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Theory of inhomogeneous fluids

R. M. Nieminen* and N. W. Ashcroft

Laboratory of Atomic and Solid State Physics and Materials Science Center, Cornell University, Ithaca, New York 14853

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A theory of nonuniform liquids is presented which is based on the Yvon-Born-Green equation for the one-particle density and the Ornstein-Zernike equation of an inhomogeneous system. The necessary closure is effected by exploiting the solution of a modified hypernetted-chain equation and making a local approximation on the (highly universal) bridge function. The theory is successfully applied to model problems that have also been studied by direct-simulation methods. A brief generalization to quantum liquids is also given.

I. INTRODUCTION

In spite of the importance of nonuniform fluids, both classical and quantum, in a variety of physical problems, the understanding of their microscopic structure and thermodynamics is far less well developed than is the corresponding situation for uniform fluids. Perhaps the foremost example of an inhomogeneous fluid is the surface of a liquid in equilibrium with its vapor, the entire system being subjected to a one-body force such as a gravitational field. As is well known, the one-particle equilibrium density changes very rapidly at the surface, especially for temperatures near the triple point. Because of the rapidity of this variation a very detailed theory of the inhomogeneous fluid is required in order to give an adequate description of the surface region.[1] The same observation holds for a whole class of interfacial phenomena another example being the solid-fluid interface in which the interactions between the atoms of the fluid and those of the solid surface also lead to highly nonuniform single-particle densities with important consequences for absorption-related phenomena.[2] Phase separation, nucleation, and spinodal decomposition are examples of nonequilibrium phenomena in inhomogeneous systems.

Many of the theories of inhomogeneous classical fluids originate from the ideas of van der Waals[3] and Rayleigh.[4] The key element in these approaches is the construction of a free-energy functional for the inhomogeneous system in terms of the one-particle density profile. With a properly chosen, though in general unknown, correlation function one then seeks a variational minimum among a class of physically acceptable density distributions. Although this procedure is justified by exact existence and uniqueness theorems,[1] analogs, for instance, of the Hohenberg-Kohn-Mermin[5] theorems for the interacting electron gas, the practical applications of the method often resort to quite drastic approximations. In circumstances where the density distributions vary *slowly* over the range of correlations in the system it is certainly plausible to assume that the thermodynamic functions of interest can be given by those of a hypothetical uniform fluid whose density is given by the equilibrium density at each space point of the real inhomogeneous fluid. When the density varies more rapidly an obvious extension is to expand the appropriate energy densities about their local values in terms of density gradients.[6] While such methods are conceptually useful,[7] and even quantitatively accurate in some cases,[8] they fail badly in others. For example, gradient expansion techniques are not adequate in cases where the density shows a nonmonotonic trend, as in the case of the structure of a fluid near a solid wall.

An extension of the van der Waals theory has recently been proposed by Ebner, Saam, and co-workers.[9-12] It achieves what may be viewed as a partial summation of the terms in the gradient expansion. In this type of density-functional (df) theory a weighted integral over density differences at different points in the fluid is involved; the requisite kernel is related to a linear-response function in the limit of small inhomogeneities and in practice is approximated by suitably chosen local-density values of the *uniform fluid* direct-correlation function. A related modification of the van der Waals theory has also been given by Bongiorno *et al.*[13,14] These transcriptions of the density-functional theory are remarkably simple and transparent and have proven useful in certain applications. Yet as we shall show below the intrinsic approximations of density-functional theory are not always valid and actually lead to quite spurious results in some instances.

An alternative approach is based on perturbation theory. The successful application of perturbation theory for uniform fluids[15] relies on the observation that the structure of such fluids is governed by the highly repulsive short-range parts of interatomic forces. The weaker attractive parts of the potentials provide the stabilizing internal pressure, at least in nonmetallic systems.[16] Their contribution to the thermodynamic functions is calculated using perturbation theory with respect to a reference fluid very often chosen to be a hard-sphere system for which very detailed results are now available. Provided that information of comparable accuracy could be obtained for a *nonuniform* reference fluid the aim would be similar, i.e., to evaluate the effects of atomic attraction perturbatively.[15]

In the case of a fluid in contact with a solid boundary there is a class of theories that utilizes an idea originating with Helfand *et al.*[17] One considers a binary fluid in which the concentration of one of the components tends to zero while the size of its "atoms" diverges. This limiting process leads to an Ornstein-Zernike-type of equation for the one-particle density near a planar wall[18] and the solution of the equation can be obtained by appealing to an analog of one of the closure approximations well known from bulk-liquid theories. These techniques have been widely applied to the study of interfacial phenomena including adsorption[19] and colloidal suspension.[20] On the other hand, recent studies[21] of dense fluids bounded by hard walls show discrepancies between different integral equation approaches and also some disagreement with computer simulation studies. These and other observations seem to indicate that generalizations of the integral equation and perturbative approaches, generally successful in describing the structure of bulk uniform fluids, are not universally applicable to their nonuniform counterparts.

As a final example in this brief overview of theoretical approaches to inhomogeneous fluids, one may cite the method of computer simulation,[22] either Monte Carlo or molecular dynamics, which, within the usual limitations imposed by the finiteness of the systems studied and the restriction on simulation sequences, gives essentially exact information to which various analytical theories may be compared. The data that are available from such studies is growing rapidly.[23]

In the case of a *free* surface, the different approaches appear to agree reasonably well for simple insulating fluids near their triple points. For example, all the variants of van der Waals theory predict a monotonic surface density profile with a width $w \approx 2\sigma$ and a surface tension $\gamma_s \approx \sigma^2/\epsilon$, where σ and ϵ are the parameters in the Lennard-Jones potential describing the interaction between particles. These results are in reasonable accord with both experiments on real fluids and computer simulations. As noted above, the situation is not so satisfactory for interfacial problems involving fluids and solids. This presents a more stringent test of theory and the various analytical methods often differ markedly in their predictions even of the qualitative features of, say, adsorption. It very often seems that solid-induced correlations appear to render quite inaccurate the simple extensions of those methods that work rather well in bulk liquids. It is mainly for this reason that we propose a new approach for calculating the structure and thermodynamic properties of a nonuniform fluid in the presence of an externally imposed potential.

The method developed in the present paper proceeds from the (exact) first Yvon-Born-Green equation for the one-particle density, rather than from an approximate free-energy functional. This equation is augmented by the Ornstein-Zernike equation of the nonuniform fluid. The necessary closure is achieved by exploiting the solution of the modified hypernetted-chain (MHNC) equations for the system which in turn require knowledge of the bridge function. Following the ideas of Rosenfeld and Ashcroft[24] we suggest here that the bridge function shows a high degree of universality,[25] *even in the nonuniform context*. It is insensitive to the actual form of the interatomic potential, but most importantly it is *short ranged* and well defined for all densities and temperatures. Of the various two-point functions it is the one perhaps most amenable to local-density approximation. Consequently we solve for the structure and thermodynamics of the inhomogeneous fluid *exactly* at the level of HNC and then introduce corrections through the bridge function regarded as a local-density dependent potential.

The method is similar in spirit to one introduced recently by Fischer and Methfessel[26] who also examine interfacial phenomena from the standpoint of the Yvon-Born-Green equation but with a different approximate closure. In their approach the pair potential ϕ is split into a repulsive short-range part and an attractive part. The attractive part is dealt with by ignoring correlations in the fluid. The repulsive part is treated in the hard-sphere approximation, the pair-correlation function being taken as that appropriate to a locally homogeneous hard-sphere system (with requisite averages being taken over a volume equal to that of a single particle). The approximations made in this approach appear to be severe, but nevertheless have the great advantage that they also lead to a method in which local densities avoid the liquid-gas coexistence region. For the gas-solid interface problem, the results of Fischer and Methfessel are in good agreement with the appropriate computer simulation data and qualitatively similar to some of the results we present below.

The paper is organized as follows: In the next section we present the necessary theory of inhomogeneous classical liquids and describe our method. Section III formulates the problem for a system with planar symmetry. Section IV is devoted to some numerical applications of the scheme; a one-dimensional-model problem is analyzed and compared with other methods and computer simulation results. A three-dimensional adsorption model is also investigated and the results also compared with those of other techniques. Section V summarizes our findings: In the Appendix we give a discussion of the application of the method to inhomogeneous (Bose) quantum fluids.

II. INTEGRAL EQUATIONS FOR NONUNIFORM FLUIDS

Consider a simple fluid subjected to an external one-body potential $V_{\text{ext}}(\vec{r})$; at fixed chemical potential the one-particle density $n(\vec{r})$ satisfies the exact equation[27]

$$\vec{\nabla} n(\vec{r}) = -\beta n(\vec{r}) \vec{\nabla} V_{\text{ext}}(\vec{r}) - \beta \int d\vec{r}' [\rho^{(2)}(\vec{r},\vec{r}') - n(\vec{r}) n(\vec{r}')] \vec{\nabla} V_{\text{ext}}(\vec{r}'), \quad (1)$$

$\beta = (k_B T)^{-1}$,

where

$$\rho^{(2)}(\vec{r},\vec{r}') = n(\vec{r}) n(\vec{r}') g(\vec{r},\vec{r}') \quad (2)$$

is the two-particle distribution function and g the radial distribution function. Using the fact that $V_{\text{ext}}(\vec{r})$ is essential for the localization of $n(\vec{r})$ in space, an equation equivalent to (1) can be derived[28,29] that involves the Ornstein-Zernike direct-correlation function $c(\vec{r},\vec{r}')$:

$$\vec{\nabla} n(\vec{r}) = -\beta n(\vec{r}) \vec{\nabla} V_{\text{ext}}(\vec{r}) + n(\vec{r}) \int d\vec{r}' c(\vec{r},\vec{r}') \vec{\nabla} n(\vec{r}'). \quad (3)$$

Notice that Eqs. (1) and (3) contain no explicit reference to the form of the interparticle potential: This information is implicitly subsumed in $\rho^{(2)}$ and c, respectively. They are both quite general statements about the equilibrium of mechanical and thermodynamic forces. For particles interacting via pairwise potentials $\phi(\vec{r},\vec{r}')$ a third, and again equivalent form, is

$$\vec{\nabla} n(\vec{r}) = -\beta n(\vec{r}) \vec{\nabla} V_{\text{ext}}(\vec{r}) - \beta \int d\vec{r}' \vec{\nabla}_{\vec{r}} \phi(\vec{r},\vec{r}') \rho^{(2)}(\vec{r},\vec{r}'), \quad (4)$$

which is familiar as the first member of the Yvon-Born-Green (YBG) hierarchy. For a uniform system Eqs. (1), (3), and (4) are trivial; for the nonuniform fluid they are an exceedingly fruitful source of information.

There have been attempts[30,31] to apply the YBG equation to nonuniform systems by invoking some approximation to $\rho^{(2)}(\vec{r},\vec{r}')$. Such an approach is simple in principle and also in practice, but the approximations to $\rho^{(2)}(\vec{r},\vec{r}')$ have on the whole been somewhat artificial constructs and have led to very different results for, say, the case of the density profile of a free liquid surface. Thus, for example, any local-density approximation to $\rho^{(2)}$ is to be viewed with caution if the local density happens to lie in the liquid-vapor coexistence region. This point is discussed further in what follows.

Following established procedures developed for homogeneous fluids, it is possible to carry out a diagrammatic expansion of the total correlation function

$$h(\vec{r},\vec{r}') = g(\vec{r},\vec{r}') - 1 \quad (5)$$

in powers of the density $n(\vec{r})$. The result is a resummation in the form[32]

$$1 + h(\vec{r},\vec{r}') = \exp[-\beta\phi(\vec{r},\vec{r}') + h(\vec{r},\vec{r}') - c(\vec{r},\vec{r}') + E(\vec{r},\vec{r}')], \quad (6)$$

where $c(\vec{r},\vec{r}')$ is defined by the Ornstein-Zernike relation

$$h(\vec{r},\vec{r}') = c(\vec{r},\vec{r}') + \int d\vec{r}'' h(\vec{r},\vec{r}'') n(\vec{r}'') c(\vec{r}'',\vec{r}'), \quad (7)$$

and the function

$$E(\vec{r},\vec{r}') = \tfrac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 c_3(\vec{r},\vec{r}_1,\vec{r}_2) n(\vec{r}_1) h(\vec{r}_1,\vec{r}') n(\vec{r}_2) h(\vec{r}_2,\vec{r}') + \cdots \quad (8)$$

is the bridge function. In (8) the higher-order correlation functions are defined by

$$c_s(\vec{r}_1,\ldots,\vec{r}_s) \equiv \frac{\delta^{s-1}[\beta V_{\text{ext}}(\vec{r}_1) + \ln n(\vec{r}_1)]}{\delta n(\vec{r}_2) \cdots \delta n(\vec{r}_s)}. \quad (9)$$

The bridge function corresponds to the sum of nonnodal elementary graphs in the diagrammatic expansion.

If $E(\vec{r},\vec{r}')$ is set to zero, then (3), (6) and (7) constitute a closed set of equations. This is the hypernetted-chain approximation (HNC) widely used in the theory of bulk liquids. More generally, let E' be an approximate form of E, assumed known. Then the first YBG equation [most practical in the form of (3)] together with Eqs. (6) and (7) again constitute a closed system of equations which, in this instance, can be solved for $h(\vec{r},\vec{r}')$, $c(\vec{r},\vec{r}')$, and $n(\vec{r})$ once the pairwise potential $\phi(\vec{r},\vec{r}')$ and external potential $V_{\text{ext}}(\vec{r})$ have been specified. As noted by Rosenfeld and Ashcroft,[24] for the homogeneous case this procedure leads to an exact solution (for g, c, etc.) for a system in which the particles interact via an effective state dependent potential $\phi(\vec{r},\vec{r}')+\beta^{-1}[E(\vec{r},\vec{r}')-E'(\vec{r},\vec{r}')]$. With the exact $E'=E$, the solution would also be exact for the true physical potential. With approximate forms E', the procedure leads to a modified hypernetted-chain equation; in what follows we shall extend the notion to a modified nonuniform hypernetted-chain equation, to be augmented by the *exact* first YBG relation.

The key factor underlying the success of the modified HNC method[24] is the observation that E in the homogeneous case is a highly universal function. The defining elementary diagrams lead to a function that in the dense-fluid regime displays a remarkable insensitivity to the assumed pair potential. It depends mainly on the density n, and it is therefore possible to describe E by a one-parameter family of curves, for example, by the family appropriate to the hard-sphere fluid. This system is characterized by the packing fraction η, a quantity that can be determined in principle, by imposing the requirements of thermodynamic consistency. This procedure works exceedingly well for a wide range of interatomic potentials, densities, and temperatures. As shown in Ref. 24 (see Fig. 1 there) the bridge function E can be regarded as a *short-ranged* repulsive contribution to the effective pair interaction. For practical purposes it matters little[33] whether one uses the exact E (for instance, the one obtained from numerical simulation studies of an appropriate reference system), or a computationally more convenient form (for instance, the Percus-Yevick result for the hard-sphere fluid).

For an inhomogeneous fluid the bridge function is no longer a function of $|\vec{r}-\vec{r}'|$; it depends on $\vec{r}$, $\vec{r}'$, and is a functional of the density profile $n(\vec{r})$. There are a number of ways to construct, at least approximately, this functional, and the built-in variational degrees of freedom can be used to impose constraints (minimization of the free energy, for example) on the solution. However, in view of the fact that at a given density $E(\vec{r})$ for uniform systems is a monotonic *short-ranged* function we propose that for the nonuniform fluid a local-density approximation on E is not only physically plausible but is also expected to be numerically accurate. We therefore set

$$E(\vec{r},\vec{r}')=E_0(|\vec{r}-\vec{r}'|;\bar{n}), \tag{10}$$

where $E_0(|\vec{r}-\vec{r}'|;\bar{n})$ is the universal bridge function for a uniform system evaluated at a density $\bar{n}$ intermediate between the densities at $\vec{r}$ and $\vec{r}'$. For example, we might choose the standard

$$\bar{n}=\tfrac{1}{2}[n(\vec{r})+n(\vec{r}')]. \tag{11}$$

It is interesting to contrast the local-density approximation to $E(\vec{r},\vec{r}')$ with similar approximations applied to other two-point functions, such as $h(\vec{r},\vec{r}')$ or $c(\vec{r},\vec{r}')$. The familiar form of density-functional theory[9-11] requires the construction of a free-energy functional by an approximate functional integration and a subsequent local-density approximation to $c(\vec{r},\vec{r}')$. However, an incautious application of this approach can lead to situations in which the local density $\bar{n}$ is such that the corresponding bulk fluid is actually unstable. For a given temperature T the point $(\bar{n},T)$ actually lies well inside the two-phase region of the phase diagram. In addition to this difficulty it may also happen (low-temperature adsorption is a case in point) that the local density is actually higher than any bulk-liquid density for the given conditions.

It is not at all clear that the bulk direct-correlation function actually exists in the unphysical (unstable) region. The standard assumption of density-functional theory is that an analytic continuation *does* exist and that a satisfactory interpolation formula can subsequently be devised to obtain $c(\vec{r},\vec{r}')$ in the unstable region. This procedure may lead to spurious results and is, we suggest, one reason why the density-functional theory of certain adsorption systems differs quite radically from the results to be presented below (Sec. III) and also from computer simulation studies.[34] In this context especially, it is important to stress that $E_0(|\vec{r}-\vec{r}'|,\bar{n})$ exists for *all* densities: the universality principle guarantees this. Further E has the extremely important advantage that it is a simple monotonic function of both its arguments.

The approach we follow requires the solution of coupled hypernetted chain and the Yvon-Born-Green equations. The method is general but at first sight appears numerically quite demanding. However, as we show below, the solutions we need can be obtained for planar of spherical interfaces in three-dimensional fluids with reasonable computational capacity. An important reason underlying the practical feasibility of the method is the inherent stability of HNC equations, as noted in Ref. 24. For computational reasons it is useful to recast the three equations to be solved in the following form:

$$c(\vec{r},\vec{r}\,')=\exp[-\beta\phi(\vec{r},\vec{r}\,')+E(\vec{r},\vec{r}\,')]\exp[y(\vec{r},\vec{r}\,')]-y(\vec{r},\vec{r}\,')-1, \qquad (12)$$

$$\vec{\nabla}n(\vec{r})=-\beta n(\vec{r})\vec{\nabla}V_{\text{ext}}(\vec{r})+\int d\vec{r}\,'c(\vec{r},\vec{r}\,')\vec{\nabla}n(\vec{r}\,'), \qquad (13)$$

and

$$y(\vec{r},\vec{r}\,')=\int d\vec{r}\,''c(\vec{r},\vec{r}\,'')n(\vec{r}\,'')c[(\vec{r}\,'',\vec{r}\,')+y(\vec{r}\,'',\vec{r}\,')]. \qquad (14)$$

Next, in effecting the local-density approximation for $E(\vec{r},\vec{r}\,')$ the hard-sphere fluid is used as a reference system since it has been studied extensively both by simulation and analytic methods.[15] For both thermodynamics and structure it is quite satisfactory[24] in bulk fluids to use the Percus-Yevick (PY) family of bridge functions. A similar viewpoint is taken here. We write

$$E(\vec{r},\vec{r}\,')=E_{\text{HS}}(|\vec{r}-\vec{r}\,'|;\eta), \qquad (15)$$

where

$$E_{\text{HS}}(r)=\begin{cases}c_{\text{PY}}(r,\eta)+\ln c_{\text{PY}}(r,\eta)+1, & r<\sigma\\ g_{\text{PY}}(r,\eta)-\ln g_{\text{PY}}(r,\eta)-1, & r>\sigma\end{cases} \qquad (16)$$

where

$$\eta=\frac{\pi}{6}\sigma^3[n(\vec{r})+n(\vec{r}\,')]/2. \qquad (17)$$

Here c_{PY} and g_{PY} are the Percus-Yevick direct correlation and pair-distribution functions, respectively[35] (for g_{PY} we use the analytical representation given by Smith and Henderson[36]).

III. FORMULATION FOR A PLANAR SYSTEM

For one-particle densities $n(z)$ varying in a single spatial dimension, the two-particle functions $c(\vec{r},\vec{r}\,')$ and $y(\vec{r},\vec{r}\,')$ in Eqs. (12)–(14) are functions of z, z', and $|\vec{R}-\vec{R}'|$, where $\vec{R}=\vec{r}-(\vec{r}\cdot\hat{z})\hat{z}$ is the component of $\vec{r}$ perpendicular to $\hat{z}$. If we define a two-dimensional Fourier transform by

$$\tilde{F}(Q,z,z')=\int_0^\infty dR\,RJ_0(QR)F(R,z,z'), \qquad (18)$$

then we readily find the following as the basic set of equations to be solved:

$$c(R,z,z')=\exp[-\beta\phi(r)+E(r,\bar{\eta})]\exp[y(R,z,z')]-y(R,z,z')-1, \qquad (19)$$

$$\frac{\partial n}{\partial z}=-\beta n(z)\frac{\partial V_{\text{ext}}}{\partial z}+\int_{-\infty}^{\infty}dz'\tilde{c}(0,z,z')\frac{\partial n}{\partial z'}, \qquad (20)$$

$$\tilde{y}(Q,z,z')=\int_{-\infty}^{\infty}dz''\tilde{c}(Q,z,z'')\times n(z'')[\tilde{y}(Q,z'',z')+c(Q,z'',z')], \qquad (21)$$

and

$$y(R,z,z')=\frac{1}{2\pi}\int_0^\infty dQ\,QJ_0(QR)\tilde{y}(Q,z,z'). \qquad (22)$$

In these equations

$$r=[R^2+(z-z')^2]^{1/2}$$

and

$$\bar{n}=\tfrac{1}{2}[n(z)+n(z')].$$

At this point it is worth noting that if $c(R,z,z')$ is known [from solution of (19)–(22)] the interfacial tension and other thermodynamic quantities can be obtained. The interfacial tension follows immediately from considerations of the requirements of mechanical equilibrium in the context of the planar geometry. For, by integrating the difference of the normal and transverse components of the pressure tensor from one uniform phase across the interface to the other, one obtains[37]

$$\gamma=\gamma_s-\int_{-\infty}^{\infty}dz\,zn(z)\frac{\partial V_{\text{ext}}}{\partial z}, \qquad (23)$$

where γ_s is the planar geometry *free* surface tension. A particularly convenient form for γ_s, which involves the direct-correlation function, is[27,38]

$$\gamma_s=\frac{\pi}{2\beta}\int_{-\infty}^{\infty}dz\int_{-\infty}^{\infty}dz'\frac{dn}{dz}\frac{dn}{dz'}\int_0^\infty dR\,R^3c(R,z,z'). \qquad (24)$$

We may also use forms (1) and (3) of the first YBG equation to analyze particle correlations, not only in a direction perpendicular to the surface, but also parallel. The importance of the transverse (or horizontal) correlations was first pointed out by Wertheim.[29] Our treatment will follow the discussion given by Evans[1]: For a planar interface we rewrite (1) [using (14) and (18)] in the form

$$-\frac{\partial n}{\partial z}=\beta\int_{-\infty}^{\infty}dz'\frac{\partial V_{\text{ext}}}{\partial z'}\tilde{S}(0,z,z'), \qquad (25)$$

where

$$\tilde{S}(0,z,z')=n(z)\delta(z-z')+n(z)n(z')[\tilde{c}(0,z,z')+\tilde{y}(0,z,z')]. \qquad (26)$$

The inverse of (25) [the equivalent of (3)] is

$$-\beta\frac{\partial V_{\mathrm{ext}}}{\partial z}=\int_{-\infty}^{\infty}dz'\,\frac{\partial n}{\partial z'}\tilde{C}(0,z,z'),\tag{27}$$

where

$$\tilde{C}(0,z,z')=\delta(z-z')/n(z)-\tilde{c}(0,z,z').\tag{28}$$

In addition, for any transverse wave vector $\vec{Q}$, the Ornstein-Zernike equation can be written

$$\int_{-\infty}^{\infty}dz'\tilde{C}(Q,z,z'')\tilde{S}(Q,z'',z')=\delta(z-z').\tag{29}$$

We now analyze Eqs. (25) and (27) by using spectral techniques. Since $\tilde{C}(0,z,z')$ can be regarded as a real symmetric matrix, it can be written in spectral form (as noted by Wertheim[29,1])

$$\tilde{C}(0,z,z')=\sum_i\lambda_i\epsilon_i^*(z)\epsilon_i(z'),\tag{30}$$

where λ_i are the eigenvalues and $\{\epsilon_i(z)\}$ is an orthonormal set of eigenfunctions. Using (29)

$$\tilde{S}(0,z,z')=\sum_i\lambda_i^{-1}\epsilon_i(z)\,E_i(z').\tag{31}$$

If the external force is

$$F(z)=-\frac{\partial V_{\mathrm{ext}}}{\partial z}\tag{32}$$

then, from (31) and (25) we have

$$\frac{\partial n}{\partial z}=\sum_i\lambda_i^{-1}\epsilon_i(z)E_i,\tag{33}$$

where

$$E_i=\beta\int_{-\infty}^{\infty}dz'F(z')\epsilon_i(z').\tag{34}$$

Next, suppose that $\partial n/\partial z$ is strongly peaked. Then we expect the eigenvalue spectrum to be dominated by discrete values, the lowest eigenvalue being most important.[39] If this assertion is correct then

$$\epsilon_0(z)=\frac{\lambda_i}{E_i}\frac{\partial n}{\partial z}\tag{35}$$

and

$$\tilde{S}(0,z,z')\cong\frac{\partial n}{\partial z}\,\frac{\partial n}{\partial z'}\Big/\beta\int_{-\infty}^{\infty}dz\,F(z)\frac{\partial n}{\partial z},\tag{36}$$

which is clearly consistent with (25). For small Q the argument is generalized to[29,1]

$$\lambda_i(\phi)=\lambda_i+Q^2\int_{-\infty}^{\infty}dz\int_{-\infty}^{\infty}dz'\epsilon_i^*(z)\epsilon_i(z')\tfrac{1}{2}\pi\times\int_0^{\infty}dR\,R^3c(R,z,z'),\tag{37}$$

where the second term arises from the expansion of $\tilde{C}(Q,z,z')$ in Q. An assumption of lowest eigenvalue dominance then leads to

$$\tilde{S}(Q,z,z')\cong\frac{\partial n}{\partial z}\,\frac{\partial n}{\partial z'}\Big/\left(\beta\int_{-\infty}^{\infty}dz\,F(z)\frac{\partial n}{\partial z}+\beta\gamma_sQ^2\right)\tag{38}$$

for small Q. In arriving at (38) we have used the Triezenberg-Zwanzig form [Eq. (24)] for the surface tension in the presence of an external potential.

Equation (38) has an Ornstein-Zernike-type of behavior for the transverse structure factor or density-density correlation function. For a free surface under gravity $[F(z)=mg]$ the correlation length

$$\xi=[\gamma_s/(n_l-n_v)mg]^{1/2}$$

(where n_l-n_v is the liquid-vapor density difference) attains macroscopic dimensions. In turn this implies nearly singular behavior in S close to $Q=0$. The form of (38) is therefore suggestive of horizontal correlations corresponding to surface (capillary) waves, these waves being thermally excited against surface tension and gravity. An external perturbation, such as a solid substrate, will tend to suppress these long-range correlations.

It is now clear that any extensions of the van der Waals theories which start from a local-density approximation for $\rho^{(2)}(\vec{r},\vec{r}')$ or $c(\vec{r},\vec{r}')$, cannot correctly generate the transverse correlations. On the other hand, the method we propose *does* reproduce the correct small-Q result and *does* contain such correlations. This strongly suggests that the theory will lead to further insights into the physics of horizontal effects associated with symmetry breaking in the perpendicular direction. Near the gas-liquid critical point these may be particularly interesting.

IV. APPLICATIONS OF THE THEORY

As a first example we apply the method described above to the case of a classical one-dimensional fluid. In a recent paper[12] Ebner *et al.* have examined a class of inhomogeneous one-dimensional fluids by a variety of methods based on the minimization of an approximate free-energy functional. The systems were also studied by Monte Carlo simulation techniques. To facilitate comparisons with their results we have solved Eqs. (12)–(14) for identical systems. We have therefore considered one-dimensional fluids in which the interactions are derived from Lennard-Jones potentials

$$\phi(z)=4\epsilon[(\sigma/z)^{12}-(\sigma/z)^6]\tag{39}$$

and are under the influence of external potential of the form

$$V_{\text{ext}}(z) = -E_0 \sinh(w/2t)/[\cosh(w/2t) + \cosh(z/t)] \, . \tag{40}$$

The effect of $V_{\text{ext}}(z)$ is to produce a localized "phase" whose density and extent can be controlled by varying E_0 and w, respectively. The parameter t controls the thickness of the edge region separating the localized phase and the asumptotic uniform fluid. We set the unperturbed uniform fluid density at

$$n(z \to \pm\infty) = 0.05\sigma^{-1} \quad \text{or} \quad n_0^* = n_0\sigma = 0.05$$

and the temperature at

$$T^* = k_B T/\epsilon = 1 \, .$$

These correspond to the conditions chosen in Ref. 12.

We generate the requisite bridge function $E(z,z')$ by taking the Percus-Yevick solution for hard rods of length σ: It is exact in one dimension. Equations (12)–(14) are then solved for $c(z,z')$, $y(z,z')$, and $n(z)$ by straightforward numerical iterations of a starting trial solution conveniently provided by setting $v(z,z') = 0$. Normally 10–15 iterations are quite sufficient to ensure good convergence.[40] The density profiles we obtain are shown in Figs. 1–3: These profiles correspond to the same choice of external potential parmeters as used by Ebner *et al.*[12] (wells 4, 2, and 3, respectively, in Ref. 12). If we compare the results with the Monte Carlo data for the same systems,[12] we find agreement within the numerical inaccuracy (~5%) of the simulation procedure.[41] Notice that the small oscillations outside the range of the wells (most pronounced in Fig. 1) are also discernable in the simulations.

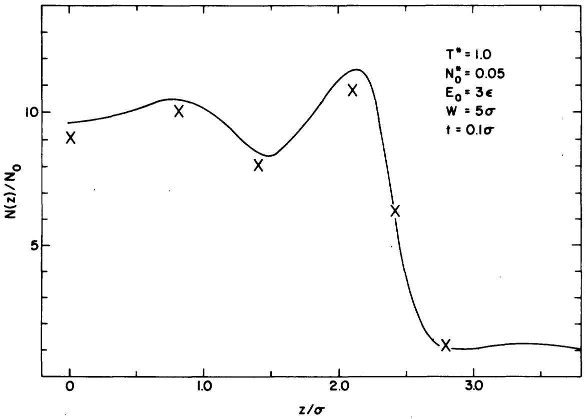

FIG. 1. Density profile for a one-dimensional Lennard-Jones fluid in an external potential corresponding to well No. 4 of Ref. 12. The crosses denote Monte Carlo simulation results also taken from Ref. 12.

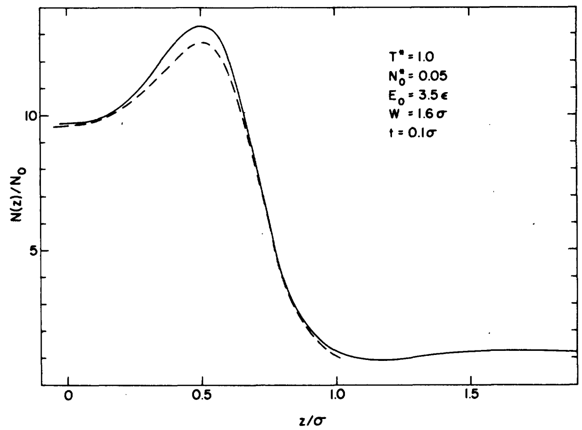

FIG. 2. Density profile for a one-dimensional Lennard-Jones fluid in an external potential corresponding to well No. 2 of Ref. 12. The dotted line is the density-functional result also taken from Ref. 12.

Ebner *et al.*[12] carried out a number of density-functional calculations for these systems: They are based on a minimization of the (formally exact) functional[1] obtained by integration of the direct-correlation function of the nonuniform systems with respect to density. This functional involves the functions

$$\bar{c}(\vec{r},\vec{r}\,') = 2\int_0^1 d\alpha\,(1-\alpha)\,c[n_\alpha(\vec{r});\vec{r},\vec{r}\,'] \tag{41}$$

and

$$\bar{c}_0(\vec{r}) = \int d\vec{r}\,'\,\bar{c}(\vec{r},\vec{r}\,') \, , \tag{42}$$

where α is a parameter representing the functional integration from a reference system [density $n_0(\vec{r})$] to the final physical state with density profile $n(\vec{r})$. Along the integration path the

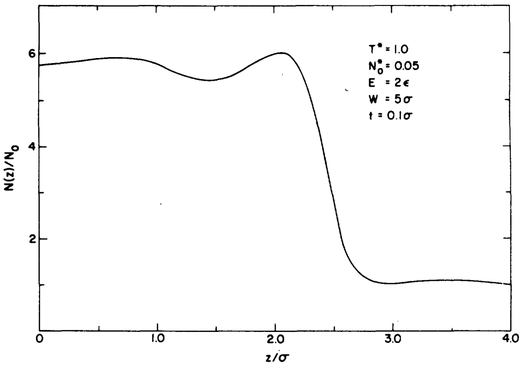

FIG. 3. Density profile for a one-dimensional Lennard-Jones fluid in an external potential corresponding to well No. 3 of Ref. 12.

density is chosen to vary as

$$n_\alpha(\vec{r}) = n_0(\vec{r}) + \alpha[n(\vec{r}) - n_0(\vec{r})] \ . \qquad (43)$$

For the density α, the direct-correlation function is $c(n_\alpha;\vec{r},\vec{r}')$. The simplest density-functional approximation then amounts to the choice

$$\bar{c}(\vec{r},\vec{r}') \cong c_h\{|\vec{r}-\vec{r}'|,[n(\vec{r})+n(\vec{r}')]/2\} \ , \qquad (44)$$

where c_h is the uniform system direct-correlation function.

The results that follow from this method are rather close to ours, suggesting that the local-density approximation (44) is indeed useful for the one-dimensional case. The reason why this might be expected may be traced to the absence of phase transitions in one-dimensional systems with short-range interactions. The construction of an approximate $c(\vec{r},\vec{r}')$ never involves contributions from a two-phase region, a difficulty that is inevitably encountered in the three-dimensional case where the crossing of the infinite compressibility gas-liquid phase boundary for a local density in the spinodal region can lead, in some cases, to spurious results.

Ebner *et al.*[12] also determined $\bar{c}(\vec{r},\vec{r}')$ by assuming that $\bar{c}(n_\alpha,\vec{r},\vec{r}')$ in Eq. (41) can be calculated by solving the Ornstein-Zernike equations for a *uniform* system taken at a density

$$\bar{n} = \tfrac{1}{2}[n_\alpha(\vec{r}) + n_\alpha(\vec{r}')] \ , \qquad (45)$$

an approximation that leads to density profiles depending on the integration path [i.e., on $n_0(\vec{r})$ in Eq. (43)]. The path independence of the exact $\bar{c}(\vec{r},\vec{r}')$ is guaranteed by uniqueness theorems.[1,5] The one-dimensional case can also be treated by the linearized Percus-Yevick (LPY) approximation but as noted in Ref. 12 this approximation fails badly for the one-dimensional case.

We turn now to a three-dimensional and somewhat more realistic example of a nonuniform system. We describe the structure of a classical fluid near a solid substrate, a problem of some importance in the understanding of adsorption, wetting, contact angles, and so forth. The model we treat is chosen to represent adsorption of argon on solid carbon dioxide. The substrate is taken to be a smoothed planar wall of atoms interacting with atoms of the fluid via a Lennard-Jones potential:

$$V_{\text{ext}}(z) = \begin{cases} 4\pi\epsilon_w n_w \sigma_w^3\left[\dfrac{1}{45}\left(\dfrac{\sigma_w}{z}\right)^9 - \dfrac{1}{6}\left(\dfrac{\sigma_w}{z}\right)^3\right], & z \geq 0 \\ \infty, & z \leq 0 \end{cases} \qquad (46)$$

with $\epsilon_w/k_B = 153$ K, $\sigma_w = 3.727$ Å, and $n_w\sigma_w^3 = 0.988$. For the atoms of argon we have a Lennard-Jones potential

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] , \qquad (47)$$

where $\epsilon/k_B = 119.73$ K and $\sigma = 3.405$ Å. (Note that the liquid-gas critical temperature for the Lennard-Jones fluid is $T_c^* = 1.32 k_B T_c/\epsilon$). This system has been studied by Saam and Ebner[11] using both density-functional and LPY techniques. It has also been examined more recently by Lane *et al.*[42] using Monte Carlo simulation methods. For temperatures $T < T_c$ and for asymptotic densities n_0 less than vapor-pressure densities $[n_0 < n_{\text{VP}}(T)]$ Saam and Ebner found a formation of unsaturated films on the substrate with thicknesses of up to ten layers. Our results[43] are shown in Figs. 4, 6, and 7: They are in good agreement with the computer simulation data, but like the simulation data they show no film growth. Figures (4)–(7) also show an interesting manifestation of the effect of interactions between atoms in the fluid. At low densities the bridge function plays a very minor role, but as density increases its presence is increasingly felt. The density profiles show generally smooth behavior with a gradual onset of maxima at roughly $z \approx \sigma$, $z \approx 2\sigma$, and $z \approx 3\sigma$ corresponding to the growth coverage from a monolayer to a multilayer configuration. For the systems studied here the second peak is quite weak and we find no evidence at all for the unlimited growth of a thick film.

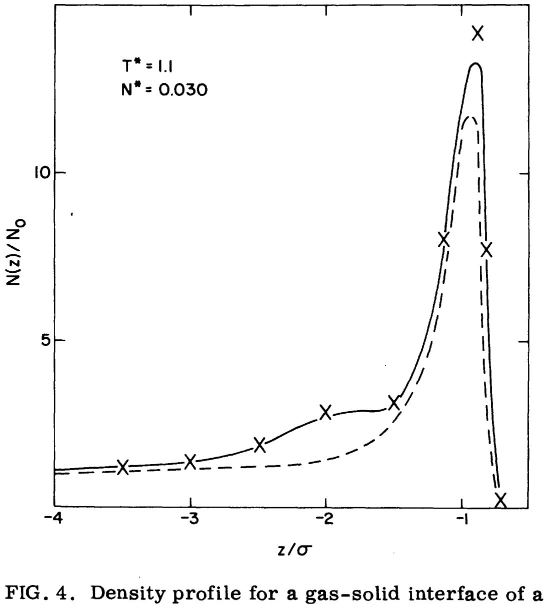

FIG. 4. Density profile for a gas-solid interface of a Lennard-Jones system (Ar/CO$_2$) at $T^* = 1.1$ and $n_0^* = 0.030$. The dotted line is the result for an ideal gas, the full curve the present result, and the crosses denote Monte Carlo simulation results taken from Ref. 41.

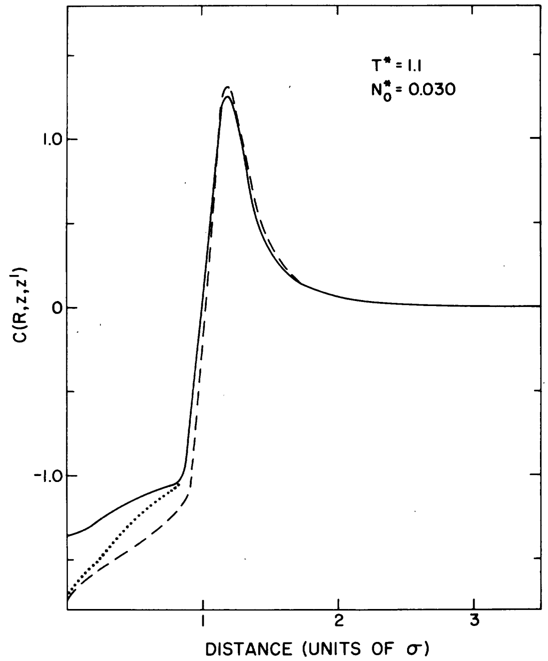

FIG. 5. Direct-correlation functions for the gas-solid interface. Full curve: Bulk gas $c(r)$; dashed curve: $c(R; z=z'=-\sigma)$ (see Fig. 4); dotted curve: $c(0; |z-z'|; z=-\sigma)$.

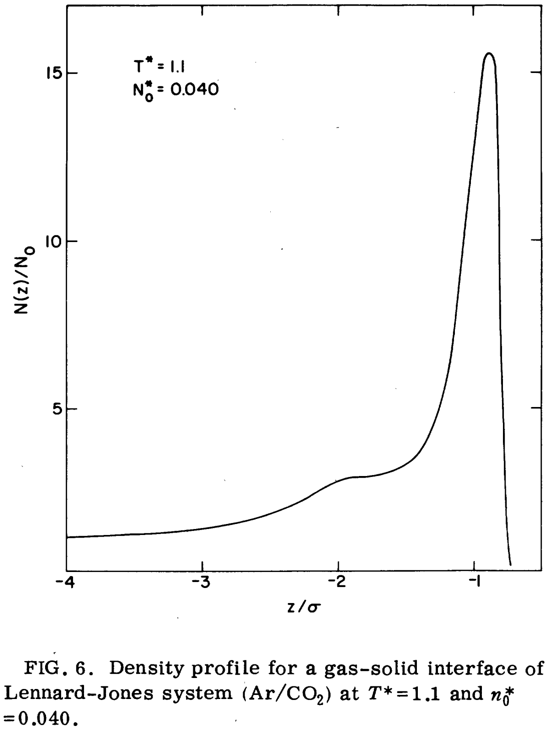

FIG. 6. Density profile for a gas-solid interface of a Lennard-Jones system (Ar/CO$_2$) at $T^*=1.1$ and $n_0^*=0.040$.

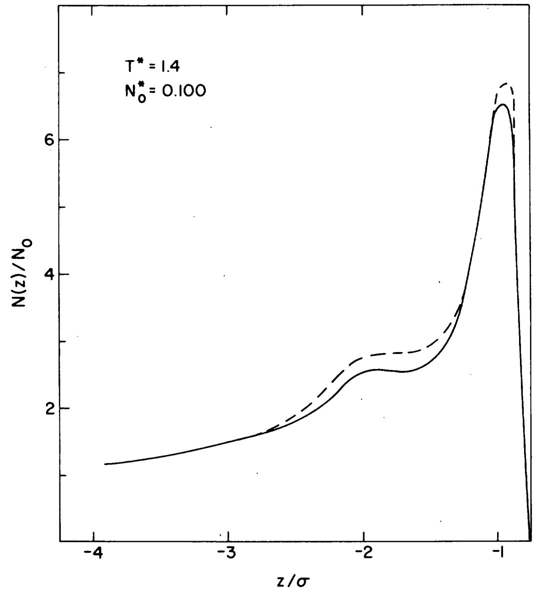

FIG. 7. Density profile for a gas-solid interface of a Lennard-Jones system (Ar/CO$_2$) at $T^*=1.4$ and $n_0^*=0.100$. The dotted curve denotes the result corresponding to the omission of the bridge function (i.e., to HNC).

Further, the peak *positions* are quite different from those obtained by Saam and Ebner, whose results indicate peaks at 1.5σ and 2.5σ. As noted, our results are in accord with computer simulation data (where the latter are available) and are also qualitatively similar to the LPY results. The latter seem to be rather good for these problems, however, this particular method is quite sensitive to the form of the approximations used and as a consequence cannot be regarded as generally reliable.

It is worth noting here that attempts to find a convergent solution to Eqs. (19)–(22) at fixed $T^*=1.1$ fail when n_0 exceeds $0.047\sigma^{-3}$. This value of n_0 is close to the coexisting gas density at $T^*=k_BT/\epsilon=1.1$ and we therefore find that the approach to saturation density and the coexistence region is signaled quite clearly by uncontrolled variation of the calculated functions between successive iterations.[44] Since in a variational scheme a solution is always expected, it is plausible that the thick unsaturated films found by Saam and Ebner near the coexistence region correspond to unstable states.

As an example[45] of the correlation functions determined by our method, we show in Fig. 5 the direct-correlation function $c(R,z,z')$ for the case of adsorption at $T^*=1.1$ and $n^*=n_0\sigma^3=0.030$. As a function of parallel separation R, we find that $c(R,z,z')$ closely resembles the bulk-gas results obtained with the modified hypernetted-chain method. This remains the case when z and z' are chosen from the high-density layer. In addition $c(R,z,z')$ shows the same kind of behavior as a function of $|z'-z|$ when $R=0$ and z' have been fixed in the high-density region. In this respect the results are again in accord with the computer simulation results which find the monolayer and bulk radial distribution functions to be very similar, suggesting a structure of a two-dimensional dense gas for the adsorbed layer. Computer simulation studies of a hard-sphere system near a hard wall also find that the pair-correlation function in planes parallel to the interface is essentially independent of distance from the interface (and also almost independent of the local density).

V. CONCLUDING COMMENTARY

We have presented above a general method for calculating the structure and thermodynamics of a nonuniform one-component fluid. It is based on the notion that the requiements of thermodynamic and mechanical stability should be incorporated in the theory from the outset. The approach avoids the use of local-density approximations for functions that are not defined in the two-phase region. We have shown that the method described above is numerically feasible by applying it to model problems where Monte Carlo and other theoretical results are already available. The results we obtain agree very well with those resulting from simulation studies. The method can be extended to other problems involving inhomogeneous fluids, for example, the structure (including transverse oscillations) of the gas-liquid interface in a gravitational field. It can also be adapted to multicomponent systems and to charged systems (the surface and interfaces of liquid metals, for example).

ACKNOWLEDGMENTS

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APPENDIX: INHOMOGENEOUS QUANTUM FLUIDS

Diagrammatic and integral equation methods developed to deal with uniform classical fluids can also be applied to the variational theory of quantum fluids.[46] The analogy between the Jastrow theory of a ground-state Bose fluid and an appropriately chosen classical fluid is especially useful, but even for Fermi liquids the added complications arising from the requirements of antisymmetry can still be handled in a HNC-type of theory.[47]

The method developed here can also be straightforwardly generalized to the ground state of a nonuniform quantum liquid.[48] We outline the application to an inhomogeneous Bose liquid (numerical calculations will clearly be of interest for interfacial phenomena involving ^{4}He). Consider an N-boson Hamiltonian:

$$H=-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2+\frac{1}{2}\sum_{i\neq j}\phi(\vec{r}_i-\vec{r}_j)+\sum_j V_{\text{ext}}(\vec{r}_j) \tag{A1}$$

and make the standard variational ansatz

$$\psi(\vec{r}_1,\ldots,\vec{r}_N)=\prod_{i=1}^{N}e^{1/2t(\vec{r}_i)}\prod_{j,k=1}^{N}\exp[\tfrac{1}{2}u(\vec{r}_i-\vec{r}_j)]\ , \tag{A2}$$

where the *one-particle function* $t(r)$ is ultimately manifested in the physical nonuniformity, and the two-particle function represents correlations between particles. Using the definitions

$$\begin{aligned} n(\vec{r})&=N\int d\vec{r}_2\cdots\int d\vec{r}_N|\psi(\vec{r},\vec{r}_2,\ldots,\vec{r}_N)|^2\ ,\\ \rho^{(2)}(\vec{r},\vec{r}\,')&=N(N-1)\int d\vec{r}_3\cdots\\ &\qquad\times\int d\vec{r}_N|\psi(\vec{r},\vec{r}\,',\vec{r}_3,\ldots,\vec{r}_N)|^2\\ &=n(\vec{r})n(\vec{r}\,')[1+h(\vec{r},\vec{r}\,')]\ , \end{aligned} \tag{A3}$$

we obtain the analog of the first YBG equations [Eq. (4)]

$$\nabla n(\vec{r})=n(\vec{r})\vec{\nabla}t(\vec{r})+\int d\vec{r}\,'\nabla_r u(\vec{r}-\vec{r}\,')\rho^{(2)}(\vec{r},\vec{r}\,')\ . \tag{A4}$$

In a similar way, if we perform a translation of the whole system we obtain the equivalent of Eq. (3):

$$\nabla n(\vec{r})=n(\vec{r})\nabla t(\vec{r})+\int \vec{d}r'c(\vec{r},\vec{r}\,')\vec{\nabla}n(\vec{r}\,')\ , \tag{A5}$$

where the direct-correlation function is again defined via the Ornstein-Zernike equation. A variational estimate for the ground-state energy is then

$$E=\langle\psi|H|\psi\rangle=\int d\vec{r}\,n(\vec{r})V_{\mathrm{ext}}(\vec{r})+\tfrac{1}{4}\int d\vec{r}\,n(\vec{r})\left(\frac{-\hbar^2}{2m}\nabla^2\right)t(\vec{r})$$
$$+\tfrac{1}{2}\int d\vec{r}\int d\vec{r}'\left[\phi(\vec{r}-\vec{r}')+\tfrac{1}{2}\left(-\frac{\hbar^2}{2m}\nabla^2 u(\vec{r}-\vec{r}')\right)\right]n(\vec{r})n(\vec{r}')[1+h(\vec{r},\vec{r}')]\,, \tag{A6}$$

Either (A4) or (A5) can now be used to eliminate $t(r)$ from (35). Using (A5), and definition (12) we obtain

$$E=\int d\vec{r}\,n(\vec{r})V_{\mathrm{ext}}(\vec{r})+\tfrac{1}{4}\int d\vec{r}\,\frac{\hbar^2}{2m}\frac{|\nabla n(\vec{r})|^2}{n(r)}+\tfrac{1}{4}\int d\vec{r}\int d\vec{r}'\bigg(U(\vec{r},\vec{r}')[1+c(\vec{r},\vec{r}')+y(\vec{r},\vec{r}')]n(\vec{r})n(\vec{r}')$$
$$-\frac{\hbar^2}{4m}c(\vec{r},\vec{r}')\nabla n(\vec{r})\cdot\nabla n(\vec{r}')\bigg)\,, \tag{A7}$$

where

$$U(\vec{r},\vec{r}')=\phi(\vec{r},\vec{r}')-\frac{\hbar^2}{4m}\vec{\nabla}^2_{\vec{r}}u(\vec{r},\vec{r}')\;. \tag{A8}$$

The energy expression [Eq. (A7)] must now be minimized, for example, by resorting to local-density approximations to $\rho^{(2)}(\vec{r},\vec{r}')$ or $c(\vec{r},\vec{r}')$ and performing variations with respect to any parameters used in specifying $n(\vec{r})$ and $n(\vec{r},\vec{r}')$. However, we can also perform the minimization exactly, at least in principle, by regarding $n(\vec{r})$, $c(\vec{r},\vec{r}')$, $y(\vec{r},\vec{r}')$, and $u(\vec{r},\vec{r}')$ as independent functions and deriving the relevant Euler-Lagrange equations by using $\int d\vec{r}\,n(\vec{r})=N$ (conservation of particles), and Eqs. (12) and (14) as constraints. The practical realization of this optimal theory, originally developed and successfully applied to *uniform* quantum fluids by Lantto and Siemens,[49] is currently under investigation.

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*Permanent address: Department of Physics, University of Jyväskylä, Finland.

[1] For reviews of the liquid-vapor interface for classical fluids, the reader is referred to R. Evans, Adv. Phys. 28, 143 (1979) and F. F. Abraham, Phys. Rep. 53, 93 (1979).

[2] J. G. Dash, *Films on Solid Surfaces* (Academic, New York, 1975).

[3] J. D. van der Waals, Z. Phys. Chem. (Frankfurt am Main) 13, 657 (1894).

[4] Lord Rayleigh, Philos. Mag. 33, 209 (1892).

[5] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); N. D. Mermin, *ibid.* 137, A1441 (1965).

[6] See, for example, A. J. M. Yang, P. D. Fleming, and J. H. Gibbs, J. Chem. Phys. 64, 3732 (1976) and references therein.

[7] B. Widom, in *Phase Transitions and Critical Phenomena*, Vol. 2, edited by C. Domb and M. S. Green (Academic, New York, 1972).

[8] B. F. McCoy and H. T. Davis, Phys. Rev. A 20, 1201 (1979).

[9] C. Ebner, W. F. Saam, and D. Stroud, Phys. Rev. A 14, 2264 (1976).

[10] W. F. Saam and C. Ebner, Phys. Rev. A 15, 2566 (1977).

[11] W. F. Saam and C. Ebner, Phys. Rev. A 17, 1768 (1978).

[12] C. Ebner, M. A. Lee, and W. F. Saam, Phys. Rev. A 21, 969 (1980).

[13] V. Bongiorno and H. T. Davis, Phys. Rev. A 13, 2213 (1975).

[14] V. Bongiorno, L. E. Scriven, and H. T. Davis, J. Colloid Interface Sci. 57, 462 (1976).

[15] A recent review is given by J. A. Barker and D. Henderson, Rev. Mod. Phys. 48, 587 (1976).

[16] In a very real sense this notion is related to the van der Waals thermodynamic model. Perturbation methods can therefore also be considered as generalizations of the van der Waals theory.

[17] E. Helfand, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. 34, 1037 (1961).

[18] For applications of this method, see for example, J. W. Perram and L. R. White, Faraday Discuss. Chem. Soc. 59, 29 (1975); D. Henderson, F. F. Abraham, and J. Barker, Mol. Phys. 31, 1291 (1976); E. Waisman, D. Henderson, and J. Lebowitz, *ibid.* 32, 1373 (1976); J. K. Percus, J. Stat. Phys. 15, 423 (1976).

[19] L. S. Smith and L. L. Lee, J. Chem. Phys. 71, 4085 (1979).

[20] See, I. K. Snook and W. van Megen, J. Chem. Phys. 72, 2907 (1980) and references therein.

[21] D. E. Sullivan and G. Stell, J. Chem. Phys. 69, 5450 (1978); D. E. Sullivan, D. Levesque, and J. J. Weis, *ibid.* 72, 1170 (1980).

[22] See, *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer, Heidelberg, 1978).

[23] Recent work includes: L. A. Rowley, D. Nicholson, and N. G. Parsonage, Mol. Phys. 31, 365 (1976); *ibid.* 31, 389 (1976); M. Kalos, J. K. Percus, and M. Rao, J. Stat. Phys. 17, 111 (1977); M. Rao, B. J. Berne, J. K. Percus, and M. H. Kalos, J. Chem. Phys. 71, 3802 (1979); I. K. Snook and D. Henderson, *ibid.* 68, 2134 (1978); I. K. Snook and W. van Megen, *ibid.* 70, 3099 (1979). See also Refs. 12 and 21.

[24] Y. Rosenfeld and N. W. Ashcroft, Phys. Rev. A 20, 1208 (1979).

[25] An approximate analytic demonstration of this principle of universality has been given recently by D. MacGowan, Phys. Lett. 76A, 264 (1980).

[26] J. Fischer and M. Methfessel, Phys. Rev. A 22, 2836 (1980).

[27] D. G. Triezenberg and R. Zwanzig, Phys. Rev. Lett.

28, 1183 (1972).

[28] R. A. Lovett, C. Y. Mou, and F. P. Buff, J. Chem. Phys. 58, 1880 (1976).

[29] M. S. Wertheim, J. Chem. Phys. 65, 2377 (1976).

[30] C. A. Croxton and R. P. Ferrier, J. Phys. C 4, 1909 (1971); G. M. Nazarian, J. Chem. Phys. 56, 1408 (1972); S. Toxvaerd, Mol. Phys. 26, 91 (1973); J. Fischer, *ibid.* 33, 75 (1977).

[31] B. Borstnik and A. Azman, Mol. Phys. 30, 1575 (1975); J. Fischer, J. Chem. Phys. 68, 3947 (1978).

[32] The result can also be obtained using the techniques of functional differentiation. See, J. K. Percus, in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964), p. II–33.

[33] For the Lennard-Jones fluid, taking $E(r,\eta)$ to be either the *exact* hard-sphere bridge function, or the Percus-Yevick approximation to it, leads to nearly identical $g(r)$ and equation of state data (for optimal choices of packing fraction).

[34] This deficiency of the density-functional theory, or of other theories attempting to incorporate local thermodynamics, has recently been discussed by D. E. Sullivan, Phys. Rev. B 20, 3991 (1979). This paper also introduces a useful van der Waals description of adsorption phenomena.

[35] M. S. Wertheim, Phys. Rev. Lett. 10, 321 (1963); E. Thiele, J. Chem. Phys. 39, 474 (1963).

[36] W. R. Smith and D. Henderson, Mol. Phys. 19, 411 (1970).

[37] See, for example, G. Navascues, Rep. Prog. Phys. 42, 1131 (1979).

[38] P. Schofield [Chem. Phys. Lett. 62, 413 (1979)] has recently shown that this form of the surface tension can be directly transformed to the Kirkwood-Buff expression [J. G. Kirkwood and F. P. Buff, J. Chem. Phys. 17, 338 (1949)]. See also Ref. 1.

[39] The higher eigenfunctions are all orthogonal to the lowest and thus have additional nodes. Using Eq. (24) we may argue that the higher eigenfunctions then have a higher characteristic energy content and are thus suppressed in thermal equilibrium.

[40] A feedback parameter (typically 50%) can be used to mix previous values with new values. Using a matrix of 60 × 60 in the (z,z') plane the calculation typically requires ~8 sec per iteration on an IBM 370/168.

[41] We point out that the Monte Carlo results for the density profile are slightly below the present results, but consistently so.

[42] J. E. Lane, T. H. Spurling, B. C. Freasier, J. W. Perram, and E. R. Smith, Phys. Rev. A 20, 2147 (1979).

[43] We solved Eqs. (19)–(22) numerically for V_{ext} given by (46). The solutions are obtained by discretizing the equations for a z mesh of 40 points with $\Delta z = 0.15\sigma$, an R mesh of 30 points with $\Delta R = 0.2\sigma$, and a Q mesh of 30 points with $\Delta Q = 0.2\sigma^{-1}$. The truncation of the Fourier transform at large Q introduces inaccuracies at small R ($R \leq 0.2\sigma$), but these and other numerical approximations have been found to have little influence on the results for asymptotic densities $n_0 \lesssim 0.3\sigma^{-3}$. For higher densities it is necessary to increase matrix sizes. For the present discretization one iteration requires ~30 sec on an IBM 370/168.

[44] This is indicative of the fact that for a free liquid surface the YBG approach leads to an eigenvalue problem in the sense that at fixed temperature Eqs. (19)–(22) have but a single solution for a pair of asymptotic (gas and liquid) densities.

[45] Detailed numerical results for the correlation functions will be deferred to a future publication.

[46] See, for example, E. Feenberg, *Theory of Quantum Fluids* (Academic, New York, 1969); G. Ripka, Phys. Rep. 56, 1 (1979).

[47] S. Fantoni and S. Rosati, Nuovo Cimento 25A, 539 (1975).

[48] For a survey of related approximations in the theory of the free surface of liquid helium see, D. O. Edwards and W. F. Saam, *Progress in Low Temperature Physics, VIIIA*, edited by D. F. Brewer (North-Holland, Amsterdam, 1978).

[49] L. J. Lantto and P. J. Siemens, Phys. Lett. 68B, 308 (1977).