Incorporating molecular scale structure into the van der Waals theory of the liquid-vapor interface

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We have developed a new and general theory of nonuniform fluids that naturally incorporates molecular scale information into the classical van der Waals theory of slowly varying interfaces. Here the theory is applied to the liquid-vapor interface of a Lennard-Jones fluid. The method combines a molecular field treatment of the effects of unbalanced attractive forces with a locally optimal use of linear response theory to approximate fluid structure by that of the associated (hard sphere like) reference fluid. Our approach avoids many of the conceptual problems that arise in the classical theory and shows why capillary wave effects are not included in the theory. The general theory and a simplified version gives results for the interface profile and surface tension for states with different temperatures and potential energy cutoffs that compare very favorably with simulation data.

I. INTRODUCTION

This paper applies our general theory of nonuniform fluids, described in several earlier publications [1, 2, 3, 4, 5], to the liquid-vapor interface of the simple Lennard-Jones fluid. Our approach here can be viewed as a generalization of the classical van der Waals (VDW) theory for the density profile of the liquid-vapor interface that (a) incorporates accurate thermodynamic data for the uniform fluid and (b) corrects the usual assumption that the interface profile is slowly varying. The new theory takes account of nonlocal molecular scale density correlations in a very natural way and can be applied to a wide variety of problems where the classical theory would fail. This perspective also provides a new and physically suggestive interpretation of the classical VDW theory for even a slowly-varying liquid-vapor interface that removes many of the conceptual problems and ambiguities that arise in standard descriptions [6]. Thus it seems appropriate to refer to it as a molecular scale van der Waals (MVDW) theory [3].

Since many aspects of the MVDW theory have been presented in some detail in previous work, here we will just outline the main features and focus on the new results we find for the structure and thermodynamics of the liquid-vapor interface. In this specific application where the interface is often slowly varying, correction (a) plays the most important role and (b) is relatively less important, though conceptually (b) represents the most important advance and permits much more general application of the theory. In particular we will show how our theory, which first determines the structure of the liquid-vapor (LV) interface, can be used to calculate thermodynamic properties such as the surface tension. These results will be compared to data from computer simulations [8, 9, 10, 11] and to a simplified version of the MVDW theory that includes only correction (a). We also discuss the role of capillary wave fluctuations [12, 13], which should be taken into account when comparing theory and experiment.

II. MOLECULAR FIELD APPROXIMATION

An essential ingredient in the MVDW theory and in our interpretation of the classical VDW theory is the introduction of an effective single particle potential or “molecular field” to describe the locally averaged effects of the unbalanced attractive forces in the nonuniform LJ fluid [4]. Since the attractive interactions are relatively slowly varying, such an averaged treatment seems physically reasonable. To that end, the LJ pair potential \( w(r) \equiv w_0(r) + w_1(r) \) is separated into rapidly and slowly varying parts associated with the intermolecular forces so that all the harshly repulsive forces arise from \( w_0 \) and all the attractive forces from \( w_1 \). We describe the LV interface using a grand ensemble with a fixed chemical potential \( \mu^v \) and temperature \( k_B T \equiv \beta^{-1} \) giving two phase coexistence with bulk liquid and vapor densities \( \rho^l \) and \( \rho^v \) respectively in an external field \( \phi(r) = 0 \).

The theory then approximates the structure of the nonuniform LJ system by that of a simpler nonuniform “reference” or “mimic” system at the same temperature but with a chemical potential \( \mu_0^v \) and purely repulsive pair interactions \( u_0(r) \). These give the same repulsive inter-molecular forces as in the LJ fluid and are well approximated for most purposes by hard sphere interactions.

The nonuniformity in the reference system is induced by an appropriately chosen effective reference field (ERF) \( \phi_R(r) \) that is supposed to take into account the locally averaged effects of the attractive interactions in the LJ fluid.

\[ \rho^l \equiv \rho^v \equiv \rho, \quad \mu^v \equiv \mu^l \equiv \mu \]
How should \( \phi_R(r) \) be chosen? Since we want the reference fluid structure to approximate that of the full fluid to the extent possible, it seems reasonable to determine \( \phi_R(r) \) formally by the requirement that the local (singlet) densities at every point \( r \) in the two fluids are equal \(^{15}\):

\[
\rho_0(r; [\phi_R], \mu_0^i) = \rho(r; [\phi], \mu^f). \tag{1}
\]

Of course this density is not known in advance, so in practice we will make approximate choices for \( \phi_R \) motivated by mean or molecular field ideas. Here the subscript 0 denotes the reference fluid, the absence of a subscript the LJ fluid, and the notation \([\phi]\) indicates that the correlation functions are functionals of the external field \( \phi \) (which in the present case is zero in the LJ system and \( \phi_R \) in the reference system). Unless we want to emphasize this point, we will suppress this functional dependence, e.g., writing Eq. (1) as \( \rho_0(r) = \rho(r) \).

### III. CLASSICAL VDW INTERFACE EQUATION

As discussed in detail in \(^3\), we can derive the classical VDW interface equation from this starting point by making two additional approximations. We briefly discuss this interpretation of the classical theory and then describe how our new MVDW theory improves on both approximations.

#### A. Simple molecular field approximation

First, the classical VDW theory uses the simple molecular field (MF) approximation for the ERF \( \phi_R \):

\[
\phi_R(r_1) = \phi(r_1) + \int dr_2 \rho_0(r_2; [\phi_R], \mu_0^i) u_1(r_{12}) + 2a \rho^f, \tag{2}
\]

where

\[
a \equiv -\frac{1}{2} \int dr_2 u_1(r_{12}) \tag{3}
\]

corresponds to the attractive interaction parameter \( a \) in the uniform fluid VDW equation, as discussed below. This is just a transcription of the usual molecular field equation for the Ising model to a continuum fluid with attractive interactions \( u_1(r) \) and can be derived in a number of different ways \(^{16, 17}\). The connection to the unbalanced attractive forces is perhaps most clearly seen in the derivation in \(^{14, 15}\), which starts from a formally exact description of the force balance in a nonuniform fluid and arrives at Eq. (2) by a series of physically motivated approximations.

For the LV interface we have \( \phi(r) = 0 \), but it is convenient in what follows to keep a general \( \phi \) which we will then set to zero. In that case we will also choose \( \mu_0^i \) so that the density \( \rho_0^i \) of the uniform reference fluid with \( \phi_R = 0 \) equals \( \rho^f \). With this choice the ERF \( \phi_R \) vanishes on the liquid side far from the interface where the density becomes equal to \( \rho^f \).

Another special case of Eq. (2) arises when \( \phi \) is a constant. Since a constant field in the grand ensemble is equivalent to a shift of the chemical potential, Eq. (2) then relates the chemical potentials in the uniform LJ and reference fluids \(^3\). Equation (2) thus yields the familiar uniform fluid VDW result

\[
\mu(\rho) = \mu_0(\rho) - 2a \rho_0, \tag{4}
\]

where \( \mu(\rho) \) and \( \mu_0(\rho) \) denote the chemical potential as a function of density \( \rho \) for the uniform LJ fluid and the reference fluid respectively. In the classical theory \( \mu(\rho) \) is defined for all \( \rho \) in terms of known reference system quantities by the right side of this equation. Since the uniform reference fluid is well defined for all densities below freezing, no problems arise from densities in the two phase region of the LJ fluid. The MVDW theory will use a slightly different expression for \( \phi_R \) in Eq. (1) below that gives a more accurate description of the thermodynamics of the uniform LJ fluid.

In general, to calculate \( \phi_R \) a self-consistent solution of Eq. (2) is required, since \( \phi_R \) appears explicitly on the left side and implicitly on the right side through \( \rho_0(r; [\phi_R], \mu_0^i) \). Thus a useful implementation of the MF idea requires a way to accurately determine the density response \( \rho_0(r; [\phi_R], \mu_0^i) \) induced by a given \( \phi_R \).

#### B. Local response to ERF

The classical VDW interface equation results when a second approximation, appropriate only for a slowly varying field, is used to estimate the density response \( \rho_0(r; [\phi_R], \mu_0^i) \). This hydrostatic approximation for the density takes account only of the local value of the field through a shift in the chemical potential \(^{14, 15, 16}\). Thus \( \rho_0(r_1; [\phi_R], \mu_0^i) \) is approximated for each \( r_1 \) by \( \rho_0^i \), the local hydrostatic density response, which satisfies

\[
\mu_0(\rho_0^i) = \mu_0^f - \phi_R(r_1). \tag{5}
\]

Hence the nonuniform density \( \rho_0(r_1) \) at each \( r_1 \) is assumed to equal \( \rho_0^i(r_1; [\phi_R], \mu_0^i) \), the density of the uniform reference fluid in zero field at the shifted chemical potential \( \mu_0^i = \mu_0^i - \phi_R(r_1) \), given by the right side of Eq. (5). When \( \phi_R(r_1) \) is a constant, this gives the exact result.

The superscript \( r_1 \) in \( \rho_0^i \) is meant to remind us that \( \rho_0^i \), like \( \rho_0^r \) or \( \rho_0^0 \), represents the density of the uniform reference fluid at a particular chemical potential \( \mu_0^i \), which from Eq. (5) depends parametrically on \( r_1 \) through the local value of the ERF. Thus when \( r_1 \) is in the bulk liquid (vapor) phase then \( \rho_0^r \) reduces to \( \rho_0^i (\rho_0^i) \). When \( \phi_R \) is very slowly varying this “local field” approximation is quite accurate and in this special case is equivalent to
the local density approximation made in the usual inter-
pretation of the VDW theory \[6\] [17]. However this ap-
proximation ignores the nonlocal excluded volume corre-
lations that can be induced by a more rapidly varying \(\phi_R\).
This represents a major limitation of the classical theory
in more general applications, and will be corrected in the
MVDW theory.

### C. Classical interface equation

The classical VDW interface equation follows immedi-
ately when \(\rho_0(r_2)\) is replaced by \(\rho_0^2\) in Eq. (6) and the
latter is substituted into Eq. (4). This yields an integral
equation for \(\rho_0^1\), which from Eq. (1) is supposed to equal
the density in the full LJ fluid:

\[
\mu_0(\rho_0^1) = \mu_0^0 - \phi(r_1) - \int dr_2 \rho_0^2 u_1(r_12) - 2a \rho^0. \tag{6}
\]

This can be exactly rewritten in a more standard form
using \(\mu(\rho)\) as defined in Eq. (3):

\[
\mu(\rho_0^1) = \mu^0 - \phi(r_1) - \int dr_2 [\rho_0^2 - \rho_0^1] u_1(r_12). \tag{7}
\]

Specializing to the case of the LV interface with planar
symmetry and \(\phi = 0\) and expanding \(\rho_0^2\) to second or-
der in a Taylor series about \(\rho_0^1\) (consistent with the as-
sumption of a slowly varying interface) yields the classical
VDW differential equation for the interface profile \(\rho_0^1:\)

\[
\mu(\rho_0^1) - \mu^0 = m \frac{d^2 \rho_0^1}{dr^2}, \tag{8}
\]

where

\[
m = \frac{1}{6} \int dr r^2 u_1(r). \tag{9}
\]

Equations (7) and (8) are completely equivalent to the
VDW theory for the LV interface as it is usually pre-
sented [7]. In our derivation the theory describes hydro-
static densities in the reference system, and \(\mu(\rho)\) is also
defined in terms of reference system quantities given on
the right side of Eq. (4). This provides a simple and con-
sistent interpretation of the classical theory that avoids
all the conceptual problems associated with densities in
the two phase region of the LJ fluid that arise in tradi-
tional approaches.

In this derivation we have obtained the VDW interface
equation directly, without first approximating the free
energy. We will later show how to determine the interface
free energy in this approach. First we will discuss our new
MVDW theory for the interface profile, which improves
on both approximations made in the classical theory.

### IV. MVDW THEORY FOR THE LV INTERFACE PROFILE

In the limit of a uniform system, Eq. (3) describes all
effects of attractive interactions in terms of the constant
parameter \(\alpha\) as in the van der Waals equation. While
this very simple approximation captures much essential
physics and gives a qualitative description of the uniform
fluid thermodynamic properties it certainly is not quan-
titatively accurate. In particular, when used to describe
a slowly varying liquid-vapor interface, it will predict
shifted (molecular field) values for the densities of the
coeexisting bulk liquid and vapor phases. The main
problem with the classical theory in this case is not so much
its description of the local density gradients, which are
often small, but its predictions for the thermodynamic
properties of the coexisting bulk phases. The first cor-
rection made in the MVDW theory is to modify Eq. (3) so
that it agrees with a given equation of state for the uni-
form system while still giving reasonable results for
nonuniform systems [8].

#### A. Modified molecular field approximation

To achieve quantitative agreement with known ther-
modynamic properties of the uniform LJ system we can
replace the constant \(\alpha\) by a function \(\alpha\) that depends
(hopefully weakly, to the extent the van der Waals theory
is reasonably accurate) on temperature and density [8].
Thus, instead of using the MF approximation for \(\mu(\rho)\)
as in Eq. (4), we assume that \(\mu(\rho)\) is known from an accu-
rate bulk equation of state. In particular, we determine
\(\mu(\rho)\) from the 33-parameter equation of state for the LJ
fluid given by Johnson, et al [18]. This provides a very
good global description of the stable liquid and vapor
phases in the LJ fluid and provides a smooth interpola-
tion in between by using analytic fitting functions. Thus
it naturally produces a modified “van der Waals loop” in
the two phase region and seems quite appropriate for our
use here in improving the simplest MF description of the
uniform fluid.

Now we relate this accurate \(\mu(\rho)\) to the known \(\mu_0(\rho)\)
through a function \(\alpha(\rho)\) defined so that

\[
\mu(\rho) = \mu_0(\rho) - 2 \rho \alpha(\rho). \tag{10}
\]

Thus the exact chemical potentials in the uniform LJ and
reference systems are related in the same way as is pre-
dicted by the simple MF approximation of Eq. (3) except
that the constant \(\alpha\) is replaced by a (temperature and
density dependent) function \(\alpha(\rho)\) chosen so that Eq. (10)
holds. We showed in [8] that the ratio \(\alpha(\rho)/\alpha\) is indeed
of order unity and rather weakly dependent on density and
temperature.

Because of the strictly local response in Eq. (6), these
results for a constant field can also be used to determine
exact results in the hydrostatic limit of a very slowly
varying field. We want to modify Eq. (6) so that in
the hydrostatic limit it will reproduce these exact values,
while still giving reasonable MF results for more rapidly
varying fields.

There is no unique way to do this, but the following
simple prescription seems very natural, and gives our fi-

nial result, which we have called the modified molecular field (MMF) approximation for the ERF [8]:

\[ \phi_R(r_1) - \phi(r_1) = \frac{\alpha(\rho_0^h)}{a} \int dr_2 \rho_0(r_2; \phi_R, \mu_0) u_1(r_{12}) + 2\alpha(\rho^f)\rho^f. \]  

(11)

Thus the molecular field integral in Eq. (2) is multiplied by a factor \(\alpha(\rho_0^h)/a\) of order unity that depends on \(r_1\) through the dependence of the hydrostatic density \(\rho_0^h\) on the local value of the field \(\phi_R(r_1)\), and the constant \(2\alpha(\rho^f)\rho^f\) is replaced by the appropriate limiting value of the modified integral. The MVDW theory assumes that the ERF is given by Eq. (11) rather than Eq. (2).

B. Nonlocal response to the ERF

The second important correction made in the MVDW theory is to determine more accurately the full nonlocal response \(\rho_0(r_1; \phi_R, \mu_0)\) to the ERF, thus correcting the local hydrostatic density \(\rho_0^h\) used in the classical theory. We introduced in a simple and generally very accurate method for calculating the structure and thermodynamics of the reference fluid in the presence of a general external field, using linear response theory in a locally optimal way to calculate the nonlocal corrections to the hydrostatic density. For a very slowly varying field the theory gives the hydrostatic density and for a hard core field the theory naturally reduces to the Percus-Yevick approximation [9].

The result is an integral equation for the density \(\rho_0(r_1)\), which we refer to as the hydrostatic linear response (HLR) equation:

\[ \rho_0(r_1) = \rho_0^h + \rho_0^r \int dr_2 c_0(r_{12}; \rho_0^h)[\rho_0(r_2) - \rho_0^h]. \]  

(12)

Here \(c_0(r_{12}; \rho_0^h)\) is the direct correlation of the uniform reference fluid at the hydrostatic density \(\rho_0^h\). This can be accurately approximated using known results for the uniform hard sphere fluid, as discussed in [8, 9]. The \(r_1\) dependence of the linear response kernel \(c_0\) through \(\rho_0^h\) is the most important new feature of the HLR equation. A discussion of the ideas leading to Eq. (12) and of its advantages over standard methods, along with numerical details of its solution, is given in [3, 5, 6].

C. Two step method and the MVDW theory

The MVDW theory for the LV interface arises from the self-consistent solution of Eqs. (5), (11) and (12). A two-step iterative method proved sufficient in all cases tested. Given a starting guess for \(\phi_R(r_1)\) one computes first in the first step the local hydrostatic density response \(\rho_0^h\) from Eq. (6). Then in a second step nonlocal corrections leading to \(\rho_0(r_1)\) are determined from (11), and this is used in Eq. (12) to give a new estimate for \(\phi_R(r_1)\). This process is iterated to self-consistency, and accurate numerical results are readily obtained.

D. Simplified MVDW interface equation

A simplified version of the MVDW theory arises when one skips the second step and assumes that \(\rho_0(r_1) = \rho_0^h\) as in the classical theory, while still using the accurate equation of state to determine \(\mu(\rho)\) from Eq. (10). While the full MVDW theory is straightforward to implement, the nonlocal corrections for the LV interface are often small and the use of the hydrostatic approximation allows for a more direct comparison with the classical theory. Using this approximation and Eqs. (11), (8), and (10), we obtain an integral equation analogous to the classical equation (8).

Expanding for simplicity to second order and assuming planar symmetry yields a generalization of the classical interface equation (8):

\[ \mu(\rho_0^h) - \mu^f = m\alpha(\rho_0^h)d^2\rho_0^h/dz^2, \]  

(13)

where

\[ m\alpha(\rho) \equiv m\alpha(\rho)/a. \]  

(14)

Following Rowlinson and Widom (RW) we can define

\[ -W(\rho) = f(\rho) - \mu^f\rho + \rho^f, \]

\[ = \rho[\mu(\rho) - \mu^f] - [\rho(\rho) - \rho^f]. \]  

(15)

Here \(f(\rho)\) is the Helmholtz free energy density from our analytic equation of state that corresponds to \(\mu(\rho)\) given by Eq. (10), where \(\mu(\rho) = df(\rho)/d\rho\) and the associated pressure \(p(\rho) = -f(\rho) + \rho\mu(\rho)\) from standard thermodynamics. We see that \(W(\rho)\) vanishes in the coexisting bulk liquid and vapor phases and note that the left side of Eq. (13) is given by \(-dW(\rho^h)/d\rho_0^h\). By interpreting the latter as a “force”, Eq. (13) is analogous to Newton’s law, with \(\rho_0^h\) the “displacement”, \(z\) the “time” and \(m\alpha(\rho)\) a density (or “displacement”) dependent “mass”.

Note that Eq. (13) differs from the analogous equation that would arise in the classical theory from assuming a density dependent “mass” in the gradient correction to the free energy. As shown by RW in their Eq. (3.10), the latter would generate an additional square gradient term in the interface equation (13). It is difficult to see how such a term could arise naturally in our approach.

We report results here for the even simpler theory that arises when \(m\alpha(\rho)\) in Eq. (13) is replaced by its classical value \(m\) given by Eq. (1). The resulting simplified interface equation has the same form as the classical equation (5). However it uses the accurate expression for \(\mu(\rho)\) given by Eq. (14), which assures a proper thermodynamic description of the coexisting bulk phases, while (inconsistently) retaining the classical expression for \(m\). This produces some changes in shape of the interface profile when
compared to that predicted by the MVDW theory, but preserves many qualitative features such as the dependence of the interface width on the thermodynamic state and the range of the attractive interactions. One major virtue of this approximation is that a very simple expression for the profile $\rho_0$ in terms of the inverse function $z(\rho_0)$ (with arbitrary origin) follows immediately from Eq. (13) by quadrature, as shown by RW:

$$z(\rho_0) - z(\rho^v) = \left(\frac{m}{2}\right)^{1/2} \int_{\rho^v}^{\rho_0} d\rho \left[ -W(\rho) \right]^{-1/2}. \quad (16)$$

Results from this simplified approach and the full MVDW theory will be discussed in Sec. III below.

E. Nonlocal correlations and capillary waves

The use of the HLR equation in the MVDW theory allows one to take account of nonlocal correlations induced by the ERF. These arise mainly from the packing of the harshly repulsive molecular cores and become significant at high density when the ERF is rapidly varying. In principle small amplitude excluded volume oscillations would be expected at high density from linear response theory far from any localized perturbation [20, 21]. The amplitude of these oscillations for a general liquid-vapor interface depends on the thermodynamic state and on the strength and range of the attractive interactions. These features control the steepness of the ERF $\phi_R(r)$, which mainly determines how significant these nonlocal corrections to the classical theory are in a given case.

For our study here of the LV interface in the LJ fluid the attractive interactions are relatively slowly varying and these corrections are numerically small in most cases. However, near the triple point the interface is very steep and noticeable oscillations on the liquid side are predicted by the theory and, with much smaller amplitude, are also seen in the computer simulations. The classical local hydrostatic approximation precludes a description of any such oscillations and gives no indication of where it can break down. So these corrections are conceptually important even for “smooth” LV interfaces.

The difference in oscillation amplitude between theory and simulation arises because the MVDW theory describes a “static” interface in the reference fluid induced by the ERF. Any theory that takes account of attractive forces only through an ERF and uses reference system correlation functions to approximate structure in the LJ system cannot properly describe the physics leading to the long-wavelength capillary wave fluctuations that occur at a real LV interface [2, 3, 13]. These induce characteristic long-ranged pair correlations in the interface region of a real fluid that are completely different from the corresponding pair correlations in the reference system, which remain short-ranged for any reasonable choice of $\phi_R(r)$. In a sufficiently large system, the capillary wave fluctuations can wash out any excluded volume oscillations at the real LV interface, and indeed the entire interface profile $\rho(r)$ itself [12]!

However the small system sizes studied in computer simulations or encountered in most experiments on interfaces in confined geometries cut off most effects of such capillary wave fluctuations. It is reasonable to interpret the MVDW theory as providing one way of defining an “intrinsic” profile unbroadened by capillary wave effects and to compare its predictions directly to the simulation or experimental data, taking account of the residual finite size capillary wave effects separately if necessary [13]. This will be discussed further below.

Workers using other approaches such as density functional theory or integral equation methods sometimes argue that their theories describe correlations in the full nonuniform LJ system, and thus may include some or perhaps all of the effects of capillary wave fluctuations [2, 3]. However such theories usually introduce approximations that relate correlation functions in the nonuniform system to interpolated or weighted correlation functions in the uniform LJ system. One must then deal with the ambiguities arising from unstable uniform densities in the two phase region. We believe most such arbitrary schemes implicitly introduce a mean field character to the theory through the use of uniform fluid correlation functions that do not contain any capillary wave effects. However the precise physical implications of such approximations are very difficult to assess. In our interpretation of MF theory, both the strengths and the limitations arising from the use of reference system correlation functions are clear from the outset.
V. RESULTS FOR INTERFACE STRUCTURE

A. MVDW theory

Figure 1 shows the interface profiles for the LJ fluid for states at three different temperatures. The dots give results of recent molecular dynamics (MD) simulations of Mecke et al. [1]. They made a careful study of the important changes in the interface profile and surface tension that arise from setting the force from the LJ potential to zero beyond a certain cutoff distance $r_c$. Since there are unbalanced attractive forces in the interface region, effects from different cutoffs are much more important than in uniform systems, where the attractive forces essentially cancel. The first two curves on the left give profiles very near the triple point at a reduced temperature $T = 0.7$ with $r_c = 5$ and 2.5 respectively. There are notable changes in the coexistence densities $\rho^c$ and $\rho^f$ from the different cutoffs. The next two curves give results at $T = 0.85$ with the same two cutoffs and the last curve on the right gives $T = 1.1$ with $r_c = 5$.

The lines give results of the MVDW theory, using the appropriate cutoff and shifted LJ potential. The effects of the cutoff on the bulk thermodynamics can be taken into account in the general equation of state of Johnson, et al. [8] used in the MVDW theory, and the ERF properly describes the averaged effects of the unbalanced attractive forces in the interfacial region. Overall there is very good agreement between simulations and the theory, which captures all qualitative effects of changes in temperature and cutoff radius.

However, the theory predicts very noticeable density oscillations on the liquid side at the lowest temperature $T = 0.7$. As discussed earlier, the amplitude of these oscillations is a sensitive function of temperature and cutoff and already by $T = 0.85$ their amplitude is greatly reduced. Such nonlocal excluded volume correlations are to be expected when the density is high and the ERF is sufficiently rapidly varying. In other contexts they play an important role in the physics of nonuniform fluids [3].

Indeed we find that the theory provide an exceptionally accurate description of $\rho_0(r; \phi_R, \mu_0^c)$, the density of the reference system in the presence of the ERF $\phi_R$. This is illustrated in Fig. 2, which compares the theory (solid lines) for $T = 0.7$ and $T = 0.75$ directly to results from grand canonical Monte Carlo simulations we carried out [4] for the reference system density (symbols) in the presence of the self-consistently determined ERF (dotted lines). Note that while the field is smooth, it is sufficiently rapidly varying in this case to produce a density response with nonlocal excluded volume correlations. These are very well described theoretically by the HLR equation used in the MVDW theory and are completely missed by the local hydrostatic approximation (dashed lines) used in the classical theory.

The differences in oscillation amplitude seen in Fig. 1 arise because the reference system cannot describe the capillary wave fluctuations seen at a real LV interface, as discussed above. Some residual effects are present even for the relatively small system sizes used in the computer simulations. We can take them into account in an approximate way by using the standard prescription for Gaussian capillary wave smearing of an “intrinsic” interface. Thus we convolute the “intrinsic” interface as given by the MVDW theory in Fig. 1 with a Gaussian distribution of local interface positions $h$:

$$P(h) = (2\pi s^2)^{-1/2} \exp(-h^2/2s^2),$$

where the width $s$ of the Gaussian is given by

$$s^2 = \frac{k_B T}{2\pi \gamma} \ln \frac{L}{L_s}. \quad (17)$$

Here $L$ is the lateral box size in the simulation and the $L_s$ is the short distance (wavelength) cutoff, which is supposed to be proportional to the bulk correlation length or the interface width [6, 7, 8]. In this case the amount of smoothing depends mainly on the choice of $L_s$, and the very reasonable choice of three times the interface width gives the data plotted in Fig. 3. The minimal choice of just the interface width gives too much smoothing when compared to the MD data.

We see that the finite size capillary wave fluctuations have very little effect on the smooth profiles at higher temperatures, but they are quite effective in damping out some of the “intrinsic” oscillations predicted near the triple point. Our purpose here is not to advocate this particular and somewhat arbitrary prescription for smoothing the results of the MVDW theory, but to point out that while excluded volume oscillations are accurately described by the MVDW theory, their influence on the LV interface profile is reduced by capillary wave effects not captured by the theory. In many other applications,
VI. SURFACE TENSION

A. Basic formalism

In the MVDW theory, we first determine fluid structure. To calculate the interface free energy or surface tension $\gamma$ for the LV system, we proceed formally and imagine a special path where the density in the LJ fluid changes linearly from that of the uniform liquid with density $\rho'$ to the final LV interface profile $\rho(r; [\phi = 0], \mu') \equiv \rho(r)$ as controlled by a coupling parameter $\lambda$ with $0 \leq \lambda \leq 1$:

$$\rho_\lambda(r) = \rho' + \lambda(\rho(r) - \rho').$$

(19)

Here $\rho_\lambda(r) \equiv \rho(r; [\phi_\lambda], \mu')$ where $\phi_\lambda(r)$ is the (generally nonzero) external field that formally produces the partially coupled profile $\rho_\lambda(r)$ defined by the right side of Eq. (19). Since $\rho_\lambda(r) = \delta \Omega_\lambda/\delta \phi_\lambda(r)$, on integration the change in the Grand canonical free energy associated with this density change is exactly given by:

$$\Omega_{\lambda=1} - \Omega_{\lambda=0} = \int dr \int_0^1 d\lambda \rho_\lambda(r) \frac{d\phi_\lambda(r)}{d\lambda}. \quad (20)$$

Here $-\beta \Omega_\lambda \equiv \ln \Xi_\lambda$ where $\Xi_\lambda$ is the Grand partition function for the system with field $\phi_\lambda$. For the LV interface we have $\phi_{\lambda=0}(r) = \phi_{\lambda=1}(r) = 0$. Since $\Omega_{\lambda=0} = -p' V$, with $p'$ the coexistence pressure, which equals that in the vapor phase, the free energy difference on the left side is the desired interfacial free energy $\gamma$, and is independent of any choice of Gibbs dividing surface $\Sigma$. Integrating by parts, we have our basic starting point:

$$\gamma = -\int dr \int_0^1 d\lambda \phi_\lambda(r) \frac{d\rho_\lambda(r)}{d\lambda},$$

(21)

or for the linear path:

$$\gamma = -\int dr [\rho(r) - \rho'] \int_0^1 d\lambda \phi_\lambda(r). \quad (22)$$

B. MVDW theory for surface tension

The MF approximation used in the MVDW theory allows us to evaluate these expressions using reference system quantities. Thus we assume from Eq. (10) that $\rho_\lambda(r) = \rho_{0\lambda}(r) \equiv \rho_0(r; [\phi_{R\lambda}], \mu'_0)$, where $\phi_{R\lambda}(r)$ is the field in the reference system producing the same profile, formally related to $\phi_\lambda(r)$ by the MMF equation (11):

$$\phi_{R\lambda}(r_1) = \phi_\lambda(r_1) + \frac{\alpha(r_1^2)}{a} \int dr_2 \rho_{0\lambda}(r_2) u_1(r_12) + 2\alpha(\rho')\rho'.$$

(23)

Using Eq. (6) and Eq. (10), we can exactly rewrite Eq. (23) in a convenient form for use in Eqs. (21) and...
In the MVDW theory $\mu(\rho)$ is determined from the accurate equation of state and is given by Eq. (10), and all densities are calculated in the reference system.

To calculate $\phi_\lambda(r_1)$ from Eq. (24) we start with the final self-consistent profile $\rho_0(r)$ and use Eq. (14) to define $\rho_{0\lambda}(r)$. We then iterate the HLR equation (12) in an “inverse” way to find the hydrostatic density $\rho_{0\lambda}$ associated with a given $\rho_{0\lambda}(r_1)$. Although we know that $\rho_{0\lambda}(r)$ is linear in $\lambda$ from Eq. (13), unless the density is slowly varying this does not imply that the same condition holds for $\rho_{0\lambda}$. With this in hand, we use Eq. (24) to determine $\phi_\lambda(r_1)$ for several intermediate values of $\lambda$. The surface tension is then calculated by carrying out the integration in Eq. (24) numerically.

C. Simplified hydrostatic approximations for the surface tension

If we ignore the difference between $\rho_{0\lambda}(r_1)$ and $\rho_{0\lambda}$ as in the classical theory and assume the latter varies linearly in $\lambda$, then we require only the final profile $\rho_{0\lambda}$ and can carry out most of the $\lambda$ integration in Eq. (21) analytically. We have already seen that this is a rather accurate approximation for the structure of the LV interface and we use this approximation only under an integral in computing the free energy. As we will see, this greatly simplifies the calculation of the free energy and also allows us to make contact with classical results and the simplified MVDW theory.

Assuming that $\rho_{0\lambda}(r_2) = \rho_{0\lambda}^2$ in Eq. (24) we have

$$\phi_\lambda(r_1) = \mu^\ell - \mu(\rho_{0\lambda}^1) - \frac{\alpha(\rho_{0\lambda}^1)}{\alpha} \int d\mathbf{r}_2 \left[ \rho_{0\lambda}(r_2) - \rho_{0\lambda}^1 \right] u_1(r_{12}),$$

and we will use this expression in Eqs. (21) or (22) to determine the surface tension. For $\lambda = 1$ we have $\phi_{\lambda-1}(r_1) = 0$, and Eq. (25) reduces to the generalized interface equation (13) on expanding $\rho_{0\lambda}$ to second order about $\rho_{0\lambda}^2$. The simplified MVDW interface equation discussed earlier whose solution is given in Eq. (14) follows on further approximating $\alpha(\rho)$ by $a$ in Eq. (23) or $m$, by $m$ in Eq. (13).

Now let carry out the $\lambda$ integration in Eq. (21) using Eq. (25) for $\phi_\lambda(r_1)$. A clear discussion of most of the technical issues in given in RW. The first two terms on the right in Eq. (23) represent the local contribution to the interface free energy and can be integrated analytically:

$$I_{local} = -\int d\mathbf{r} \int_0^{r_2} d\lambda \frac{d\rho_{0\lambda}}{d\lambda} \left[ \mu^\ell - \mu(\rho_{0\lambda}^2) \right]$$

$$= -\int d\mathbf{r} \int_0^{r_2} d\rho_{0\lambda} \frac{dW(\rho_{0\lambda})}{d\rho_{0\lambda}}$$

$$= -\int d\mathbf{r} W(\rho_{0\lambda}^2),$$

where $W(\rho)$ is given in Eq. (15). The last term in Eq. (25) gives the nonlocal contribution to the free energy. Using Eq. (19) for $\rho_{0\lambda}$ we require
only $\rho_0^i$ and from Eq. (22) we find

$$I_{nonlocal} = \int d\mathbf{r}_1 \left[ \rho_0^1 - \rho_0^1 \right] K(\mathbf{r}_1) \int d\mathbf{r}_2 \left[ \rho_0^2 - \rho_0^2 \right] u_1(\mathbf{r}_1)$$

(27)

where

$$K(\mathbf{r}) = 2 \int_0^1 d\lambda \lambda \alpha(\rho_{0\lambda})/a.$$  

(28)

Thus we have

$$\gamma = I_{local} + I_{nonlocal},$$

(29)

and both terms require only $\rho_0^i$. In the simplified MVDW theory discussed earlier, we set $\alpha = a$ or $K(\mathbf{r})=1$ in Eq. (27) and expand $\rho_0^2$ about $\rho_0^1$ to second order. Using Eq. (13) with $m_\alpha = m$, we see that these additional approximations imply that $I_{nonlocal} = I_{local}$, as given in Eq. (24). RW show in this case we can use the even simpler expression

$$\gamma = \int_{\rho_0^1}^{\rho_0^2} d\rho[\rho W(\rho)]^{1/2},$$

(30)

which does not require explicit knowledge of $\rho_0^i$.

**D. Results**

Figure 5 gives the surface tension predicted by the MVDW theory (with no capillary wave smoothing of the profile), that arising from use of the hydrostatic approximation as in Eq. (24) and (27), and that given by the simplified MVDW theory in Eq. (30). We see that the MVDW theory gives very good agreement with the simulation data. The simplified MVDW theory is much less accurate. Since all theories give essentially the same results for $I_{local}$, the problem with the simplified theory must arise from its treatment of nonlocal effects through the approximation $I_{nonlocal} = I_{local}$, which we see becomes increasingly inaccurate at lower temperatures. Equation (27) provides a more accurate but still simple alternative to use of the full MVDW theory.

**VII. CONCLUSIONS**

The MVDW theory provides a simple and physically motivated approach that can describe the structure and thermodynamics of a fluid in a general external field. It optimally combines two standard approximations, a molecular field treatment of attractive interactions, modified to give accurate thermodynamic data for the uniform fluid, along with a linear response treatment of correlations in the reference fluid. The present application of the theory to the LV interface permits a new interpretation of the classical VDW theory that removes some ambiguities in standard treatments and shows how key features of the classical theory can be improved in a natural way. The accuracy of the MVDW theory in this application provided additional support for the physical ideas behind the theory and for its quantitative utility.

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We carried out a standard Grand Canonical MC simulation. There are three types of moves: insertion of a particle, removal of a particle and a Canonical local movement of a particle. The ratio of the moves was 1:1:20, which we did not try to optimize. Both a hard sphere fluid of appropriate diameter in the field and the reference LJ fluid in the same field were studied. Both simulations give essentially indistinguishable results. The hard sphere simulation is considerably faster and the figure has those results.

Other density paths can be used, and in some cases may be preferable. See Y.-G. Chen and J. D. Weeks (unpublished)