

## Statistical mechanics of a nonuniform fluid with long-range attractions

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A recursive method is described for generating the Helmholtz free energy and pair-correlation function of a nonuniform fluid, in powers of the Kac inverse-range parameter  $\gamma$ . The results agree with earlier calculations using graphical and functional-integral methods. The ordering of the free energy is functionally consistent with a similar ordering of the density profile. The lowest-order or "van der Waals" theory is equivalent to a mean-field average of the attractive intermolecular energies and use of local thermodynamics in a reference hard-sphere fluid. The next level of approximation is the "random-phase approximation," which is shown to produce logarithmic anomalies in the free energy and density profile similar to those expected on the basis of capillary-wave theory. The occurrence of these anomalies results from the existence of a long-wavelength divergence in the transverse Fourier transform of the lowest-order pair-correlation function.

### I. INTRODUCTION

It is well known<sup>1</sup> that van der Waals' equation of state for uniform fluids is obtained as a rigorous limiting result in the case of molecules whose pair potential consists of a short-range repulsive part plus a weak and long-range attractive tail. The limit corresponds<sup>2</sup> to the neglect of microscopic fluctuations in the attractive interactions, which in turn arise from correlations in number-density fluctuations, and hence can be viewed as a "mean-field" theory. Extensions of this theory, accounting systematically for the effects of microscopic fluctuations, have been generated<sup>3-6</sup> by ordering in powers of the Kac<sup>7</sup> parameter  $\gamma$  characterizing the strength and inverse range of the attractive pair potential. The lowest-order van der Waals theory can also be generalized to nonuniform fluids, as first described by van Kampen<sup>8</sup> and Percus.<sup>9</sup> The resulting integral-equation theory yields a description of the liquid-vapor interface which reduces in certain limits<sup>10,11</sup> to that given by the van der Waals,<sup>12</sup> Cahn-Hilliard<sup>13,14</sup> "square-gradient" approach. We have elsewhere<sup>15-17</sup> discussed the application of this theory to fluid-solid interfaces, in particular to the phenomenon of wetting of such interfaces, where we have further commented on its relation to square-gradient formulations and on the limitations of the latter. It is natural to seek extensions of this theory by utilizing  $\gamma$  as a formal parameter of smallness, paralleling the treatment of uniform fluids. Such is the topic of the present

article.

In Sec. II we describe a recursive method for evaluating the Helmholtz free energy and pair-correlation function in powers of  $\gamma$ . The method derives from the fact that each order of approximation of these functions generates the next-order correction by seeking consistency between two basic functional relations [cf. Eqs. (2.7) and (2.11)]. This provides a simpler route to at least the lowest-order terms in  $\gamma$  ordering than obtained by generalizing either graphical approaches<sup>3,4</sup> or the so-called functional-integral method<sup>5,6</sup> to nonuniform states.

The ordering of the free energy, whereby each successive term starts with one higher power of  $\gamma^3$ , induces a corresponding ordering in the density profile, which is discussed in Sec. III. The use of "local thermodynamics"<sup>2</sup> in determining the lowest-order profile is formally justified by a functional expansion<sup>18</sup> procedure similar to one discussed by Yang *et al.*<sup>19</sup> As in our previous work<sup>15-17</sup> however, it is emphasized that local thermodynamics is applicable only to a reference fluid interacting by short-range repulsive forces. The attractive forces, which vary on the same length scale as the density profile, yield nonlocal contributions and must be evaluated separately.

In Sec. IV we examine the first correction to the lowest-order van der Waals theory, which corresponds to the so-called "random-phase approximation" RPA,<sup>6</sup> specifically focusing attention on the genesis of capillary-wave-like<sup>20-22</sup> diver-

gences at this level. Here we are motivated by the fact that considerable discussion<sup>21–26</sup> has taken place in recent years, addressing questions first raised by Widom,<sup>27</sup> on the relation between the results of van der Waals type of theories and those given by capillary-wave arguments. The former lead<sup>19</sup> to a well-defined density profile for a planar liquid-vapor interface in the absence of external gravitational forces, while capillary-wave theory predicts that the profile becomes increasingly diffuse as the gravitational strength  $g$  approaches zero. The prevalent view, argued for in detail on a semimacroscopic basis by Weeks,<sup>21</sup> is that theories of a van der Waals type pertain to a “bare” or “intrinsic”<sup>27</sup> interface, while capillary-wave theory describes long-wavelength fluctuations in the position of this “bare” interface. There have been some previous attempts<sup>23(a),24,25</sup> to justify this view on a more microscopic basis, although it has been argued<sup>23(b),26</sup> that the approaches of Refs. 23(a) and 24 are invalid. Furthermore, some doubts have recently been expressed<sup>26</sup> about the correctness of capillary-wave predictions.

Here we show that the RPA produces logarithmic anomalies in the interfacial tension  $\bar{\gamma}$  and density profile  $\rho(z)$  similar to those resulting from capillary-wave-like fluctuations in a bare interface described by the van der Waals theory. Specifically,  $\bar{\gamma}$  displays an anomaly of the form  $-g \ln g$ , in agreement with capillary-wave predictions.<sup>20–22</sup> The density profile at this level of approximation diverges for small  $g$  as

$$\rho(z) \sim \ln g. \quad (1.1)$$

These results have been obtained previously by calculations<sup>25,28</sup> in the more restricted context of a system characterized by a Landau-Ginzburg-Wilson Hamiltonian, for which analytical methods first described by Zittartz<sup>28</sup> are available. The present work extends these findings to a considerably more general fluid Hamiltonian model [see (2.1) and (2.2)]. Furthermore, the results (1.1) and for the interfacial tension in RPA are shown to follow directly from the presence of a long-wavelength divergence in the transverse Fourier transform of the lowest-order pair-correlation function, the existence of which was first demonstrated on general grounds by Wertheim.<sup>29</sup>

The prediction in (1.1) that  $\rho(z)$  diverges for small  $g$  disagrees with capillary-wave theory,<sup>20–22</sup> which instead predicts that  $\rho(z)$  is bounded for all  $z$  while its spatial derivative  $d\rho(z)/dz$  should vanish as  $g \rightarrow 0+$  according to

$$\frac{d\rho(z)}{dz} \sim (-1/\ln g)^{1/2}. \quad (1.2)$$

It is likely that the result (1.1) is predicated by use of strict perturbative ordering in powers of the Kac parameter  $\gamma$ . An equivalent result was found by Jasnow and Rudnick<sup>25</sup> from calculations on a “renormalized” RPA.<sup>30,31</sup> These authors, however, were able to justify<sup>32</sup> a resummation yielding the correct result (1.2) by introducing the bare interface position as a degree of freedom in their model. We shall comment briefly on the possible use of an analogous procedure within the framework of the present theory in our conclusion Sec. V. It can be argued that the basis for such a resummation should also be revealed through analysis of higher-order terms in  $\gamma$ -ordered expansions [see, e.g., the present (2.25)]. While this is a difficult task which we do not attempt here, we include in Sec. IV an argument closely related to that which yields the RPA result (1.1) and based on the existence of a long-wavelength divergence<sup>29</sup> in the transverse pair-correlation function, which demonstrates that (1.2) should emerge on properly accounting for the “core condition”<sup>4</sup> satisfied by the pair-correlation function.

In summary, the use of  $\gamma$  ordering provides a systematic means of extending the van der Waals theory, accounting at higher order in the smallness parameter  $\gamma$  for fluctuations which can be identified with capillary-wave-like fluctuations leading to characteristic singularities in the free energy and density profile. The fact that such anomalies occur at higher order in  $\gamma$  is significant, since an *ad hoc* density functional approach,<sup>23,24</sup> which produces *both* a mean-field-like profile and capillary-wave-like effects of order unity, is probably inconsistent. We conclude in Sec. V with further comments on the implications of the present results.

## II. INVERSE-RANGE EXPANSIONS: FREE-ENERGY AND PAIR-CORRELATION FUNCTION

We consider a fluid whose molecules interact by means of a spherically symmetric pair potential  $\phi_2(r)$ , which can be decomposed into a repulsive term  $\phi_2^{(0)}(r)$  and an attractive tail  $w_2(r)$ :

$$\phi_2(r) = \phi_2^{(0)}(r) + w_2(r). \quad (2.1)$$

We shall refer to  $\phi_2^{(0)}(r)$  as a “hard-sphere” potential, although the inclusion of softer short-range repulsive forces does not alter our conclusions. It

is supposed that  $w_2(r)$  has a Kac parametrization,<sup>1-7</sup>

$$w_2(r) = \gamma^3 \Phi(\gamma r). \quad (2.2)$$

The bulk free energy and pair-correlation function of such a fluid can be systematically ordered in powers of  $\gamma$ , by either graphical means<sup>3,4</sup> or by the functional-integral method.<sup>5</sup> Generally speaking, the terms in these expansions involve  $n$ -particle distribution functions of the reference hard-sphere system, denoted in the following by superscript zero, and "chain bonds" depending on  $w_2(r)$ . The results of graph theory can be generalized in a straightforward fashion to the case of a nonuniform fluid, characterized by an arbitrary spatially varying number density  $\rho(\vec{r})$ , simply on replacing the constant bulk density associated with every field point  $i$  in a Mayer graph by the factor  $\rho(\vec{r}_i)$ .<sup>33</sup> The corresponding generalization<sup>6</sup> of the functional-integral approach, so that the reference-system distribution functions depend on the *same* density profile  $\rho(\vec{r})$  as the fluid with attractions added, is less straightforward.

A simple recursive or "bootstrapping" method can be devised to generate the  $\gamma$ -ordered expansions. We start by considering the free-energy functional  $W$ <sup>18,19</sup>, which is related to the Helmholtz free energy  $A$  by

$$W = A - \int d\vec{r} \rho(\vec{r}) \phi_{\text{ex}}(\vec{r}), \quad (2.3)$$

where  $\phi_{\text{ex}}(\vec{r})$  is the external field acting on the fluid. Alternatively,  $W$  is related to the grand canonical partition function  $\Xi$  by

$$W = \Omega + \int d\vec{r} \rho(\vec{r}) [\mu - \phi_{\text{ex}}(\vec{r})], \quad (2.4)$$

where  $\mu$  is the total chemical potential and  $\Omega \equiv -kT \ln \Xi$ . We now consider varying the attractive part of the pair potentials by introducing a "charging parameter"  $\nu$  such that the pair attractions corresponding to strength  $\nu$  are given by  $\nu w_2(r)$ . At the end we set  $\nu=1$ , while  $\nu=0$  corresponds to the reference fluid with no attractions. In order to maintain a density profile  $\rho(\vec{r})$  which does not change as  $\nu$  varies between 0 and 1, and which corresponds to that of the fully charged fluid, it is also necessary to generalize the external potential to the form

$$\phi_{\text{eff}}(\vec{r}; \nu) = \phi_{\text{ex}}(\vec{r}) + \Delta \phi_{\text{eff}}(\vec{r}; \nu), \quad (2.5)$$

where the increment  $\Delta \phi_{\text{eff}}(\vec{r}; \nu)$  satisfies

$$\begin{aligned} \Delta \phi_{\text{eff}}(\vec{r}; \nu=1) &= 0, \\ \Delta \phi_{\text{eff}}(\vec{r}; \nu=0) &\equiv \Delta \phi_{\text{eff}}(\vec{r}). \end{aligned} \quad (2.6)$$

The increment  $\Delta \phi_{\text{eff}}(\vec{r})$  at  $\nu=0$  is such that  $\phi_{\text{eff}}(\vec{r}; \nu=0) \equiv \phi_{\text{eff}}(\vec{r})$  is the total external potential which acts on the hard-sphere reference fluid to impose on it a density profile equal to  $\rho(\vec{r})$ . Working in the grand canonical ensemble, it is then easily found that the free energy  $W(\nu)$  corresponding to strength  $\nu$  is given by

$$W(\nu) = W^{(0)} + \frac{1}{2} \int_0^\nu d\nu' \int \int d\vec{r}_1 d\vec{r}_2 \rho_2(\vec{r}_1, \vec{r}_2; \nu') \times w_2(r_{12}), \quad (2.7)$$

where  $W^{(0)}$  is the free energy of a hard-sphere fluid with density profile  $\rho(\vec{r})$ , and  $\rho_2(\vec{r}_1, \vec{r}_2; \nu')$  is the pair-correlation function of the fluid at strength  $\nu'$ . A similar charging-parameter integration to obtain the free energy of nonuniform fluids has been described by Evans and Schirmacher,<sup>34</sup> without, however, recognizing the essential role played by  $\phi_{\text{eff}}(\vec{r}; \nu)$ . The approach to be described below systematizes one discussed in Ref. 34.

At large separations  $\vec{r}_2 - \vec{r}_1$ , the pair-correlation function becomes

$$\rho_2(\vec{r}_1, \vec{r}_2; \nu') \approx \rho(\vec{r}_1) \rho(\vec{r}_2). \quad (2.8)$$

If this asymptotic result for  $\rho(\vec{r}_1, \vec{r}_2; \nu')$  is used for all separations in the integrand of (2.7), we get

$$\begin{aligned} W(\nu) &\approx W^{(0)} + \frac{\nu}{2} \int \int d\vec{r}_1 d\vec{r}_2 \rho(\vec{r}_1) \rho(\vec{r}_2) w_2(r_{12}) \\ &\equiv W_\nu(\nu), \end{aligned} \quad (2.9)$$

which clearly corresponds to a "mean-field" approximation to the free energy. Let us examine this approximation by substituting the Kac-parametrized form of  $w_2(r)$  from (2.2). Assuming for the moment that the density varies only on the length scale  $\gamma^{-1}$ , i.e.,  $\rho(\vec{r}) = \rho(\vec{R})$  with  $\vec{R} = \gamma \vec{r}$ ,<sup>15,16</sup> and rescaling variables of integration in (2.9), the latter becomes

$$\begin{aligned} W_\nu(\nu) &= W^{(0)} + \frac{\nu}{2} \int \frac{d\vec{R}_1}{\gamma^3} \int d\vec{R}_2 \rho(\vec{R}_1) \\ &\quad \times \rho(\vec{R}_2) \Phi(R_{12}). \end{aligned} \quad (2.10)$$

In a bulk translationally invariant phase with constant density, the integration  $d\vec{r}_1 = d\vec{R}_1 / \gamma^3$  simply yields a factor of the volume, and the resulting approximation to the free energy per unit volume is  $O(\gamma^0)$ . Subtracting out this bulk contribution, the remaining term in (2.10) is proportional to the in-

terfacial area *divided* by  $\gamma$ .<sup>16</sup> As discussed in Ref. (16), such a formal  $\gamma^{-1}$  divergence nonetheless preserves a physically correct magnitude for the ratio of total interfacial to bulk free energy on accounting for a required scaling of the external parameters in the thermodynamic limit (see Sec. IV below), and in this view can be considered a removable singularity.<sup>35</sup> Hence we shall still refer to (2.9) or (2.10) as the  $O(\gamma^0)$  approximation to  $W(\nu)$ . It should be noted that (2.9) will generally also produce terms of higher order in  $\gamma$ , due to the occurrence of density variations on a shorter length scale than  $\gamma^{-1}$ , such as found in the vicinity of walls,<sup>15-17</sup> and also due to the fact that the density profile itself, regardless of the length scale on which its components vary, has an expansion in powers of  $\gamma$  (see Sec. III). Notice, however, that all corrections to the uncorrelated approximation for  $\rho_2(\vec{r}_1, \vec{r}_2; \nu)$  in (2.8), on which (2.9) is based, approach zero at large  $|\vec{r}_2 - \vec{r}_1|$  and thus yield contributions to  $W(\nu)$  which are higher than  $O(\gamma^0)$ ; in particular, it will be seen below that corrections to the functional form (2.9) for  $W(\nu)$  are of dominant order  $\gamma^3$ . Thus (2.9) accounts for *all* contributions to the free energy through terms of  $O(\gamma^2)$ .

We can generate corrections to the approximations (2.8) and (2.9) by using the fact that the second functional derivative of  $W(\nu)$  with respect to density gives the direct correlation function  $c_2(\vec{r}_1, \vec{r}_2; \nu)$  (Refs. 18 and 19):

$$\begin{aligned} \frac{\delta^2 \beta W(\nu)}{\delta \rho(\vec{r}_1) \delta \rho(\vec{r}_2)} &= \delta(\vec{r}_1 - \vec{r}_2) / \rho(\vec{r}_1) \\ &\quad - c_2(\vec{r}_1, \vec{r}_2; \nu) \\ &\equiv \hat{c}_2(\vec{r}_1, \vec{r}_2; \nu), \end{aligned} \quad (2.11)$$

where  $\beta = 1/kT$ . Applying this relation to the lowest-order result (2.9) yields

$$\hat{c}_2(\vec{r}_1, \vec{r}_2; \nu) \approx \hat{c}_2^{(0)}(\vec{r}_1, \vec{r}_2) + \nu \beta w_2(r_{12}), \quad (2.12)$$

where

$$\hat{c}_2^{(0)}(\vec{r}_1, \vec{r}_2) = \frac{\delta^2 \beta W^{(0)}}{\delta \rho(\vec{r}_1) \delta \rho(\vec{r}_2)} \quad (2.13)$$

is the modified hard-sphere direct correlation function. Equation (2.12) is of course the familiar "Ornstein-Zernike" approximation to  $\hat{c}_2(\vec{r}_1, \vec{r}_2; \nu)$ .

The pair-correlation function is related to the latter by

$$\int d\vec{r}_3 \hat{F}_2(\vec{r}_1, \vec{r}_3; \nu) \hat{c}_2(\vec{r}_3, \vec{r}_2; \nu) = \delta(\vec{r}_1 - \vec{r}_2), \quad (2.14)$$

where  $\hat{F}_2(\vec{r}_1, \vec{r}_2; \nu)$  is the modified two-particle Ursell function<sup>3</sup>

$$\begin{aligned} \hat{F}_2(\vec{r}_1, \vec{r}_2; \nu) &= \rho_2(\vec{r}_1, \vec{r}_2; \nu) - \rho(\vec{r}_1) \rho(\vec{r}_2) \\ &\quad + \rho(\vec{r}_1) \delta(\vec{r}_1 - \vec{r}_2). \end{aligned} \quad (2.15)$$

We can write (2.14) in symbolic notation as

$$\hat{F}_2(\nu) * \hat{c}_2(\nu) = 1 \quad (2.16a)$$

or

$$\hat{F}_2(\nu) = [\hat{c}_2(\nu)]^{-1}, \quad (2.16b)$$

where  $\hat{F}_2(\nu)$ ,  $\hat{c}_2(\nu)$ , and 1 are regarded as matrices in an infinite continuous vector space labeled by the particle positions  $\vec{r}$ ; the symbol \* denotes convolution, i.e., matrix product, in this representation. It follows from the approximation (2.12) that, symbolically

$$\hat{F}_2(\nu) \approx [1 + \nu \beta \hat{F}_2^{(0)} * w_2]^{-1} * \hat{F}_2^{(0)} \quad (2.17a)$$

$$= \hat{F}_2^{(0)} + \hat{F}_2^{(0)} * \zeta(\nu) * \hat{F}_2^{(0)} \quad (2.17b)$$

$$\equiv \hat{F}_{2,v}(\nu),$$

where  $\hat{F}_2^{(0)} \equiv [\hat{c}_2^{(0)}]^{-1}$  is the hard-sphere modified Ursell function, and  $\zeta(\nu) = \zeta(\vec{r}_1, \vec{r}_2; \nu)$  is the "chain bond"<sup>3,4</sup> defined as

$$\zeta(\nu) = -\nu \beta w_2 * [1 + \nu \beta \hat{F}_2^{(0)} * w_2]^{-1}. \quad (2.18)$$

Note that (2.15) and (2.17) provide a refined approximation for  $\rho_2(\vec{r}_1, \vec{r}_2; \nu)$ , correcting the uncorrelated value in (2.8). If this result is used in (2.7), we obtain a refined approximation to the free energy

$$\begin{aligned} W(\nu) &\approx W_v(\nu) - \frac{\nu}{2} w_2(0) \int d\vec{r}_1 \rho(\vec{r}_1) \\ &\quad + \beta^{-1} D(\nu), \\ &\equiv W_{\text{RPA}}(\nu), \end{aligned} \quad (2.19)$$

where  $W_v(\nu)$  is given by (2.9),  $w_2(0) = w_2(r=0)$ , and  $D(\nu)$  is the following "chain sum,"

$$\begin{aligned}
D(\nu) = \frac{1}{2} & \left[ \beta\nu \int \int d\vec{r}_1 d\vec{r}_2 \hat{F}_2^{(0)}(\vec{r}_1, \vec{r}_2) w_2(\vec{r}_{12}) \right. \\
& - \frac{(\beta\nu)^2}{2} \int \int \int \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 \hat{F}_2^{(0)}(\vec{r}_1, \vec{r}_2) w_2(r_{23}) \hat{F}_2^{(0)}(\vec{r}_3, \vec{r}_4) w_2(r_{41}) \\
& \left. + \frac{(\beta\nu)^3}{3} \int \dots \int d\vec{r}_1 \dots d\vec{r}_6 \hat{F}_2^{(0)}(\vec{r}_1, \vec{r}_2) w_2(r_{23}) \hat{F}_2^{(0)}(\vec{r}_3, \vec{r}_4) w_2(r_{45}) \hat{F}_2^{(0)}(\vec{r}_5, \vec{r}_6) w_2(r_{61}) - \dots \right]. \quad (2.20a)
\end{aligned}$$

This can be written in matrix notation as (see also Ref. 6)

$$\begin{aligned}
D(\nu) &= \frac{1}{2} \text{Tr}[\ln(1 + \beta\nu \hat{F}_2^{(0)} * w_2)] \\
&= \frac{1}{2} \text{Tr}[\ln\{\hat{F}_2^{(0)} * [\hat{F}_{2,v}(\nu)]^{-1}\}], \quad (2.20b)
\end{aligned}$$

where Tr denotes trace and the second line follows from (2.17a). The approximation to the free energy given by (2.19) and (2.20) has previously been derived graphically,<sup>3,4</sup> by the functional-integral method<sup>5,6,36</sup> (considering the contribution from density fluctuations in Gaussian approximation), and, at least for uniform fluids, by the so-called mode expansion.<sup>37</sup> This corresponds to the random-phase approximation (RPA).

In the context of  $\gamma$  ordering,<sup>3,4</sup> (2.17) accounts for the leading-order terms in the expansion of the two-particle Ursell function. This expansion generally involves the decomposition of  $\hat{F}_2(\vec{r}_1, \vec{r}_2; \nu)$  into "short-range" (SR) and "long-range" (LR) parts,

$$\hat{F}_2(\vec{r}_1, \vec{r}_2; \nu) = \hat{F}_2^{\text{SR}}(\vec{r}_1, \vec{r}_2; \nu) + \hat{F}_2^{\text{LR}}(\vec{R}_1, \vec{R}_2; \nu). \quad (2.21)$$

To lowest order,  $\hat{F}_2^{\text{SR}}$  is equal to the reference-system Ursell function  $\hat{F}_2^{(0)}$ , and hence is independent of  $\gamma$  [considering the density profile on which it functionally depends to be arbitrary, cf. our comments following (2.10)]. The second term on the right of (2.17b) represents the lowest-order approximation for  $\hat{F}_2^{\text{LR}}$ . The dominant order in  $\gamma$  of this term, for fixed values of  $\vec{R}_1 = \gamma\vec{r}_1$  and  $\vec{R}_2 = \gamma\vec{r}_2$ , can be determined on approximating each reference-system Ursell function appearing there and in (2.18) by a  $\delta$  function of its arguments [cf. (3.18) below<sup>3-5</sup>], and is found to be  $O(\gamma^3)$ . The combination of these lowest-order results for the SR and LR terms of  $F_2$  yields a contribution to the free energy, specifically the term  $D(\nu)$  defined above, which is of dominant order  $\gamma^3$ . [In using this designation one must bear in mind, cf. the dis-

cussion following (2.10), that the interfacial part of the free energy is actually reduced by one factor of  $\gamma$ .<sup>16</sup>] Here we observe at lowest order an illustration of the more general fact<sup>3,4</sup> that the SR part of  $\hat{F}_2$  for fixed  $\vec{r}_2 - \vec{r}_1$  must be combined with the LR part to one higher order in  $\gamma^3$  for fixed  $\vec{R}_2 - \vec{R}_1$  to give thermodynamic contributions of the same order in  $\gamma^3$ .

The same procedure as used above to refine the mean-field free energy (2.9) into the RPA result (2.19) can also be applied to the latter. On taking two functional derivatives of (2.19) with respect to density, we first derive a higher-order approximation for the modified direct correlation function:

$$\begin{aligned}
\hat{c}_2(\vec{r}_1, \vec{r}_2; \nu) &\approx \hat{c}_2^{(0)}(\vec{r}_1, \vec{r}_2) + \nu\beta w_2(r_{12}) \\
&\quad + x(\vec{r}_1, \vec{r}_2; \nu), \quad (2.22)
\end{aligned}$$

where

$$x(\vec{r}_1, \vec{r}_2; \nu) = \frac{\delta^2 D(\nu)}{\delta\rho(\vec{r}_1)\delta\rho(\vec{r}_2)}. \quad (2.23)$$

The latter function can be shown to have a SR part of dominant order  $\gamma^3$  and a LR part of dominant order  $\gamma^6$ . The modified two-particle Ursell function is found by applying (2.16); the next correction to this function, beyond the lowest-order result in (2.17), is obtained by keeping only terms linear in  $x(\vec{r}_1, \vec{r}_2; \nu)$ . Hence we find, in symbolic notation,

$$\hat{F}_2(\nu) \approx \hat{F}_{2,v}(\nu) - \hat{F}_{2,v}(\nu) * x(\nu) * \hat{F}_{2,v}(\nu). \quad (2.24)$$

This can be shown, on manipulating the functional derivatives involved in the definition of  $x(\vec{r}_1, \vec{r}_2; \nu)$ , to agree with graph-theoretical results<sup>3,4</sup>; specifically, this gives  $\hat{F}_2^{\text{SR}}(\vec{r}_1, \vec{r}_2; \nu)$  to  $O(\gamma^3)$  and  $\hat{F}_2^{\text{LR}}(\vec{R}_1, \vec{R}_2; \nu)$  to  $O(\gamma^6)$ . On inserting the pair-correlation function obtained from this result and (2.15) into the integral of (2.7), after a bit of effort we find

$$\begin{aligned}
W(\nu) &\approx W_{\text{RPA}}(\nu) \\
&- \frac{1}{8\beta} \int \dots \int d\vec{r}_1 \dots d\vec{r}_6 \left[ \frac{\delta^2 \hat{F}_2^{(0)}(\vec{r}_3, \vec{r}_4)}{\delta\rho(\vec{r}_1)\delta\rho(\vec{r}_2)} \right] \hat{F}_2^{(0)}(\vec{r}_1, \vec{r}_5) \zeta(\vec{r}_5, \vec{r}_6; \nu) \hat{F}_2^{(0)}(\vec{r}_6, \vec{r}_2) \zeta(\vec{r}_3, \vec{r}_4; \nu) \\
&- \frac{1}{12\beta} \int \dots \int d\vec{r}_1 \dots d\vec{r}_6 \hat{F}_3^{(0)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) \zeta(\vec{r}_1, \vec{r}_4; \nu) \zeta(\vec{r}_2, \vec{r}_5; \nu) \zeta(\vec{r}_3, \vec{r}_6; \nu) \hat{F}_3^{(0)}(\vec{r}_4, \vec{r}_5, \vec{r}_6), \quad (2.25)
\end{aligned}$$

where  $\hat{F}_3^{(0)}(\vec{r}_1, \vec{r}_2, \vec{r}_3)$  is the modified three-particle Ursell function for hard spheres.<sup>3,4,18,33</sup> Equation (2.25) has been given previously by Stell,<sup>4(b)</sup> and provides the exact correction term of dominant order  $\gamma^6$ .

The present recursive method is based simply on use of the two exact relations, (2.7), which gives  $W(\nu)$  as a functional integral involving the pair-correlation function (the integrand of  $d\nu'$  in this relation can be identified as the excess internal energy at strength  $\nu'$ ), and (2.11) expressing the direct correlation function as the second functional derivative of  $\beta W(\nu)$  with respect to density. These two relations are the functional generalizations of the well-known internal energy and compressibility routes, respectively, to bulk thermodynamics.<sup>3</sup> Each order of approximation to the free energy and pair-correlation function generates its successor by attempting to satisfy both of these relations, i.e., by seeking thermodynamic consistency, which, however, can only be achieved asymptotically. On initializing the sequence of approximations at the mean-field level, each successive correction to  $W(\nu)$  starts with one higher power of  $\gamma^3$ , thus providing a simple derivation and reinterpretation of  $\gamma$ -ordering theory.<sup>3-6</sup> In principle, further corrections to  $W(\nu)$  and  $\hat{F}_2^{(0)}(\vec{r}_1, \vec{r}_2; \nu)$  beyond those given explicitly here can be generated in the same fashion, although the analysis quickly becomes very tedious.

### III. DENSITY PROFILE

The terms in the  $\gamma$ -ordered expressions for the free energy and pair-correlation function given in Sec. II contain the density profile  $\rho(\vec{r})$  as well as hard-sphere quantities, e.g.,  $W^{(0)}$  and  $\hat{F}_2^{(0)}(\vec{r}_1, \vec{r}_2)$ , which are functionals of  $\rho(\vec{r})$ . In principle, knowing these functional dependences,  $\rho(\vec{r})$  can be determined by applying the fundamental relation<sup>18,19,29</sup>

$$\frac{\delta W}{\delta\rho(\vec{r})} = \mu - \phi_{\text{ex}}(\vec{r}), \quad (3.1)$$

where, from now on, it is implicit that  $\nu=1$ .

It is useful to separate out the pure hard-sphere contribution  $W^{(0)}$  from the last equation. Recalling (2.5) and (2.6), we have analogous to (3.1)

$$\frac{\delta W^{(0)}}{\delta\rho(\vec{r})} = \mu - \phi_{\text{eff}}(\vec{r}). \quad (3.2)$$

That is,  $\rho(\vec{r})$  can be equivalently viewed as the density profile of a pure hard-sphere fluid at total chemical potential  $\mu$  in the presence of the external potential  $\phi_{\text{eff}}(\vec{r})$ .<sup>15-17</sup> Strictly, the last equation amounts to no more than a definition of  $\phi_{\text{eff}}(\vec{r})$ ; combined with (3.1), it can be expressed as

$$\phi_{\text{eff}}(\vec{r}) = \phi_{\text{ex}}(\vec{r}) + \frac{\delta}{\delta\rho(\vec{r})} (W - W^{(0)}). \quad (3.3)$$

In particular, using the RPA approximation to  $W$  from (2.19) and (2.20), this yields the prescription

$$\begin{aligned}
\phi_{\text{eff}}(\vec{r}_1) - \phi_{\text{ex}}(\vec{r}_1) &\approx \int d\vec{r}_2 w_2(r_{12}) \rho(\vec{r}_2) \\
&- \frac{1}{2} w_2(0) + \beta^{-1} \frac{\delta D}{\delta\rho(\vec{r}_1)}, \quad (3.4)
\end{aligned}$$

where the last term on the right is, more explicitly

$$\begin{aligned}
\frac{\delta D}{\delta\rho(\vec{r}_1)} &= -\frac{1}{2} \int \int d\vec{r}_2 d\vec{r}_3 \zeta(\vec{r}_2, \vec{r}_3) \\
&\times \frac{\delta \hat{F}_2^{(0)}(\vec{r}_2, \vec{r}_3)}{\delta\rho(\vec{r}_1)} \quad (3.5)
\end{aligned}$$

Equation (3.2) together with (3.3) or (3.4) provides a "closed" equation for the density profile on expressing  $\delta W^{(0)}/\delta\rho(\vec{r})$  in terms of  $\rho(\vec{r})$ . In a bulk uniform fluid, with  $\phi_{\text{ex}}(\vec{r})=0$  and both  $\rho(\vec{r})=\rho$ ,  $\phi_{\text{eff}}(\vec{r})=\phi_{\text{eff}}$  constant everywhere, the latter step is formally trivial and leads to the equation of state

$$\mu^{(0)}(\rho) = \mu - \phi_{\text{eff}}, \quad (3.6)$$

where  $\mu^{(0)}(\rho)$  is the bulk chemical potential of hard spheres at density  $\rho$  [denoted in our earlier work<sup>15-17</sup> as  $\mu_h(\rho)$ ]. Under these circumstances, on retaining only the first or mean-field term on the right of (3.4), (3.6) becomes the familiar van

der Waals equation of state.<sup>1</sup>

The last equation can be generalized to the nonuniform régime by use of  $\gamma$ -ordering methods. We restrict consideration to external fields which are only slowly varying, i.e., on the length scale  $\gamma^{-1}$ , thus ignoring, e.g., the presence of walls.<sup>15-17</sup> Hence we set  $\phi_{\text{ex}}(\vec{r}_1) = \phi_{\text{ex}}(\vec{R}_1)$ ,  $\vec{R}_1 \equiv \gamma \vec{r}_1$ . It will be found, self-consistently, that the resulting density variation occurs only on this length-scale, so that  $\rho(\vec{r}_1) = \rho(\vec{R}_1)$ . Using the same argument as applied in (2.10), the first term on the right in (3.4) is seen to be  $O(\gamma^0)$  for fixed  $\vec{R}_1$ . The second term is a constant proportional to  $\gamma^3$ , cf. (2.2). The third term can be shown by  $\gamma$ -ordering techniques [see, e.g., the discussion following (2.21)] to be of leading order  $\gamma^3$  for fixed  $\vec{R}_1$ . Hence, to zeroth order

in  $\gamma$ ,  $\phi_{\text{eff}}(\vec{R}_1)$  consists of only the mean-field term in (3.4),

$$\phi_{\text{eff}}(\vec{R}_1) = \phi_{\text{ex}}(\vec{R}_1) + \int d\vec{R}_2 \Phi(\vec{R}_{12}) \rho(\vec{R}_2) + O(\gamma^3). \quad (3.7)$$

One anticipates that, to the same order, (3.6) still applies with  $\mu^{(0)}(\rho)$  simply generalized to the "local" hard-sphere chemical potential  $\mu^{(0)}(\rho(\vec{R}_1))$ . This has been used, without formal proof, in our earlier work,<sup>15-17</sup> and will here be verified by a method similar to that described in Appendix A of Ref. 19. We consider the functional Taylor-series expansion<sup>18</sup> of  $\delta W^{(0)}/\delta \rho(\vec{r}_1)$  about its value  $\mu^{(0)}(\rho(\vec{R}_1))$  in a uniform reference system of density everywhere equal to  $\rho(\vec{R}_1)$ . This gives

$$\begin{aligned} \frac{\delta \beta W^{(0)}}{\delta \rho(\vec{r}_1)} &= \beta \mu^{(0)}(\rho(\vec{R}_1)) + \int d\vec{r}_2 \hat{c}_{2,B}^{(0)}(r_{12}) [\rho(\vec{R}_2) - \rho(\vec{R}_1)] \\ &+ \frac{1}{2} \int d\vec{r}_2 d\vec{r}_3 \hat{c}_{3,B}^{(0)}(r_{12}, r_{13}) [\rho(\vec{R}_2) - \rho(\vec{R}_1)] [\rho(\vec{R}_3) - \rho(\vec{R}_1)] + \dots, \end{aligned} \quad (3.8)$$

where we have used (2.13) and where

$$\hat{c}_3^{(0)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \frac{\delta^3 \beta W^{(0)}}{\delta \rho(\vec{r}_1) \delta \rho(\vec{r}_2) \delta \rho(\vec{r}_3)} \quad (3.9)$$

is the modified three-particle direct correlation function for hard spheres. The subscript  $B$  on this function and on  $\hat{c}_{2,B}^{(0)}(r_{12})$  in (3.8) denotes that they are to be evaluated in a bulk, translationally invariant system of constant density  $\rho(\vec{R}_1)$ . Furthermore, since these are *hard-sphere* direct correlation functions, they can be presumed to decay quickly to zero when their arguments are separated merely by microscopic distances. Hence, the standard gradient expansion<sup>19</sup> of the slowly varying densities  $\rho(\vec{R}_j)$ ,  $j=2,3$ , in the integrands of (3.8), i.e.,

$$\begin{aligned} \rho(\vec{R}_j) - \rho(\vec{R}_1) &= \gamma \vec{r}_{1j} \cdot \nabla_{\vec{R}_1} \rho(\vec{R}_1) \\ &+ \frac{\gamma^2}{2} (\vec{r}_{1j} \cdot \nabla_{\vec{R}_1})^2 \rho(\vec{R}_1) + \dots \end{aligned} \quad (3.10)$$

is justified in this case on the basis of  $\gamma$  ordering. Here,  $\nabla_{\vec{R}_1}$  denotes the gradient with respect to the scaled variable  $\vec{R}_1 = \gamma \vec{r}_1$ . Inserting (3.10) into (3.8), the rest of the development otherwise proceeds in the same manner described by Yang *et al.*,<sup>19</sup> resulting in

$$\begin{aligned} \frac{\delta \beta W^{(0)}}{\delta \rho(\vec{r}_1)} &= \beta \mu^{(0)}(\rho(\vec{R}_1)) \\ &+ \gamma^2 A^{(0)}(\rho(\vec{R}_1)) \nabla_{\vec{R}_1}^2 \rho(\vec{R}_1) \\ &+ \frac{\gamma^2}{2} A^{(0)'}(\rho(\vec{R}_1)) [\nabla_{\vec{R}_1} \rho(\vec{R}_1)]^2 + O(\gamma^4), \end{aligned} \quad (3.11)$$

where

$$A^{(0)}(\rho(\vec{R}_1)) = \frac{1}{6} \int d\vec{r}_{12} \hat{c}_{2,B}^{(0)}(r_{12}) r_{12}^2, \quad (3.12)$$

and  $A^{(0)'}(\rho) \equiv \partial A^{(0)}(\rho) / \partial \rho$ .

Equation (3.11) confirms the expectation that  $\delta W^{(0)}/\delta \rho(\vec{r}_1)$  is given by the local hard-sphere chemical potential to  $O(\gamma^0)$ . Including all the terms displayed in (3.11), substitution of this equation together with the mean field  $\phi_{\text{eff}}(\vec{R}_1)$  from (3.7) into (3.2) yields an integro-differential equation for  $\rho(\vec{R}_1)$  valid to  $O(\gamma^2)$ . We denote the resulting, "van der Waals" approximation to the density profile as  $\rho_0(\vec{R}_1)$ . These results differ from those of Yang *et al.*<sup>19</sup> in that the only "local thermodynamic" functions which arise here, i.e.,  $\mu^{(0)}(\rho(\vec{R}_1))$  and  $A^{(0)}(\rho(\vec{R}_1))$ , refer strictly to a hard-sphere fluid. (One significance<sup>15,17</sup> of this, of

course, is that we thereby do not encounter any problems arising from interpretation of local thermodynamic quantities at densities corresponding to metastable or unstable portions of the bulk fluid phase diagram.) The contribution of intermolecular attractions is contained in the nonlocal term of (3.7). There is no *formal* justification for carrying out a further gradient expansion of  $\rho(\vec{R}_2)$  in the integrand of this term, since truncation of such an expansion will omit an infinite number of terms of  $O(\gamma^0)$ . Performing such an expansion<sup>10,11,17</sup> to second-order gradients of  $\rho(\vec{R}_1)$  and neglect of the  $O(\gamma^2)$  terms in (3.11), leads to what is usually called “van der Waals, Cahn-Hilliard, square-gradient” theory.<sup>12–14,27</sup>

The presence of walls leads to the existence of an additional “short-range” component in the density profile, analogous to the decomposition (2.21) of the pair correlation function into SR and LR parts. This more general situation can also be analyzed by a functional expansion method similar to that used in this section. We shall not go into this here, except to point out that, to strict  $O(\gamma^0)$  terms, the LR component of the density profile is decoupled from the SR part and satisfies the same equations as given above, with the inclusion of a wall cutoff in the integrand of (3.7).<sup>15</sup> In this case, the further approximation of gradient expanding the density profile in this integrand, in addition to being formally incorrect, gives rise to practical errors.<sup>16,17</sup> The SR component of the density profile is determined by other means,<sup>15</sup> *not* involving the application of local thermodynamics, which clearly cannot be sensibly applied to functions which undergo the type of sharp oscillations expected in the vicinity of a wall.

As noted above, the last two terms in the RPA approximation (3.4) for  $\phi_{\text{eff}}(\vec{R}_1)$  are  $O(\gamma^3)$ , and hence will induce a correction of  $O(\gamma^3)$  in the density profile. It is more generally evident that the successive corrections to the free energy discussed in Sec. II, each starting with one higher power of  $\gamma^3$ , will lead via (3.3) to an ordering of the effective potential in powers of  $\gamma^3$ , and hence to an ordering of the density profile which can be written as

$$\rho(\vec{R}) = \rho_0(\vec{R}) + \rho_1(\vec{R}) + \rho_2(\vec{R}) + \dots, \quad (3.13)$$

where  $\rho_n(\vec{R})$  is of leading order  $\gamma^{3n}$ . We shall explicitly analyze the first correction  $\rho_1(\vec{R})$  in Sec. IV. We conclude this section with the remark, which will be of relevance in Sec. IV, that the present results for the density profile can also be obtained by use of the integro-differential equa-

tion<sup>29,38</sup>

$$\nabla\rho(\vec{r}_1) = -\beta \int d\vec{r}_2 \hat{F}_2(\vec{r}_1, \vec{r}_2) \nabla\phi_{\text{ex}}(\vec{r}_2), \quad (3.14)$$

or by the equivalent equation, which follows from the Ornstein-Zernike relation (2.14),

$$\beta\nabla\phi_{\text{ex}}(\vec{r}_1) = -\int d\vec{r}_2 \hat{c}_2(\vec{r}_1, \vec{r}_2) \nabla\rho(\vec{r}_2). \quad (3.15)$$

We have reverted to expressing positions as  $\vec{r}_i$ , since these equations apply under arbitrary spatial variation of the density and external field.<sup>29,38</sup> An additional equivalence exists between the last two equations and the following pair:

$$\nabla\rho(\vec{r}_1) = -\beta \int d\vec{r}_2 \hat{F}_2^{(0)}(\vec{r}_1, \vec{r}_2) \nabla\phi_{\text{eff}}(\vec{r}_2), \quad (3.16)$$

$$\beta\nabla\phi_{\text{eff}}(\vec{r}_1) = -\int d\vec{r}_2 \hat{c}_2^{(0)}(\vec{r}_1, \vec{r}_2) \nabla\rho(\vec{r}_2), \quad (3.17)$$

which can be generally verified using the definitions of  $\hat{c}_2(\vec{r}_1, \vec{r}_2)$ ,  $\hat{c}_2^{(0)}(\vec{r}_1, \vec{r}_2)$ , and  $\phi_{\text{eff}}(\vec{r})$ , Eqs. (2.11), (2.13), and (3.3), respectively, together with the appropriate functional chain rule<sup>18,29,38</sup> for the gradient operator. Of later significance, one can specifically verify that (3.14) and (3.16) are equivalent in lowest order, with  $\hat{F}_2(\vec{r}_1, \vec{r}_2)$  approximated by  $\hat{F}_{2,v}(\vec{r}_1, \vec{r}_2)$  defined in (2.17), and  $\phi_{\text{eff}}(\vec{r})$  given in mean-field approximation. Functional expansion of  $\hat{F}_2^{(0)}(\vec{r}_1, \vec{r}_2)$  in (3.16) then leads to results identical to those discussed earlier in this section. For example, the leading term  $\mu^{(0)}(\rho(\vec{R}_1))$  in (3.11) is equivalent to use of the “local” approximation

$$\hat{F}_2^{(0)}(\vec{r}_1, \vec{r}_2) \approx \chi^{(0)}(\rho(\vec{R}_1)) \delta(\vec{r}_1 - \vec{r}_2), \quad (3.18a)$$

with

$$\chi^{(0)}(\rho) = \left[ \frac{\partial\beta\mu^{(0)}(\rho)}{\partial\rho} \right]^{-1}. \quad (3.18b)$$

Notice, again, that we only apply local thermodynamics to hard-sphere quantities.

#### IV. CAPILLARY-WAVELIKE ANOMALIES IN RPA

In this section we carry out a partial analysis of the RPA contributions to the free energy and density profile. Here we specialize to the situation of a planar liquid-vapor interface in the presence of a weak gravitational field  $mgz$  acting in the  $z$  direction. Strictly, to be consistent with a density profile varying on the length scale  $\gamma^{-1}$ , the gravita-

tional strength  $g$  should be replaced by the scaled variable  $\gamma g$  (we consider that  $\gamma$  has been rendered dimensionless, e.g., by expressing  $\gamma^{-1}$ , the range of attractive interactions, in units of a microscopic length such as hard-sphere diameter). Such a scaling goes along with the requirement<sup>1,2</sup> that each linear dimension  $L_i$  of the system be correspondingly scaled to  $L_i/\gamma$  as  $\gamma \rightarrow 0$ , yielding a change of gravitational potential over the system,  $\propto gL_i$ , which is invariant under scaling.<sup>35</sup> For notational convenience in this section, we henceforth use units in which  $\gamma = 1$ , recognizing also the purely *formal* smallness of  $\gamma$ .<sup>16</sup>

The density profile can now be considered as varying only in the  $z$  direction, and therefore denoted  $\rho(z)$ . Correspondingly, the two-particle Ursell functions  $\hat{F}_2(\vec{r}_1, \vec{r}_2)$  and  $\hat{F}_2^{(0)}(\vec{r}_1, \vec{r}_2)$  are translationally invariant in the  $xy$  plane and hence can be expressed in terms of transverse Fourier transforms, e.g.,

$$\hat{F}_2(\vec{r}_1, \vec{r}_2) = \frac{1}{(2\pi)^2} \int d\vec{k} \hat{F}_2(z_1, z_2, k) e^{-i\vec{k} \cdot \vec{s}_{12}}, \quad (4.1)$$

where  $\vec{k}$  is the Fourier wave vector in the  $xy$  plane and  $\vec{s}_{12}$  is the projection of  $\vec{r}_2 - \vec{r}_1$  onto this plane. Central to the following analysis is the result, first deduced by Wertheim<sup>29</sup> and later extended by others,<sup>21,22</sup> that the transformed Ursell function  $\hat{F}_2(z_1, z_2, k)$  under the present conditions should display a small- $k$  divergence

$$\hat{F}_2(z_1, z_2, k) \sim \frac{\rho'(z_1)\rho'(z_2)}{\beta\bar{\gamma}k^2 + \beta mg \Delta\rho}, \quad k \rightarrow 0 \quad (4.2)$$

where  $\rho'(z) = d\rho(z)/dz$ ,  $\Delta\rho = \rho(-\infty) - \rho(+\infty)$  is the difference in coexisting bulk densities, and  $\bar{\gamma}$  is the interfacial tension. The work in Refs. 21, 22, and 29 has shown that the asymptotic result (4.2) follows generally from any theory of the liquid-vapor interface in a weak gravitational field, for which the relevant density profile and Ursell function are related by (3.14) and for which the profile approaches a well-defined limit<sup>29</sup> or indeed slowly washes out<sup>21</sup> as  $g \rightarrow 0+$ . Since as noted at the end of Sec. III, these conditions are satisfied by the lowest-order van der Waals density profile  $\rho_0(z)$  and the corresponding approximate Ursell function  $\hat{F}_{2,v}(\vec{r}_1, \vec{r}_2)$ , the relation (4.2) must in particular hold for the transverse Fourier transform of the latter,

$$\hat{F}_{2,v}(z_1, z_2, k) \sim \frac{\rho'_0(z_1)\rho'_0(z_2)}{\beta\bar{\gamma}_0 k^2 + \beta mg \Delta\rho_0}, \quad k \rightarrow 0 \quad (4.3)$$

where  $\bar{\gamma}_0$  denotes the interfacial tension of the van der Waals theory. This result has also been explicitly verified<sup>26,28</sup> in the Landau-Ginzburg-Wilson submodel of van der Waals theory. [This model is derived<sup>2,28</sup> by neglecting higher than second-order terms in the wave-vector expansion of the Fourier transform of  $w_2(r)$ , equivalent to the familiar square-gradient approximation, and representing the hard-sphere chemical potential  $\beta\mu^{(0)}(\rho)$  by its expansion to terms cubic in  $\rho - \rho_c$ , where  $\rho_c$  is the fluid critical density.] In the following we demonstrate how the divergence of  $\hat{F}_{2,v}(z_1, z_2, k)$  in (4.3) leads to capillary-wave-like anomalies in the higher-order RPA contributions to the density profile and free energy. Essentially the same mechanism for the production of anomalies is implicit in earlier analyses<sup>25,28,32</sup>; the more general nature of the Hamiltonian model considered here and the explicit connection drawn to the work pioneered in Ref. 29, justifies the present account.

We consider first the quantity  $D$  occurring in the RPA free energy, (2.19) and (2.20). Application of some matrix identities allows (2.20b) to be written as

$$D = \frac{1}{2} \{ \ln[\det(\hat{F}_2^{(0)})] - \ln[\det(\hat{F}_{2,v})] \}, \quad (4.4)$$

where  $\text{Det}$  denotes determinant. As described in Sec. II,  $D$  yields a contribution of dominant order  $\gamma^3$  to the free energy, irrespective of the order of approximation of the density profile on which the matrices  $\hat{F}_2^{(0)}$  and  $\hat{F}_{2,v}$  in (4.4) functionally depend. To leading order, therefore, we can take the profile implicit in (4.4) as that given by the zeroth-order van der Waals theory,  $\rho_0(z)$ . Correspondingly, the Ursell function  $\hat{F}_{2,v}$  in the above equation satisfies (4.3) for small  $k$ . To extract the contribution of this divergence, we suppose that  $\hat{F}_{2,v}(z_1, z_2, k)$  has a spectral decomposition<sup>21,22,29</sup>

$$\hat{F}_{2,v}(z_1, z_2, k) = \sum_{i=0} \epsilon_i^*(z_1) \epsilon_i(z_2) f_{i,v}(k), \quad (4.5)$$

where the  $\epsilon_i(z)$  are a complete set of appropriate orthonormal eigenfunctions. Then the second term on the right-hand side of (4.4) can be written as

$$\begin{aligned} D_2 &\equiv -\frac{1}{2} \ln[\det(\hat{F}_{2,v})] \\ &= -\frac{\mathcal{A}}{2(2\pi)^2} \int d\vec{k} \sum_{i=0} \ln f_{i,v}(k), \end{aligned} \quad (4.6)$$

where  $\mathcal{A}$  is the area of the interface. Since the hard-sphere Ursell function  $\hat{F}_2^{(0)}(z_1, z_2, k)$  does not

suffer a small- $k$  divergence analogous to (4.2), we shall ignore the remaining term in (4.4),  $\propto \ln[\text{Det}(\hat{F}_2^{(0)})]$ .

As others<sup>21,22,29</sup> have argued, (4.3) corresponds in the limit  $g \rightarrow 0+$  to a "ground state" eigenfunction  $\epsilon_0(z) = \rho_0'(z)$ , apart from normalization constant, and eigenvalue

$$D_2 \sim \frac{\mathcal{A}}{4\pi} \int_0^{k_m} dk k \ln(\beta\bar{\gamma}_0 k^2 + \beta mg \Delta\rho_0) = \frac{\mathcal{A}}{8\pi\beta\bar{\gamma}_0} \{(\beta\bar{\gamma}_0 k_m^2 + \beta mg \Delta\rho_0)[\ln(\beta\bar{\gamma}_0 k_m^2 + \beta mg \Delta\rho_0) - 1] - \beta mg \Delta\rho_0[\ln(\beta mg \Delta\rho_0) - 1]\}. \quad (4.8)$$

Here we have imposed a finite upper cutoff  $k_m$  (Refs. 20, 22, and 28) to prevent an ultraviolet divergence of the integrand, which is necessitated by neglect of the  $i > 0$  eigenvalues in (4.6). A procedure for estimating such a cutoff in terms of a microscopic correlation length has been described in Ref. 32, for the case of the Landau-Ginzburg-Wilson submodel, based on the known large- $k$  behavior of the full eigenvalue spectrum in this model. More generally, the large- $k$  behavior of  $\hat{F}_2(z_1, z_2, k)$  is expected to depend on details of the model [e.g., the nature of the potential  $w_2(r)$ ], so we shall simply suppose that a microscopic  $k_m$  has been suitably defined.<sup>20-22,28</sup>

Thus it is found that the term  $D$  contributes a

$$W_v[\rho_0(z) + \rho_1(z)] = W_v[\rho_0(z)] + \int d\vec{r}' [\mu_0 - \phi_{\text{ex}}(z')] \rho_1(z') + O(\gamma^6), \quad (4.9)$$

where  $\mu_0$  is the van der Waals approximation to the total chemical potential. On using (2.4) to compute the grand potential  $\Omega$ , whose surface contribution is  $\bar{\gamma}\mathcal{A}$  where  $\bar{\gamma}$  is the interfacial tension,<sup>16</sup> the terms containing  $\rho_1(z)$  cancel, so that the only anomaly in  $\bar{\gamma}$  through terms of order  $\gamma^3$  is that occurring in (4.8).

Turning now to the behavior of  $\rho_1(z)$  itself, the crucial quantity affecting this behavior is the last term on the right in (3.4) for  $\phi_{\text{eff}}(\vec{r}_1)$ , i.e.,  $\delta D/\delta\rho(\vec{r}_1)$ , which is given more explicitly in (3.5). As in the above analysis of  $D$ , to leading order the density profile implicit in this term can be approximated by its zeroth-order limit  $\rho_0(z)$ . Consistent with this evaluation, we can use the local approximation (3.18) for the hard-sphere Ursell function, obtaining

$$\frac{\delta D}{\delta\rho(\vec{r}_1)} \approx -\frac{1}{2} \zeta(\vec{r}_1 = \vec{r}_2) \left[ \frac{\partial\chi^{(0)}}{\partial\rho} \right]_{\rho=\rho_0(z_1)}, \quad (4.10)$$

$$f_{0,v}(k) \approx \frac{1}{\beta\bar{\gamma}_0 k^2 + \beta mg \Delta\rho_0} \quad (4.7)$$

to leading order in  $k$ . Using this leading estimate for  $f_{0,v}(k)$  in (4.6) and ignoring the contributions of  $f_{i,v}(k)$  for  $i > 0$ , which are not expected to display small- $k$  divergences, we find

bounded anomaly  $\sim -g \ln g$  to the RPA free energy; this is of the same form obtained by accounting for capillary-wave fluctuations in a "bare" interface described by the van der Waals theory. It should be noted that the density profile in the mean-field component  $W_v$  of the RPA free energy (2.19) must be carried to  $O(\gamma^3)$ , i.e., must include the first correction  $\rho_1(z)$  of (3.13), to account for all terms of order  $\gamma^3$  in  $W$ . Potentially, this could contribute further anomalies to the RPA free energy, beyond that given in (4.8), due to the anticipated divergence of  $\rho_1(z)$ . It is clear, however, that we need only linearize  $W_v$  in  $\rho_1(z)$  to account for its  $O(\gamma^3)$  contribution. Using (3.1), we obtain

It is evident from the relation between the Ursell function  $\hat{F}_{2,v}(\vec{r}_1, \vec{r}_2)$  and the chain bond in (2.17b), and from the "local," nondivergent nature of  $\hat{F}_2^{(0)}(\vec{r}_1, \vec{r}_2)$ , that  $\zeta(\vec{r}_1, \vec{r}_2)$  should exhibit the same small- $k$  divergence of its transverse Fourier transform as shown by  $\hat{F}_{2,v}(z_1, z_2, k)$  in (4.3). Concerning ourselves with extracting only this divergent contribution, neglect of the first term on the right in (2.17b) and use once more of (3.18) gives us

$$\begin{aligned} \frac{\delta D}{\delta\rho(\vec{r}_1)} &\sim -\frac{1}{2} \left[ \frac{\partial\chi^{(0)}/\partial\rho}{(\chi^{(0)})^2} \right]_{\rho=\rho_0(z_1)} \hat{F}_{2,v}(\vec{r}_1 = \vec{r}_2) \\ &= \frac{1}{2} \left[ \frac{\partial^2\beta\mu^{(0)}}{\partial\rho^2} \right]_{\rho=\rho_0(z_1)} \hat{F}_{2,v}(\vec{r}_1 = \vec{r}_2). \end{aligned} \quad (4.11)$$

We now assess the capillary-wave contribution to  $\hat{F}_{2,v}(\vec{r}_1 = \vec{r}_2)$  by inverse Fourier transforming the divergent small- $k$  limit in (4.3):

$$\begin{aligned}
\hat{F}_{2,v}(\vec{r}_1 = \vec{r}_2) &= \frac{1}{(2\pi)^2} \int d\vec{k} \hat{F}_{2,v}(z_1 = z_2, k) \\
&\sim \frac{[\rho'_0(z_1)]^2}{2\pi} \int_0^{k_m} dk \frac{k}{(\beta\bar{\gamma}_0 k^2 + \beta mg \Delta\rho_0)} \\
&= \frac{[\rho'_0(z_1)]^2}{4\pi\beta\bar{\gamma}_0} \ln \left[ \frac{\beta\bar{\gamma}_0 k_m^2 + \beta mg \Delta\rho_0}{\beta mg \Delta\rho_0} \right].
\end{aligned} \tag{4.12}$$

The last two equations therefore lead to a  $\ln g$  term in the effective potential at the RPA level of approximation. Since this term is proportional to the square of  $\rho'_0(z)$ , its occurrence is confined to the region of the interface. Note, however, that it cannot be claimed that the evaluation in (4.12) of the *small-r* behavior of the Ursell function from knowledge of the *small-k* properties of its Fourier transform is by any means rigorous. The correctness of this assessment of the capillary-wave divergence in  $\hat{F}_{2,v}(\vec{r}_1 = \vec{r}_2)$ , nonetheless, is supported by its agreement with an explicit calculation by Zitzartz<sup>28</sup> in the case of the Landau-Ginzburg-Wilson submodel, for which the full eigenvalue spectrum of  $\hat{F}_{2,v}(z_1, z_2, k)$  is available.

One further step is needed to show that the  $\ln g$  divergence of  $\delta D / \delta\rho(\vec{r}_1)$  gives rise to a similar divergence in  $\rho_1(z)$ . First notice that, applying the expansion of  $\rho(z)$  in (3.13), the full RPA expression for the effective potential in (3.4) can be written, to  $O(\gamma^3)$ ,

$$\begin{aligned}
\phi_{\text{eff}}(z_1) &= \phi_{\text{eff},0}(z_1) + \int d\vec{r}_2 w_2(r_{12}) \rho_1(z_2) \\
&\quad - \frac{1}{2} w_2(0) + \beta^{-1} \frac{\delta D}{\delta\rho(\vec{r}_1)} + O(\gamma^6) \\
&\equiv \phi_{\text{eff},0}(z_1) + \phi_{\text{eff},1}(z_1) + O(\gamma^6),
\end{aligned} \tag{4.13}$$

where  $\phi_{\text{eff},0}(z_1)$  denotes the mean-field approximation (3.7), considered as a functional of the zeroth-order density  $\rho_0(z)$ . The effective potential can alternatively be functionally expanded to terms linear in  $\rho_1(z)$ , by use of the relation [cf. (2.13) and (3.2)]

$$\frac{\beta\delta(\mu - \phi_{\text{eff}}(\vec{r}_1))}{\delta\rho(\vec{r}_2)} = \hat{c}_2^{(0)}(\vec{r}_1, \vec{r}_2). \tag{4.14}$$

Hence

$$\begin{aligned}
\beta[\mu_1 - \phi_{\text{eff},1}(z_1)] &= \int d\vec{r}_2 \hat{c}_2^{(0)}(\vec{r}_1, \vec{r}_2) |_{\rho_0(z_1)} \\
&\quad \times \rho_1(z_2) + O(\gamma^6),
\end{aligned} \tag{4.15}$$

where  $\mu_1$  is the correction to the total chemical potential given by RPA, and  $\hat{c}_2^{(0)}(\vec{r}_1, \vec{r}_2)$  on the right

of the last equation is evaluated as a functional of  $\rho_0(z)$ . Combining the expressions for  $\phi_{\text{eff},1}(z)$  given by (4.13) and (4.15) yields the following solution for  $\rho_1(z)$  in terms of functionals of  $\rho_0(z)$ :

$$\begin{aligned}
\rho_1(z_1) &= \int d\vec{r}_2 \hat{F}_{2,v}(\vec{r}_1, \vec{r}_2) \\
&\quad \times \left[ \beta[\mu_1 + \frac{1}{2}w_2(0)] - \frac{\delta D}{\delta\rho(\vec{r}_2)} \right].
\end{aligned} \tag{4.16}$$

Notice that integration over the horizontal coordinates of  $\vec{r}_2$  in this equation reduces  $\hat{F}_{2,v}(\vec{r}_1, \vec{r}_2)$  to its transverse Fourier transform at  $k=0$ ,  $\hat{F}_{2,v}(z_1, z_2, k=0)$ , which includes a  $1/g$  divergence as indicated in (4.3). It can be shown, however, that such a  $1/g$  term does *not* contribute to (4.16), and hence that  $\rho_1(z)$  exhibits the same logarithmic singularity as  $\delta D / \delta\rho(\vec{r}_2)$ . Specifically, the term in (4.16) resulting from the limiting behavior of  $\hat{F}_{2,v}(z_1, z_2, k=0)$  given by (4.3) is proportional to the integral

$$I \equiv \int dz_2 \rho'_0(z_2) \left[ \beta[\mu_1 + \frac{1}{2}w_2(0)] - \frac{\delta D}{\delta\rho(\vec{r}_2)} \right]. \tag{4.17}$$

Defining the function  $d(z)$  by [cf. (2.20)]

$$D = \int d\vec{r} d(z), \tag{4.18}$$

use of a functional chain rule<sup>29,38</sup> converts (4.17) into

$$I = -\beta\Delta\rho_0[\mu_1 + \frac{1}{2}w_2(0)] + \Delta d, \tag{4.19}$$

where  $\Delta d \equiv [d(-\infty) - d(+\infty)]$  is the difference in coexisting bulk values of  $d(z)$ . As a final exercise, whose details we shall omit, it can be shown that, on neglecting any gravitational effects in bulk and requiring equality of the total pressures of the coexisting phases, evaluated in RPA, the quantity  $I$  given by the last equation is zero.

Thus it is demonstrated that  $\rho_1(z)$ , the leading  $O(\gamma^3)$  term in the density profile, has a contribution proportional to  $\ln g$ . As noted in Sec. I, a similar nonanalyticity in the profile was found by Jasnow and Rudnick<sup>25</sup> in the context of a "renormalized" RPA applied to the Landau-Ginzburg-Wilson model of the interface. We shall comment in the next section on the method described in Refs. 25 and 32 to justify a resummation yielding the correct capillary-wave anomaly (1.2). We close the present section by describing an alternative point of view, which relates the difference between

(1.1) and (1.2) to the question of the “core condition”<sup>4</sup> on the pair-correlation function. We refer here to the well-known fact that the harsh repulsive forces between molecules should cause the pair probability  $\rho_2(\vec{r}_1, \vec{r}_2)$  to vanish at small separations  $|\vec{r}_2 - \vec{r}_1|$ . This condition, however, is not satisfied by the strict  $\gamma$ -ordered expansions discussed in this paper. As noted in Sec. II, the LR part of the two-particle Ursell function must be carried to one higher order in  $\gamma^3$  than the SR part to yield thermodynamic contributions of the same order, while only if both SR and LR parts are evaluated to the *same* order in  $\gamma^3$ , is the core condition satisfied.<sup>3,4</sup> Let us now consider applying the same steps as involved in (4.12) to determine the zero-separation value of the *exact* unmodified Ursell function

$$F_2(\vec{r}_1, \vec{r}_2) = \rho_2(\vec{r}_1, \vec{r}_2) - \rho(z_1)\rho(z_2). \quad (4.20)$$

This differs from  $\hat{F}_2(\vec{r}_1, \vec{r}_2)$  only by the term  $\rho(z_1)\delta(\vec{r}_1 - \vec{r}_2)$ , and therefore exhibits the same small- $k$  divergence of its transverse Fourier transform as given in (4.2). By applying the same reasoning as in (4.12),  $F_2(\vec{r}_1 = \vec{r}_2)$  would be expected to contain a divergent term proportional to  $[\rho'(z_1)]^2 \text{In}g$ . However, the vanishing of  $\rho_2(\vec{r}_1 = \vec{r}_2)$  and the expected boundedness of the density profile shows, in view of (4.20), that  $F_2(\vec{r}_1 = \vec{r}_2)$  should properly be bounded. Thus, to prevent a divergence in this function,  $\rho'(z)$  must satisfy (1.2). This argument, of course, does not by itself provide an explicit means for calculating the detailed form of the density profile.

## V. CONCLUSIONS

We have shown that a microscopic model based on a Kac-parametrized pair potential leads to systematic expansions for interfacial structure and thermodynamics, providing a framework for interrelating several, sometimes disparate, ideas in nonuniform-fluid theory. Specifically, the van der Waals theory has been placed in the formal context of a zeroth-order, fluctuationless result in expansion of the density profile and free energy in powers of  $\gamma^3$ . The next level  $O(\gamma^3)$  theory, the RPA, accounts approximately for the effects of density fluctuations, including some which give rise to capillary-wave-like anomalies in interfacial structure and thermodynamics. We have observed

that the interfacial behavior at lowest order influences the production of anomalies at higher order via the presence of a long-wavelength divergence in the two-particle Ursell function. This provides microscopic justification for Weeks<sup>21</sup> thesis that the same fluctuations responsible for the small- $k$  divergence of  $\hat{F}_2(z_1, z_2, k)$  also cause  $\rho'(z)$  to vanish as  $g \rightarrow 0+$ . This idea has been disputed by Evans,<sup>26</sup> but only on the grounds that the *van der Waals* density profile  $\rho_0(z)$  is well behaved as  $g \rightarrow 0+$ , discounting the contribution of fluctuation corrections to this profile.

Several important questions are remaining. Clearly, the contribution of higher-order terms in  $\gamma$  ordering, e.g., the  $O(\gamma^6)$  free energy in (2.25) and its associated density profile, should be examined. In view of the proliferation of chain bonds  $\xi(\vec{r}_1, \vec{r}_2)$  in the last two terms in (2.25), each displaying a long-wavelength divergence, one could envisage capillary-wave-like anomalies developing in profusion from these terms, although some elimination of these divergences may occur by a mechanism similar to or generalizing that described in (4.16)–(4.19). The occurrence of compounded anomalies, however, is presumably related to and should illuminate the basis for resummation from (1.1) to (1.2). In Refs. 25 and 32, the result (1.2) was derived, to an order of approximation consistent with the RPA, using the method of Gervais and Sakita<sup>39</sup> to introduce the “bare” interface position as a degree of freedom in the model (Landau-Ginzburg-Wilson) partition function. In the context of a Kac-parametrized Hamiltonian model such as considered here, an analogous procedure could in principle be adapted to the functional-integral method.<sup>2,5,6</sup> At the RPA level of approximation, fluctuation corrections to van der Waals theory are generated by Gaussian functional integrals,<sup>5,6,36</sup> so that to this order the prediction of anomalies in agreement with the original Gaussian model of Buff, Lovett, and Stillinger<sup>20</sup> is to be anticipated. As noted at the beginning of Sec. II, however, the functional-integral method is somewhat unwieldy in deriving equations for the deriving profile, at least at its present stage<sup>6</sup> of development for nonuniform fluids. It is also expected that in higher-order theory there is coupling of “ordinary” (nondivergent) to capillary-wave-like fluctuations,<sup>25</sup> so that the ability to define an “intrinsic” interface becomes less clear. We have suggested above that a key role in establishing (1.2) is played by the core condition on the pair-correlation function. This aspect deserves further exploration,

both in the framework of  $\gamma$ -ordered expansions (particularly in view of our earlier remarks on how the core condition is developed asymptotically in such expansions) as well as in other directions. For example, it is anticipated that an "optimized"<sup>40</sup> version of the RPA, equivalent to a mean-spherical-like approximation,<sup>4</sup> should yield essentially correct capillary-wave-like effects.

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- <sup>1</sup>P. C. Hemmer and J. L. Lebowitz, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 5B.
- <sup>2</sup>J. K. Percus, in *Studies in Statistical Mechanics*, edited by E. W. Montroll and J. L. Lebowitz (North-Holland, Amsterdam, 1981).
- <sup>3</sup>J. L. Lebowitz, G. Stell, and S. Baer, *J. Math. Phys.* **6**, 1282 (1965).
- <sup>4</sup>(a) G. Stell, in *Statistical Mechanics*, Part A, edited by B. J. Berne (Plenum, New York, 1977). (b) See Eq. (94a) of this reference. This equation contains several misprints (G. Stell, private communication), which are corrected by the present (2.25).
- <sup>5</sup>J. B. Jalickee, A. J. F. Siegert, and D. J. Venzetti, *J. Math. Phys.* **10**, 1442 (1969).
- <sup>6</sup>T. F. Meister, and B. U. Felderhof, *Physica (Utrecht)* **102A**, 145 (1980).
- <sup>7</sup>M. Kac, *Phys. Fluids* **2**, 8 (1959); M. Kac, G. Uhlenbeck, and P. C. Hemmer, *J. Math. Phys.* **4**, 216 (1963).
- <sup>8</sup>N. G. van Kampen, *Phys. Rev.* **135**, A362 (1964).
- <sup>9</sup>J. K. Percus, *Trans. N. Y. Acad. Sci.* **26**, 1062 (1964); J. K. Percus, Lecture Notes on Nonuniform Fluids 1975 (unpublished).
- <sup>10</sup>B. Widom, *J. Stat. Phys.* **19**, 563 (1978).
- <sup>11</sup>C. Varea, A. Valderrama, and A. Robledo, *J. Chem. Phys.* **73**, 6265 (1980).
- <sup>12</sup>J. D. van der Waals, *Z. Phys. Chem.* **13**, 657 (1894) [translated into English by J. S. Rowlinson, *J. Stat. Phys.* **20**, 197 (1979)].
- <sup>13</sup>J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **28**, 258 (1958).
- <sup>14</sup>S. Fisk and B. Widom, *J. Chem. Phys.* **50**, 3219 (1969). See also the excellent discussion by B. Widom, in *Statistical Mechanics and Statistical Methods in Theory and Application*, edited by U. Landman (Plenum, New York, 1977).
- <sup>15</sup>D. E. Sullivan, *Phys. Rev. B* **20**, 3991 (1979).
- <sup>16</sup>D. E. Sullivan, *J. Chem. Phys.* **74**, 2604 (1981).
- <sup>17</sup>D. E. Sullivan, *Faraday Symp. Chem. Soc.* **16**, (in press).
- <sup>18</sup>J. L. Lebowitz and J. K. Percus, *J. Math. Phys.* **4**, 116 (1963); J. K. Percus, in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964).
- <sup>19</sup>A. J. M. Yang, P. D. Fleming, and J. H. Gibbs, *J. Chem. Phys.* **64**, 3732 (1976). Notice that what we call  $W$  and  $\Omega$  correspond, respectively, to  $kTF'$  and  $-kTW$  of this reference.
- <sup>20</sup>F. P. Buff, R. A. Lovett, and F. H. Stillinger, *Phys. Rev. Lett.* **15**, 621 (1965).
- <sup>21</sup>J. D. Weeks, *J. Chem. Phys.* **67**, 3106 (1977).
- <sup>22</sup>M. H. Kalos, J. K. Percus, and M. Rao, *J. Stat. Phys.* **17**, 111 (1977).
- <sup>23</sup>(a) H. T. Davis, *J. Chem. Phys.* **67**, 3636 (1977). (b) H. T. Davis, *J. Chem. Phys.* **70**, 600 (1979).
- <sup>24</sup>F. F. Abraham, *Chem. Phys. Lett.* **58**, 259 (1978).
- <sup>25</sup>D. Jasnow and J. Rudnick, *Phys. Rev. Lett.* **41**, 698 (1978).
- <sup>26</sup>R. Evans, *Mol. Phys.* **42**, 1169 (1981).
- <sup>27</sup>B. Widom, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1972), Vol. 2.
- <sup>28</sup>J. Zittartz, *Phys. Rev.* **154**, 529 (1967).
- <sup>29</sup>M. S. Wertheim, *J. Chem. Phys.* **65**, 2377 (1976).
- <sup>30</sup>J. Rudnick and D. Jasnow, *Phys. Rev. B* **17**, 1351 (1978).
- <sup>31</sup>Renormalization-group (RG) techniques overcome the well-known divergences (Refs. 1 and 3) suffered by  $\gamma$ -ordered expansions near the three-dimensional critical point. The presence of capillary-wave-like effects in the theory, however, is not modified in an essential way by the use of renormalized expansions. To elucidate these effects we feel it is preferable at this stage to avoid the additional theoretical apparatus required by RG methods.
- <sup>32</sup>D. Jasnow, T. Ohta, and J. Rudnick, *Phys. Rev. B* **20**, 2774 (1979).
- <sup>33</sup>G. Stell, in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964).
- <sup>34</sup>R. Evans and W. Schirmacher, *J. Phys. C* **11**, 2437 (1978); see also R. Evans, *Adv. Phys.* **28**, 143 (1979).
- <sup>35</sup>Formally, the interfacial tension  $\bar{\gamma}$  in  $\gamma$ -ordered expansions has the form  $\bar{\gamma} = \sigma/\gamma$ , where  $\sigma$  is finite as  $\gamma \rightarrow 0$  (Ref. 16). In macroscopic contexts,  $\bar{\gamma}$  is usually determined by observing the ratio of the capillary length (Ref. 29)  $l \equiv (\bar{\gamma}/mg\Delta\rho)^{1/2}$  to a sample dimension  $L$ , e.g., depth or radius of a capillary tube. Substituting for  $\bar{\gamma}$  and rescaling (Sec. IV)  $g$  to  $\gamma g$  and  $L$  to  $L/\gamma$ ,

this ratio remains well behaved as  $\gamma \rightarrow 0$ .

<sup>36</sup>J. M. Deutch and R. Zwanzig, *J. Chem. Phys.* **46**, 1612 (1967); R. D. Mountain and R. Zwanzig, *J. Chem. Phys.* **48**, 1451 (1968).

<sup>37</sup>H. C. Andersen and D. Chandler, *J. Chem. Phys.* **53**, 547 (1970).

<sup>38</sup>R. Lovett, C. Y. Mou, and F. P. Buff, *J. Chem. Phys.* **65**, 570 (1976).

<sup>39</sup>J. L. Gervais and B. Sakita, *Phys. Rev. D* **11**, 2943 (1975).

<sup>40</sup>H. C. Andersen and D. Chandler, *J. Chem. Phys.* **55**, 1497 (1971).