitational "vertical."

The distribution of matter within the container de-

scribed by U_w is specified by the singlet density function $\rho^{(1)}(\mathbf{r})$. This function and its higher-order analogs $\rho^{(2)}$, $\rho^{(3)}$, ... are given by the formal expression

$$\rho^{(n)}(\mathbf{r}_1 \cdots \mathbf{r}_n) = Z_G^{-1} \sum_{N=n}^{\infty} [y^N / (N-n)!]$$

$$\times \int d\mathbf{r}_{n+1} \cdots \int d\mathbf{r}_N \exp(-\beta \Phi_t) . \quad (2.4)$$

If y is properly chosen for the given temperature then both liquid and vapor macroscopic phases can coexist within the system. The location of those phases is sensitive to the form of U. Gravity normally would cause the denser liquid to settle on the bottom of the vessel with the vapor above. However if gravity is sufficiently weak, or indeed absent altogether, then the distribution of the phases would be controlled by U_w, and would depend specifically on whether or not the liquid could wet the vessel walls.

For present purposes we will suppose that gravity controls the location of the phases, with liquid macroscopically confined to the bottom of the container $(g > 0)$. Away from the container walls the interface will be planar and horizontal and thus the singlet density $\rho^{(1)}$ should depend only on the coordinate z. If g is small enough to allow one to disregard hydrostatic compression within the bulk liquid and vapor, then $\rho^{(1)}(z)$ for increasing z should decline essentially from ρ_l to ρ_v (the coexisting liquid and vapor densities) over an interval defining the interfacial zone. It has been the contention of the capillary wave viewpoint that this zone width increases without bound as $g \to 0$, reflecting instability of the interface in that limit with respect to long wavelength transverse distortions.

For simplicity in the following development we will assume that the molecules are spherically symmetric so that vectors $\mathbf{r}_1 \cdots \mathbf{r}_N$ only specify positions. The case of nonspherical polyatomic molecules raises certain technical complications not really germane to the basic matter at hand. It should be borne in mind however that the presumption of spherical symmetry does not necessarily restrict Φ to pairwise additive form.

For any instantaneous configuration $\mathbf{r}_1 \cdots \mathbf{r}_N$ of the molecules in the system surround the center of each molecule by a sphere with radius s. If the temperature T is well below its critical value T_c then $\rho_l \gg \rho_v$, and a rather wide range of s values

$$s_1(T) < s < s_2(T) \quad (2.5)$$

will exist such that volume Ω uncovered by s spheres in the system is (a) globally connected throughout essentially all of the upper vapor phase, and (b) sparse and disconnected throughout the liquid phase. In the language of percolation processes,[6] we would say that Ω is above its percolation threshold in the vapor phase, but below that threshold in the liquid phase. Figure 1 provides a simple two-dimensional illustration.

The lower limit s_1 in Eq. (2.5) is the point at which the disconnected voids in the interior of the liquid grow and merge to produce a globally connected region. Analogously s_2 is the point at which s spheres in the vapor interior become so large that they disconnect Ω.
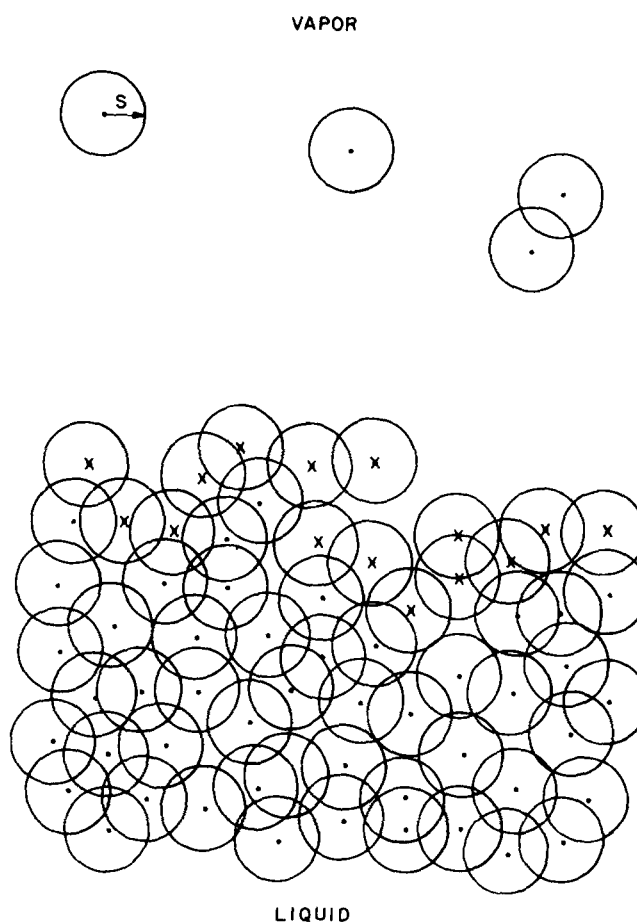

FIG. 1. Covering of system molecules with s spheres. The radius s is chosen so that uncovered volume is globally connected over the vapor phase, but disconnected throughout the liquid. The outermost layer of particles on the liquid has been indicated by crosses.

For any s satisfying Eq. (2.5) there exist paths entirely in Ω that go all the way across the macroscopic vapor phase, while at the same time *no* such paths cross the macroscopic liquid phase.

It must be stressed that s_1 and s_2 are strictly speaking attributes of the homogeneous liquid and vapor phases, each at the respective coexistence density, in the infinite system limit $(V \to \infty)$. These are the unique singular points at which the limit functions for the two phases $(\alpha = l, v)$,

$$\omega_\alpha(s) = \lim_{V \to \infty} \left\langle \sum_i \Omega_i^2(s) \right\rangle \Big/ V^2 , \quad (2.6)$$

change from positive at small s to identically zero at large s. The averaging indicated in this last equation is over all configurations of particles suitably weighted for the homogeneous phases, and the Ω_i are the distinct connected pieces of uncovered volume in the respective phases.

As T increases toward T_c the densities ρ_l and ρ_v respectively decrease and increase toward the common limit ρ_c, the critical density. Correspondingly the limits $s_1(T)$ and $s_2(T)$ in Eq. (2.5) would be expected respec-

tively to increase and to decrease as T rises, approaching a common value s_c:

$$\lim_{T \to T_c} s_1(T) = \lim_{T \to T_c} s_2(T) = s_c \ . \qquad (2.7)$$

Because we have

$$s_1(T) < s_c < s_2(T) \ , \qquad (2.8)$$

for all $T < T_c$ it is natural to choose s_c as the covering sphere radius at *all* temperatures. We shall utilize this unique choice throughout the remainder of this analysis.

Because Ω becomes disconnected at the liquid surface there exists a set L_1 of particles whose s_c spheres provide the requisite interface-spanning boundary (at least this is true with overwhelming probability in the large system limit). This set has been indicated by crosses through particle centers in the schematic Fig. 1. The particles in L_1 constitute an outermost layer on the liquid phase whose average number $\langle N_1 \rangle$ should be proportional to the nominal area of the liquid–vapor interface

$$\langle N_1 \rangle = A n_1(T, g) \ . \qquad (2.9)$$

Although the L_1 layer of s_c spheres may contain folds, it is pore-free and each of those s_c spheres is in contact with that macroscopic portion of Ω which pervades the vapor phase.

Should a reason exist to do so it would be possible to define successive layer sets $L_2, L_3, \ldots$, thereby resolving the liquid phase into vertically stratified subsets. This could be accomplished in principle by peeling away a last-identified layer set, and examining the remaining particles for that group whose s_c spheres have thereby become freshly exposed.

III. CAPILLARY WAVES

Let $\langle z \rangle$ denote the average value of z for particles in set L_1. Although $\langle z \rangle$ should lie close to z_0, the position of the Gibbs dividing surface,[7] these quantities need not be equal. It is our intention to use the instantaneous vertical deviations from $\langle z \rangle$ of particles in L_1 to define capillary wave coordinates. Specifically, the amplitude $a(\mathbf{k})$ for the surface mode with wave vector $\mathbf{k}$ will be defined to be

$$a(\mathbf{k}) = \sum_{l=1}^{N_1} (z_l - \langle z \rangle) \exp(i\mathbf{k} \cdot \mathbf{u}_l) \ ,$$
$$(3.1)$$
$$\mathbf{u}_l \equiv (x_l, y_l) \ .$$

Here we implicitly have assumed that the horizontal cross section of the system is rectangular and that the two-dimensional wave vectors $\mathbf{k}$ belong to the corresponding reciprocal lattice.

The number of capillary waves ($|\mathbf{k}| \le k_{\max}$) applicable to any system configuration clearly should be N_1, the number of particles in set L_1. This will vary from one configuration to another, and in that respect the capillary waves are no different from the fluctuating total number of particles N in the open system. In the large interface limit where $\mathbf{k}$ sums pass to integrals we can easily calculate the average maximum wave vector to be

$$\langle k_{\max} \rangle = [4\pi n_1(T, g)]^{1/2} \ . \qquad (3.2)$$

It is not at all obvious how n_1 and thus $\langle k_{\max} \rangle$ will vary with T at fixed $g > 0$. It is certainly true that as T rises from the triple point temperature T_t the bulk liquid becomes less dense (at least for normal liquids). That fact by itself would suggest that particles in L_1 undergo lateral thermal expansion which would then reduce n_1. However as T rises there is also an increasing tendency for cracks or fissures to open up in the surface of the liquid thereby exposing particles beneath (which then belong to L_1). This latter effect clearly tends to increase n_1. It is difficult to predict *a priori* which of these influences predominates near T_t, and the result may be sensitive to details of the intermolecular potential Φ. As a very tentative guess we speculate that the fissuring mechanism dominates near the critical temperature T_c thus causing the mean number of capillary waves to increase there.

Provided that Φ is bounded for all particle configurations not involving coincidence of positions ($r_{ij} = 0$), then $n_1(T, g)$ probably could be made to increase without bound by increasing g indefinitely. The resulting hydrostatic compression of the liquid phase would extend to its outermost layer, so that L_1 would consist of laterally very crowded particles. The reverse limit $g \to 0$ is a more delicate matter but we will suppose (and this is supported by results below) that for every $T < T_c$ the areal density limit exists

$$\lim_{g \to 0} n_1(T, g) = n_1(T, 0) < \infty \ . \qquad (3.3)$$

It is worth stressing that the boundary to Ω provided by the s_c spheres of set L_1 need not be at all simple. Overhangs, handles, tunnels, etc. can all be accommodated. Equation (3.1) continues in any case to supply a valid definition of the capillary wave amplitudes.

IV. INHERENT DENSITY PROFILE

We take the inherent density profile $\rho_0(z)$ to be the particle distribution subject to the vanishing of all $a(\mathbf{k})$

$$0 = \sum_{l=1}^{N_1} (z_l - \langle z \rangle) \exp(i\mathbf{k} \cdot \mathbf{u}_l) \ . \qquad (4.1)$$

These conditions provide a set of N_1 linear conditions on the N_1 vertical deviations $z_l - \langle z \rangle$. The determinant of coefficients in Eq. (4.1),

$$D = \det[\exp(i\mathbf{k}_j \cdot \mathbf{u}_l)] \ , \qquad (4.2)$$

will only vanish for a special set of lateral positions $\mathbf{u}_1 \cdots \mathbf{u}_{N_1}$ that has zero measure. With unit probability therefore the restraints of Eq. (4.1) require all members of L_1 to inhabit precisely the horizontal plane $z = \langle z \rangle$. This implies that L_1 contributes a deltafunction component to $\rho_0(z)$, specifically

$$n_1^{(0)} \delta(z - \langle z \rangle) \ , \qquad (4.3)$$

where $n_1^{(0)}$ is the areal density of particles in L_1 subject to the constraints of Eq. (4.1). Because the surface is now free of area-increasing distortions which could permit it to accommodate more particles, we expect to have

$$n_1^{(0)} < n_1 \ . \qquad (4.4)$$

The planar arrangement of particles in L_1 amounts to

a wall against which the remainder of the liquid abuts. In such circumstances the expected distribution of particles below the L_1 set at $z = \langle z \rangle$ is oscillatory but damped with increasing depth.[5] These successive maxima in $\rho_0(z)$ no doubt could be correlated strongly with distributions of members of the sets $L_2, L_3, \ldots$.

For $z > \langle z \rangle$, $\rho_0(z)$ relaxes to a value characteristic of the vapor phase, but presumably with some local structure near the interface. Far below T_c the predominating influence in the dilute vapor ought to be the net attraction each solitary particle feels for the semi-infinite bulk liquid phase. The corresponding mean potential varies as z^{-3} (or with retardation effects taken into account, z^{-4}). Figure 2 indicates roughly how our inherent density profile would appear for T not too close to T_c. Notice that particles not in L_1 are, by construction, excluded from the vicinity of $z = \langle z \rangle$.

When T approaches T_c by comparison, the liquid becomes markedly less dense and would have less tendency to manifest oscillatory density fluctuations. Both liquid and vapor as bulk phases develop long-range density correlations whose characteristic size is measured by the correlation length ξ that diverges at T_c. In this case, for small g, $\rho_0(z)$ is expected to approach respectively the bulk vapor or liquid density in an essentially exponential manner as $z \to \pm\infty$, with the same length ξ controlling the approach rate. Figure 3 illustrates the form of $\rho_0(z)$ qualitatively expected in this critical regime.

In neither case, Fig. 2 nor Fig. 3, does $\rho_0(z)$ have a monotonic shape associated with density profiles of the van der Waals type. Such monotonicity could conceivably obtain if $\rho_0(z)$ were suitably "smoothed." Weeks[8] has suggested in effect that van der Waals profiles correspond to removal from complete statistical averaging only of those capillary waves whose wavelengths exceed the bulk correlation length ξ, i.e.,

$$|\mathbf{k}| < 2\pi/\xi . \qquad (4.5)$$

This strategem would place the resulting profile $\rho_{vdw}(z)$ in an intermediate position between our $\rho_0(z)$ and the observable quantity $\rho^{(1)}(z)$. On the one hand, $\rho_{vdw}(z)$ would have less obviously oscillatory character at low temperature while continuing to exhibit ξ as its "width"

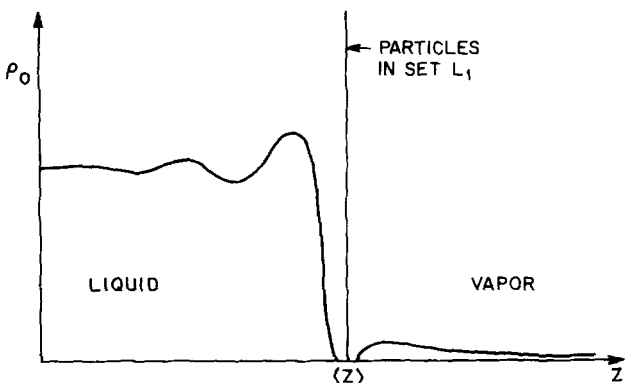FIG. 2. Qualitative behavior of the inherent density profile when the temperature is well below T_c.
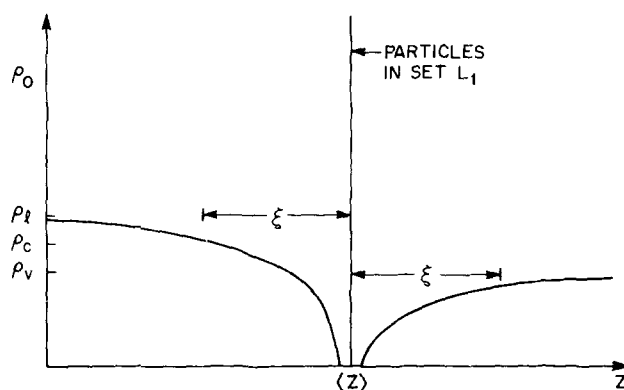

FIG. 3. Qualitative behavior of the inherent density profile when g is small and the system is close to critical. The bulk-phase correlation length has been denoted by ξ.

near T_c. On the other hand, it is free of the unbounded widening that $\rho^{(1)}(z)$ displays as $g \to 0$. Whether or not $\rho_{vdw}(z)$ satisfies a functional equation of the van der Waals type is a question outside the scope of this article.

V. SURFACE TENSION

If we remove only the one constraint in Eq. (4.1) corresponding to the capillary wave coordinate $a(\mathbf{k})$ this mode will begin to execute thermal fluctuations. In the g regime relevant to laboratory experiments it then makes sense to appeal to the format of the usual capillary wave model[1] to write

$$\langle |a(\mathbf{k})|^2 \rangle_0 = \tfrac{1}{2}(n_1^{(0)})^2 A k_B T / [\gamma_0(k)k^2 + mg\Delta\rho] ,$$
$$\Delta\rho = \rho_l - \rho_v . \qquad (5.1)$$

This defines the "bare" surface tension $\gamma_0(k)$ for the inherent density profile. The limiting value $\gamma_0(0)$ for long wavelengths could be extracted from the stress tensor components for the inherent density profile.

The bare surface tension function $\gamma_0(k)$ differs from the corresponding quantity $\gamma(k)$ for the fully unconstrained surface on account of interactions between capillary modes, and because of the inequality of Eq. (4.4). For this unconstrained situation the analog of Eq. (5.1) is

$$\langle |a(\mathbf{k})|^2 \rangle = \tfrac{1}{2}n_1^2 A k_B T / [\gamma(k)k^2 + mg\Delta\rho] . \qquad (5.2)$$

The experimentally measureable surface tension is to be identified as

$$\gamma_{expt} = \lim_{k \to 0} \gamma(k) , \qquad (5.3)$$

and it can be extracted from the stress tensor components for the unconstrained interface with density profile $\rho^{(1)}(z)$.

If Weeks' concept[8] is correct that the van der Waals picture implicitly involves partial surface mode averaging [as indicated in Eq. (4.5)], then the corresponding γ_{vdw} would be expected to lie between $\gamma_0(0)$ and $\gamma(0)$.

It is a fundamental postulate of the capillary wave model[1] that small $\mathbf{k}$ modes act independently of one another. This implies in particular that

$$\left\langle \prod_{j=1}^{n} |a(\mathbf{k}_j)|^2 \right\rangle \simeq \prod_{j=1}^{n} \langle |a(\mathbf{k}_j)|^2 \rangle \tag{5.4}$$

provided all $\mathbf{k}_j$ are distinct and $|\mathbf{k}_j| \to 0$. Deviations from this factored form when one or more of the $\mathbf{k}_j$'s is not small provides a measure of mode coupling. The diverging interface width as $g \to 0$ mentioned in the Introduction rests on this postulate as well as on the validity of the specific "hydrodynamic" expression in Eq. (5.2).

VI. DISCUSSION

The liquid-vapor interface has been examined several times previously by means of computer simulation.[9-12] While at least some of the results have been supportive of the capillary wave picture[11,12] the analyses were not of course structured in the manner that the present paper would suggest. We believe that in the future it would be beneficial to introduce our s_c-sphere construction into such simulations, to identify the L_1 surface-layer set, and to extract the inherent density profile $\rho_0(z)$.

With regard to the value of s_c, it seems clear that some numerical experimentation would be necessary. In principle this would require an arbitrarily close approach to the critical point, an admittedly difficult task for a finite-system simulation study. In practice it probably would suffice to work somewhat below T_c (say $0.9 T_c$), at which point s_1 and s_2 could be identified separately for the homogeneous liquid and vapor phases. In the spirit of the law of rectilinear diameters which states that near T_c

$$\rho_c \simeq \tfrac{1}{2}(\rho_l + \rho_v) \tag{6.1}$$

(the term linear in $\Delta T = T_c - T$ is small), it is reasonable to take

$$s_c \simeq \tfrac{1}{2}(s_1 + s_2) . \tag{6.2}$$

This approximate s_c should be quite adequate for use in the inhomogeneous system near the triple point temperature T_t.

Although it might require substantial programming skill to accomplish, a recognition algorithm would next need to be implemented to identify the surface-layer set L_1. The distribution of N_1 would then follow, and that of k_{max} could be inferred.

The Monte Carlo simulation technique appears to be well suited to determination of the inherent density profile. As an initial condition some appropriate number N_1 of particles would be confined to a plane $(z = \langle z \rangle)$, with no gaps between their s_c spheres. Subsequent configurational moves would then be carried out in the usual fashion *except* that any move would have to be rejected which (a) opened a gap in the s_c-sphere barrier provided

by set L_1, or (b) tried to add a particle to L_1 off of the $z = \langle z \rangle$ plane. The N_1 members of L_1 naturally would be subject only to lateral moves. After an appropriate equilibration period, subsequent averaging over the configurations generated would yield an inherent density profile for the chosen N_1.

From the standpoint of the underlying theory, the case of immiscible liquids offers an interesting conceptual challenge. If A and B denote the two species involved, then there is ambiguity over which, or whether both, should be employed to define capillary wave modes for the liquid-liquid interface. By considering each species separately, two distinct covering sphere radii s_{cA} and s_{cB} could be defined in terms of the uncovered-volume percolation processes at the critical mixing point. Then the respective first-layer sets L_{1A} and L_{1B} could be identified, with respective mean positions $\langle z \rangle_A$ and $\langle z \rangle_B$. How then are capillary wave modes best to be defined in generalizing Eq. (4.1) above? Should the L_{1A} and L_{1B} particles be treated symmetrically in such a mode definition? Should two surface mode branches be distinguished with A's and B's moving normal to the surface respectively in phase and out of phase? These fascinating questions will have to await deeper understanding of interfacial structure and dynamics before answers can confidently be supplied.

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