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Statistical Mechanics of Interfaces

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On the basis of van der Waals theory for interfaces we evaluate explicitly the small-wavevector behavior of the pair correlation function along an interface. A correction to the density profile is also found. The results obtained are in full accord with capillary wave theory when wave amplitudes are regarded as small.

KEY WORDS: Interface; capillary wave theory; van der Waals theory; γ-ordering; direct correlation function; pair correlation function; surface tension; Sullivan model; density profile.

1. INTRODUCTION

The theory of interfaces may be regarded from two viewpoints. One viewpoint is the capillary wave theory.(1-3) In this theory one may assume that there is a rather abrupt change from one phase to another forming an intrinsic interface. This interface will move and is deformed by capillary waves that can be described by hydrodynamics. These waves are created by thermal fluctuations. Due to this, the density will fluctuate near the interface, and the fluctuations will produce a region where the average density changes gradually. The width of this region will increase with decreasing field of gravity across the interface, and in the limit of zero gravity the resulting width of the interface becomes infinite.

The other viewpoint is the van der Waals theory for interfaces.(4) In this theory the interface is regarded as planar, and in the direction perpendicular to it the density will change gradually from one phase to the other. The form of the density profile is determined by a mean field treatment of the effect of attractive forces. The width of the density profile is finite, and it will stay finite also with zero gravity.

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From the viewpoint of the physics involved both theories are reasonable. The problem is that they describe two different aspects of interface properties that are not easy to combine by a common theory. However, several workers have tried to bridge the gap between the two viewpoints. Then mean field models are supplemented by allowing fluctuations of density around the mean field value. It has been shown that thermal fluctuations give rise to behavior that to a certain extent may be identified with capillary waves. In this respect Zittartz and later Evans studied the Landau–Ginzburg–Wilson model, which is a submodel of van der Waals theory.(5) Renormalization group methods using ε-expansion have also been applied to this model to study interface properties.(6) Wertheim(7) made an analysis of the pair correlation function along an interface and showed that quite generally it should have the long-range behavior that capillary waves have. This was later extended by others.(2,8) Sullivan(9) considered an expansion in the inverse range of attractive interaction, the γ-ordering, to obtain a perturbation on van der Waals theory. The γ-ordering is well established for uniform fluids.(10) However, it diverges in the critical region. This divergence may be tamed by some resummation of graphs, and considerable improvement over the van der Waals equation of state for the three-dimensional case of a Lennard-Jones fluid has been obtained.(11) The γ-ordering has also been a foundation for the developments by Høye and Stell in the theory for polar and polarizable fluids.(12),[2] Closely related to the γ-ordering is the work by Andersen, Chandler, and Weeks.(15)

In our work we want to apply the γ-ordering to interfaces. In principle, graph expansions are formally the same for uniform and nonuniform fluids. The difference is that the latter creates much bigger problems when one wants to do more explicit evaluations, since density is no longer a constant throughout the system. The present work is inspired by computer results obtained by Stecki and coworkers.(16) These results seemed to indicate that the short-range part of the direct correlation function at the interface is, to a good approximation, as in the bulk phase, using local density. In view of this we can proceed as in the bulk phase and establish the direct correlation function. From this we evaluate the leading behavior of the pair correlation function along the interface. A correction to the van der Waals density profile is also found. Our γ-ordering follows the one used by Sullivan.(9) Thus, some of our results overlap with those of Ref. 9. However, we make a more explicit computation of various quantities on the basis of the van der Waals theory, and a more detailed comparison with capillary wave theory is performed. To do this we treat capillary wave

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[2] See Stell *et al.*(13) for a comprehensive review of dielectric fluids. For a brief review see Høye.(14)

amplitudes as if they were small. Within this approximation or assumption we find that leading contributions beyond the van der Waals theory are in quantitative agreement with capillary wave theory.

In Section 2 we establish the correlation function along an interface according to the capillary wave picture, regarding the wave amplitudes as small. In Section 3 the van der Waals theory for interfaces is considered. In Section 4 we derive the direct correlation function. In Section 5 we evaluate the pair correlation function and find its asymptotic form, which can be interpreted as capillary waves in agreement with the result of Section 2. We perform the derivations in Section 5 in a way similar to the one Wertheim(7) employed to derive his general result for the pair correlation function along an interface. The agreement with capillary waves hinges upon the use of a general formula for the surface tension in terms of the direct correlation function.(17) In Section 6 we show explicitly that the van der Waals theory gives a surface tension in agreement with the general formula, i.e., we compute the excess to the bulk pressure with the planar equilibrium interface present.(18) The general formula, however, is based upon curving the interface and then evaluating the change in pressure or free energy accompanying this operation. Thus we show that the direct correlation function derived in Section 4 also is consistent with the van der Waals theory with respect to surface tension. In Section 7 we consider the Sullivan model, which has certain simplifying features.(18,19) There we find that the correlation function is essentially the Green's function of a one dimensional Schrödinger equation with a potential bump at the interface. In Section 8 we evaluate the leading γ-ordered correction to the average density profile. The result of this matches with capillary wave theory when the amplitudes are regarded as small.

2. CAPILLARY WAVE PICTURE

The motion of molecules at the surface between two phases will create fluctuations in it. From a macroscopic viewpoint these fluctuations may be described by capillary waves along the surface. These waves may be regarded as independent harmonic oscillators. For harmonic oscillators the equipartition principle holds. This means that at equilibrium each degree of freedom contributes the energy $\frac{1}{2}k_B T$ on average (k_B is Boltzmann's constant and T is temperature).

The forces determining the potential energy of a surface are the surface tension γ and gravity g (if the latter is present). Let the surface be a square with sides of length L along the y and z axes. A standing wave is described by the amplitude (in the x direction)

$$A = a \sin k_y y \sin k_z z \tag{1}$$

For a square surface whose side length is L the allowed values k_y and k_z will be $2\pi n/L$, where n is an integer.

Consider first gravity. Let M be the mass of each molecule, and $\Delta\rho$ the difference in number density for the coexisting two phases. The potential energy per unit area of a liquid column of height A is then $\frac{1}{2}(\Delta\rho)\, MgA^2$. Integration over the surface gives the total potential energy from gravity

$$W_g = \tfrac{1}{8}(\Delta\rho)\, Mga^2L^2 \tag{2}$$

A capillary wave increases the area of the surface, and due to surface tension this contributes to the potential energy. The relative increase of the surface is

$$\left[1 + \left(\frac{\partial A}{\partial y}\right)^2 + \left(\frac{\partial A}{\partial z}\right)^2\right]^{1/2} - 1 = \frac{1}{2}\left[\left(\frac{\partial A}{\partial y}\right)^2 + \left(\frac{\partial A}{\partial z}\right)^2\right] \tag{3}$$

Differentiating (1) and integrating over the surface, one finds the increase in surface area to be $\frac{1}{8}k^2a^2L^2$. The potential energy due to surface tension γ is thus

$$W_s = \tfrac{1}{8}k^2\gamma a^2L^2 \tag{4}$$

with

$$k^2 = k_y^2 + k_z^2$$

As mentioned above, the resulting average potential energy at equilibrium should be $\frac{1}{2}k_BT$. Adding (2) and (4), this means

$$\tfrac{1}{2}k_BT = \tfrac{1}{8}(k^2\gamma + \Delta\rho\ Mg)\, a^2L^2 \tag{5}$$

or

$$\tfrac{1}{4}a^2L^2 = 1/(\beta\gamma k^2 + \beta gM\,\Delta\rho) \tag{6}$$

with

$$\beta = 1/k_BT \tag{7}$$

The fluctuating capillary waves yield long-range correlations along the fluid interface. We want to compute the contribution from each mode. In accordance with the van der Waals type picture of a fluid interface, we assume that there will be a density profile $\rho(x)$ across it. Displacing the interface a small distance A will change the density at position x to

$$\rho(x-A) = \rho(x) - A\rho'(x), \qquad \rho'(x) = d\rho/dx \tag{8}$$

According to (6), a and thus A will decrease with increasing interface L, so for a single mode expansion (8) is valid. The pair distribution function is the average of the product of densities at two points. Subtracting the product of the average densities at these same two points, one obtains the pair correlation function $h(12)$. The contribution to it from a single mode is thus

$$\begin{aligned}\rho_1\rho_2 h_k(12) &= \langle \rho(x_1 - A_1)\,\rho(x_2 - A_2)\rangle - \rho(x_1)\,\rho(x_2)\\ &= \langle A_1 A_2\rangle\,\rho'(x_1)\,\rho'(x_2) \qquad (9)\end{aligned}$$

Here A_i ($i = 1, 2$) is the height of the interface at position (y_i, z_i) as given by (1).

Averaging keeping the relative distance in the yz plane fixed, it is clear that

$$\langle A_1 A_2\rangle = \tfrac{1}{4}a^2 \cos k_y y \cos k_z z \qquad (10)$$

with

$$y = y_2 - y_1 \qquad \text{and} \qquad z = z_2 - z_1$$

Summing over the allowed values of k_y and k_z, one obtains $h(12)$. For large $L \to \infty$ the sum may be replaced by an integral. With allowed values $2\pi n/L$ of k_y and k_z, the sum may be replaced by $(L/2\pi)^2 \int d\mathbf{k}$, where $d\mathbf{k} = dk_y\,dk_z$. This combined with (9) and (10) yields

$$\rho_1\rho_2 h(12) = \rho'(x_1)\,\rho'(x_2)\frac{1}{(2\pi)^2}\int \frac{1}{4}a^2L^2 \cos k_y y \cos k_z z\, d\mathbf{k} \qquad (11)$$

According to (6), the a^2 is a symmetric function in $\mathbf{k}$. Thus, the $\cos k_y y \cos k_z z$ can be replaced with $\exp[\pm i(k_y y + k_z z)]$ in (11), and from this it is easy to see that the Fourier transform of $h(12)$ will be

$$\rho_1\rho_2\tilde{h}(12, \mathbf{k}) = \frac{\rho'(x_1)\,\rho'(x_2)}{\beta\gamma k^2 + \beta g M\,\Delta\rho} \qquad (12)$$

when (6) is used to substitute for $\tfrac{1}{4}a^2L^2$.

It may be noted here that expression (11) is not quite the appropriate $\rho_1\rho_2 h(12)$, since it assumes that linearization (8) holds also when adding the various Fourier components. To be strict, linearization requires that the resulting wave height is small compared to the width of the intrinsic density profile. As is well known, this does not hold in the small $g \to 0$ limit and large separation along the surface for the points considered. In fact, the width of the resulting average density profile diverges when $g \to 0$. A more appropriate computation of $\rho_1\rho_2 h(12)$ using the capillary wave picture may be found in the work by Bedeaux *et al.*$^{(3)}$ They consider a Gaussian model with a sharp intrinsic interface. However, the individual Fourier components as given by (12) are the ones of primary interest to us when we want to relate the van der Waals theory to the capillary wave picture. Our derivations correspond to linearization (8), which holds for the individual Fourier components.

3. VAN DER WAALS THEORY FOR INTERFACES

The van der Waals theory for interfaces is based upon a generalization of the van der Waals theory for the homogeneous phase using a mean field approach.$^{(4)}$ It is assumed that one has a reference system whose equation of state is considered known. The reference system is perturbed by an attractive potential that may be considered weak and long-ranged such that its influence upon the equation of state will be that of a mean field. This assumption can be extended to inhomogeneous systems where the density changes with position. Computing the reference system free energy, one then assumes that it will be, as for the homogeneous system, function of local density, neglecting the effect of density gradients, which are considered small in this respect. However, the attractive interaction is more long-ranged. This has the effect that the mean field is not just a function of local density, but will depend upon the neighboring surroundings. This gives a nonlocal contribution to the free energy. Altogether the expression for Helmholtz free energy F within this theory will have the form

$$-\beta F/A = \int I_0(\rho(x))\,dx + \tfrac{1}{2}\int \rho(x)\,\chi(x-x')\,\rho(x')\,dx' \tag{13}$$

When considering interfaces the system is assumed homogeneous in the yz directions covering an area A. The $I_0(\rho)$ represents the contribution to F from the reference system, which, for instance, may be hard spheres. The latter term in (13) represents the mean field contribution from the surroundings of a given point. The attractive interaction we may call $\psi(r)$, assuming it to be spherically symmetric. Defining

$$v(r) = -\beta\psi(r) \tag{14}$$

we have

$$\chi(x) = \int v(r)\,dy\,dz \tag{15}$$

The density at equilibrium is determined via the global chemical potential g_g, which is a constant throughout the system. An external field

$\phi(x)$ may be present. The local chemical potential $g_{\text{loc}} = g_g - \phi(x)$, which will vary through the system, can be derived as the functional derivative of (13),

$$g_{\text{loc}} = \frac{\delta(F/A)}{\delta\rho(x)}$$

$$\beta g_{\text{loc}}(x) = \beta g_g - \beta\phi(x) = \beta g_0(\rho(x)) - \int \chi(x-x')\,\rho(x')\,dx' \qquad (16)$$

with

$$\beta g_0(\rho) = -\partial I_0(\rho)/\partial\rho$$

This integral equation with $g_g = \text{const}$ determines the density profile $\rho(x)$ in the van der Waals theory.

The theory outlined above may also be given a statistical mechanical justification. For the homogeneous case the van der Waals theory is well established in this respect.(10) Formally in terms of the structure of graph expansions this may be extended to the inhomogeneous case. Such a situation was studied, e.g., by Høye and Stell(20) in their work on polar fluids in electric fields. By this generalization the graphs will be the same, but constant density ρ has to be replaced with nonconstant density $\rho(x)$ at the vertices, and this usually complicates explicit computations severely. In view of an expansion where the inverse range of the attractive interaction $\psi(r)$ is considered as the perturbing parameter, the interpretation of the two terms of Eq. (13) is clear. The first term is, as mentioned before, the contribution from the reference system with the approximation that the density is kept fixed when evaluating graphs by which the result for the homogeneous system can be used, i.e., one uses a local density $\rho(x)$ assuming that the range of the graphs is small. The other term in (13) will be contribution from the graph with two vertices $\rho(x)$ and $\rho(x')$ connected by a potential bond. The potential bond is considered to be of longe range, by which variations in $\rho(x)$ during integration have to be taken into account. By an expansion in the inverse range of interaction, Eq. (13) thus represents the leading order contribution, other contributions being of higher order.(10)

4. THE DIRECT CORRELATION FUNCTION

The direct correlation function of a system may be obtained by functional differentiation of Helmholtz free energy twice with respect to $\rho(x)$. In the homogeneous case this is the same as the usual fluctuation theorem that relates the compressibility of a system to the direct correlation function or the pair correlation function. With

$$\tilde{C}(0)=\frac{1}{\rho(x_1)}\delta(x_1-x_2)-\tilde{c}(12,0) \tag{17}$$

$$\tilde{C}(0)=\frac{\delta^2(-\beta F/A)}{\delta\rho(x_1)\,\delta\rho(x_2)} \tag{18}$$

where $c(12)$ is the direct correlation function integrated over the relative y and z coordinates. By use of (16), keeping in mind that g_g is fixed, we get

$$\tilde{C}(0)=\frac{\delta(-\beta\phi(x_1))}{\delta\rho(x)}=\frac{1}{\mu(\rho(x_1))}\delta(x_1-x_2)-\chi(x_1-x_2) \tag{19}$$

with

$$\frac{1}{\mu(\rho)}=\frac{\partial(\beta g_0(\rho))}{\partial\rho} \tag{20}$$

Within the approximation used in (13) for the reference system, the first term on the right-hand side of (19) is nothing but the $\tilde{C}(0)$ for this latter system. The pair correlation function, which again follows from this, will also be short range (here approximated by a δ-function).

Now expression (19) has an additional contribution given by the attractive potential, and we want to evaluate its influence upon the pair correlation function at the interface. Then we need the details of the direct correlation function in the y and z directions. To get them, the free energy should be functionally differentiated twice with respect to $\rho(\mathbf{r})$, the density, which may vary in all three dimensions. [We have regarded Eqs. (13) and (16), which lead to (19), as one-dimensional functionals of $\rho(x)$.] Such a differentiation yields

$$C(12,y,z)=\frac{1}{\mu(\rho(x_1))}\delta(\mathbf{r}_1-\mathbf{r}_2)-v(r) \tag{21}$$

with $v(r)$ given by (14). The direct correlation function $c(12, y, z)$ is related to this by

$$C(12,y,z)=\frac{1}{\rho(\mathbf{r}_1)}\delta(\mathbf{r}_1-\mathbf{r}_2)-c(12,y,z) \tag{22}$$

with $y=y_1-y_2$ and $z=z_1-z_2$. Since expression (21) only depends upon the relative distance along the yz plane, we can Fourier transform it to obtain

$$\tilde{C}(12, \mathbf{k}) = \frac{1}{\mu(\rho(x_1))} \delta(x_1 - x_2) - \tilde{v}(x_1 - x_2, \mathbf{k}) \tag{23}$$

where $\tilde{v}(x, \mathbf{k})$ is the Fourier transform of $v(r)$ with respect to y and z coordinates. Clearly, from (15)

$$\chi(x) = \tilde{v}(x, 0) \tag{24}$$

and thus in Eq. (19)

$$\tilde{C}(0) = \tilde{C}(12, 0) \tag{25}$$

5. PAIR CORRELATION FUNCTION

The pair correlation function is related to the direct correlation function via the Ornstein–Zernike (OZ) equation. Due to translational invariance the equation can be Fourier-transformed with respect to y and z, by which it reads

$$\int \tilde{H}(13, \mathbf{k})\, \tilde{C}(32, \mathbf{k})\, dx_3 = \delta(x_1 - x_2) \tag{26}$$

where

$$\tilde{H}(13, \mathbf{k}) = \rho(x_1)\, \delta(x_1 - x_3) + \rho(x_1)\, \rho(x_3)\, \tilde{h}(12, \mathbf{k}) \tag{27}$$

Equation (26) may be regarded as a matrix equation with continuous indices x_1, x_3, and x_2. In this respect the matrix $\tilde{H}$ will be the inverse of $\tilde{C}$. Matrices may be inverted by evaluating eigenvalues and eigenvectors. The eigenvalues of $\tilde{H}$ will clearly be the inverse of those of $\tilde{C}$, while the eigenvectors will be in common, since $\tilde{H}$ and $\tilde{C}$ will be diagonal simultaneously. Here we are interested in the dominating behavior of $\tilde{H}$ for small $\mathbf{k}$, since this, like (12), asymptotically yields the correlations for large distances along the surface. Thus, we look for the smallest eigenvalue of $\tilde{C}$. At first sight it may seem hard to obtain information about this. However, Eq. (16), which determines the density profile $\rho(x)$, is the key to resolving this problem. This equation can be differentiated with respect to the position x to yield

$$\frac{d(-\beta\phi(x))}{dx} = \frac{\partial \beta g_0}{\partial \rho} \rho'(x) - \int \frac{d}{dx} [\chi(x - x')]\, \rho(x')\, dx' \tag{28}$$

We may specialize to a gravity field, i.e., $\phi(x)=gMx$. Due to the symmetry of $\chi(x-x')$ in x and x', the differentiation with respect to x can be done with respect to x', and partial integration may be performed. In addition, using (20), we find

$$-\beta gM=\int\left[\frac{1}{\mu(\rho(x))}\,\delta(x-x')-\chi(x-x')\right]\rho'(x')\,dx' \tag{29}$$

Comparing with (19) and (23), we see that this is nothing but

$$-\beta gM=\int \tilde{C}(12,0)\,\rho'(x_2)\,dx_2 \tag{30}$$

Specialized to $g=0$, this yields

$$0=\int \tilde{C}(12,0)\,\rho'(x_2)\,dx_2 \tag{31}$$

This is the crucial equation, which tells us that $\rho'(x)$ is an eigenvector of $\tilde{C}(12,0)$ with eigenvalue 0. This is also the lowest of the eigenvalues, since they are not allowed to be negative. Physically, this eigenvector or eigenfunction represents nothing but a translation of the interface in the x direction, which also is a solution of Eq. (16) for the profile $\rho(x)$ when $g=0$.

Now consider the situation with g and $\mathbf{k}$ small but different from zero. Their effect upon the smallest eigenvalue may then be handled with standard perturbation methods. Equation (31) is the zeroth-order problem. With $g\neq 0$, Eq. (30) can be used to find the lowest eigenvalue for small g. Clearly, the operator $\tilde{C}$ depends upon g, since the equilibrium profile does. However, for small g its eigenfunctions may be approximated by those for $g=0$, since an error here to first order will show up only to second order in the eigenvalue. [Note that $\rho'(x_2)$ for $g\neq 0$ is not precisely an eigenfunction of (30).] The left-hand side of (30) may be expanded in eigenfunctions, yielding

$$-\beta gM=a\rho'(x_1)+\cdots \tag{32}$$

where

$$a=\frac{1}{N}\int(-\beta gM)\,\rho'(x)\,dx=\frac{1}{N}\beta gM\,\Delta\rho \tag{33}$$

with normalization

$$N=\int[\rho'(x)]^2\,dx$$

As before, $\Delta\rho$ is the difference in density between the two coexisting phases. [By expansion of a function $f(x)=\sum_i a_i\psi_i(x)$ the $a_i=\int f\psi_i\,dx/\int\psi_i^2\,dx$, since ψ_i are the eigenfunctions of a symmetric operator.] For small g, terms other than the one shown can be neglected. The reason is that the lowest eigenvalue for the operator in (30) will be close to zero ($\sim g$), while the next lowest is expected to be of $O(1)$. Equation (32) used in (30) yields

$$\frac{1}{N}\beta gM(\Delta\rho)\,\rho'(x_1)=\int\tilde{C}(12,0)\,\rho'(x_2)\,dx_2 \tag{34}$$

From this we conclude that the lowest eigenvalue of $\tilde{C}(12,0)$ is

$$\lambda_0=(1/N)\,\beta gM\,\Delta\rho \tag{35}$$

Then we turn to the situation with $\mathbf{k}\neq 0$. The change in $\tilde{C}$ of $O(k^2)$ for small k may be regarded as a perturbation, which from (23) is found to be $(x=x_1-x_2)$

$$\Delta\tilde{v}(12)=\tilde{C}(12,\mathbf{k})-\tilde{C}(12,0)=\tilde{v}(x,0)-\tilde{v}(x,\mathbf{k}) \tag{36}$$

The change in the lowest eigenvalue can be found by standard first-order perturbation theory. Adding this to (35), we find that the lowest eigenvalue for small k becomes

$$\lambda_0=(\beta/N)(gM\,\Delta\rho+\gamma'k^2) \tag{37}$$

$$\beta\gamma'=(1/k^2)\int\rho'(x_1)\,\Delta\tilde{v}(12)\,\rho'(x_2)\,dx_1\,dx_2 \tag{38}$$

In the next part we will identify γ' with the surface tension γ of the van der Waals theory.

In accordance with Eq. (26), we want the inverse of $\tilde{C}$, which is $\tilde{H}$. This is found by first transforming $\tilde{C}$ to diagonal form, then taking the inverse, and so transforming back. The $\tilde{C}$ is made diagonal by the matrix operator S, whose matrix elements are the normalized eigenfunctions $\psi_n(x)$ of $\tilde{C}$. Since $\tilde{C}$ is symmetric, the inverse matrix S^{-1} will be the transpose of S. The elements of the diagonal matrix $\Lambda=S\tilde{C}S^{-1}$ will be

$$\begin{aligned}\Lambda_{nm}&=\int\psi_n(x_1)\,\tilde{C}(12,\mathbf{k})\,\psi_m(x_2)\,dx_1\,dx_2\\&=\lambda_m\int\psi_n(x_1)\,\psi_m(x_1)\,dx_1=\lambda_m\delta_{nm}\end{aligned} \tag{39}$$

The elements of its inverse are

$$(\Lambda^{-1})_{nm}=(1/\lambda_m)\,\delta_{nm} \tag{40}$$

Backward transformation then yields $\tilde{H} = S^{-1}\Lambda^{-1}S$,

$$\tilde{H}(12, \mathbf{k}) = \sum_n \frac{1}{\lambda_n} \psi_n(x_1)\, \psi_n(x_2) \tag{41}$$

This is formally the exact answer to the inversion problem. However, by our analytic approach explicit knowledge is restricted to $n = 0$. But this is sufficient for the purpose of obtaining the small g and $\mathbf{k}$ behavior, in which case the $n = 0$ term in (41) will be dominating. Using (37) for λ_0 and the corresponding eigenfunction of (31) for $\psi_0(x)$, we finally find

$$\tilde{H}(12, \mathbf{k}) = \frac{\rho'(x_1)\, \rho'(x_2)}{\beta\gamma' k^2 + \beta g M\, \Delta\rho} \tag{42}$$

since the normalized function $\psi_0(x)$ is

$$\psi_0(x) = N^{-1/2} \rho'(x) \tag{43}$$

with N given below (33).

Comparing with Eq. (12) via (27), one sees that Eq. (42) is nothing but the result of the capillary wave theory. With the identification $\gamma' = \gamma$ that we will establish in the next part, they are fully identical. This thus makes a bridge connecting the van der waals theory and capillary wave theory. We see that capillary waves are built into the van der Waals theory via the correlation function that emerges when it is perturbed beyond the more obvious mean field result. It may be noted that the flat intrinsic profile $\rho(x)$ of the van der Waals theory is kept unchanged in this approximation.

6. SURFACE TENSION

We want to identify the γ' in (42) with the surface tension γ that follows from the van der Waals theory. First we reexpress (36) somewhat. Noting that $v(r)$ has spherical symmetry and expanding for small $\mathbf{k}$, we find $[\boldsymbol{\sigma} = (y, z)]$

$$\begin{aligned} \Delta\tilde{v}(12) &= \int v(r)[-i\mathbf{k}\boldsymbol{\sigma} + \tfrac{1}{2}(\mathbf{k}\boldsymbol{\sigma})^2 + \cdots]\, d\boldsymbol{\sigma} \\ &= \tfrac{1}{2} \int (k_y^2 y^2 + k_z^2 z^2)\, v(r)\, d\boldsymbol{\sigma} = \tfrac{1}{2} k^2 \int y^2 v(r)\, d\boldsymbol{\sigma} \end{aligned} \tag{44}$$

which inserted in (38) yields

$$\beta\gamma' = \tfrac{1}{2} \int \rho'(x_1)\, y^2 v(r)\, \rho'(x_2)\, dy\, dz\, dx_1\, dx_2 \tag{45}$$

Next we turn to the surface tension from the van der Waals theory. Adding $\beta g_g \int \rho(x)\, dx$ to the Helmholtz free energy (13), we get

$$\Omega = \int_{-L}^{L} I_0(\rho(x))\, dx + \tfrac{1}{2} \int_{-L}^{L} \int_{-\infty}^{\infty} \rho(x)\, \chi(x-x')\, \rho(x')\, dx'\, dx + \beta g_g \int_{-L}^{L} \rho(x)\, dx \tag{46}$$

where we now specify the system to be of finite length, avoiding end effects by letting the x' integration be unrestricted. (The limit $L \to \infty$ is then considered.) The last term of (46) is β/A times the Gibbs free energy. For the case with $\rho(x) = \text{const}$ the Ω is thus nothing but $\beta p(2L)$, where p is the pressure. With an interface present the Ω will deviate from this, and the deviation is the surface tension times $-\beta$. Thus

$$\beta\gamma = \beta p(2L) - \Omega \tag{47}$$

The bulk pressure is clearly determined by

$$\beta p = I(\rho) + \tfrac{1}{2} a \rho^2 + \beta g_g \rho \tag{48}$$

where the ρ is the density of either one of the two coexisting phases, i.e., $\rho = \rho(\pm\infty)$, and a is the integrated strength of the attractive interaction multiplied by $-\beta$.

$$a = \int \chi(x)\, dx \tag{49}$$

The functional (46) has its maximum when the profile $\rho(x)$ is the one at equilibrium determined by Eq. (16) with external potential $\phi(x) = 0$. Likewise the functional (47) has its minimum for the same density profile, since p only acts as an added constant. Equation (47) may be rewritten as

$$\beta\gamma = S - R \tag{50}$$

with

$$\begin{aligned} S &= \int_{-\infty}^{\infty} K(\rho(x))\, dx + \tfrac{1}{2} a \int_{-L}^{L} [\rho(x)]^2\, dx \\ R &= \tfrac{1}{2} \int_{-L}^{L} \int_{-\infty}^{\infty} \rho(x_1)\, \chi(x_1 - x_2)\, \rho(x_2)\, dx_1\, dx_2 \end{aligned} \tag{51}$$

where

$$K(\rho(x)) = -I_0(\rho(x)) - \tfrac{1}{2} a [\rho(x)]^2 - \beta g_g \rho(x) + \beta p \tag{52}$$

Clearly, due to (48),

$$K(\rho(\pm L)) \to 0 \qquad \text{when} \quad L \to \infty \tag{53}$$

by which the limits of integration may be replaced by $\pm\infty$.

A variation of the density profile away from its equilibrium can be made by replacing x by $x(1+\varepsilon)$. Due to the extremum, the γ will be unchanged to first order in ε. With $x' = x(1+\varepsilon)$ in the integral for S, one sees that its value changes to

$$S/(1+\varepsilon) + \tfrac{1}{2}\varepsilon a L\{\rho(+L)^2 + [\rho(-L)]^2\}$$

In the integral for R we make the expansion

$$\rho(x(1+\varepsilon)) = \rho(x) + \varepsilon x \rho'(x) + \cdots$$

So, to first order in ε we find

$$\beta\gamma = \beta\gamma + \varepsilon(-S+Q) + \cdots \tag{54}$$

where

$$\begin{aligned} Q = {} & \tfrac{1}{2} a L\{[\rho(+L)]^2 + [\rho(-L)]^2\} \\ & - \tfrac{1}{2}\int_{-L}^{L}\int_{-\infty}^{\infty} [x_1\rho'(x_1)\,\chi(x_1-x_2)\,\rho(x_2) \\ & + \rho(x_1)\,\chi(x_1-x_2)\,x_2\rho'(x_2)]\,dx_1\,dx_2 \end{aligned} \tag{55}$$

Here we can perform partial integration to obtain $[\rho(\pm L) \to \rho(\pm\infty)$ as $L \to \infty]$

$$Q = 2R + \frac{1}{2}\int_{-L}^{L}\int_{-\infty}^{\infty} \rho(x_1) x \frac{d}{dx}[\chi(x)]\,\rho(x_2)\,dx_1\,dx_2 \tag{56}$$

with $x = x_1 - x_2$.

From (54) one clearly must have $S = Q$. This together with (56) inserted in (50) yields

$$\beta\gamma = Q - R = \frac{1}{2}\int_{-L}^{L}\int_{-\infty}^{\infty} \rho(x_1)\frac{d}{dx}[x\chi(x)]\,\rho(x_2)\,dx_1\,dx_2 \tag{57}$$

To go further, we use expression (15) for $\chi(x)$ to obtain

$$\begin{aligned} \frac{d}{dx}[x\chi(x)] &= \int \frac{\partial}{\partial x}[xv(r)]\,dy\,dz \\ &= -\int y\frac{\partial^2}{\partial y\,\partial x}[xv(r)]\,dy\,dz \end{aligned} \tag{58}$$

where partial integration with respect to y is used. Now we come to the point where the spherical symmetry of $v(r)$ is utilized. With $\partial v/\partial x = (x/r)\, dv/dr$, etc., one has

$$y\, \partial v/\partial x = x\, \partial v/\partial y \tag{59}$$

We operate on this with $y\, \partial/\partial x$ to obtain

$$y^2 \frac{\partial^2 v}{\partial x^2} = y \frac{\partial^2}{\partial y\, \partial x}(xv) \tag{60}$$

Noting that $\partial^2/\partial x^2 = -\partial^2/\partial x_1\, \partial x_2$ $(x = x_1 - x_2)$, we can substitute this result in (58) to yield

$$\frac{d}{dx}[x\chi(x)] = \int y^2 \frac{\partial^2 v(x)}{\partial x_1\, \partial x_2}\, dy\, dz \tag{61}$$

This latter result is finally inserted in Eq. (57) and partial integrations with respect to both x_1 and x_2 are performed whereby the surface terms do not contribute. We finally obtain the result

$$\beta\gamma = \tfrac{1}{2} \int \rho'(x_1)\, y^2 v(r)\, \rho'(x_2)\, dy\, dz\, dx_1\, dx_2 \tag{62}$$

This is precisely expression (45). Accordingly, $\gamma' = \gamma$, which we wanted to show. It may be noted that our derivations have resulted into a more compact expression for γ when compared with Eqs. (46)–(48). Here we note that result (62) agrees with the more general result expressing γ in terms of the direct correlation function and $\rho'(x)$.(17) According to expressions (21) and (22), the $v(r)$ in (62) can be replaced by $c(12, y, z)$, since $\delta(\mathbf{r}_1 - \mathbf{r}_2)$ will not contribute.

7. SULLIVAN MODEL

The Sullivan model is the van der Waals theory for the surface when the $\chi(x)$ is chosen to be of exponential form.(19) The nice feature of this special model is that the equations simplify; e.g., Eq. (16) for the equilibrium density profile can be transformed into a second-order differential equation. Likewise here we will find that the evaluation of the pair correlation function can be done more explicitly. In fact the problem transforms into the one-dimensional Schrödinger equation with a potential.

The main problem is to evaluate the $\tilde{H}$ from Eq. (26) with $\tilde{C}$ as given by (23). For this purpose we introduce a short-hand notation, rewriting (26) as

$$\tilde{H} * \tilde{C} = I \tag{63}$$

where the asterisk denotes integration with respect to the common coordinate x_3, and I is the unit matrix $\delta(x_1 - x_2)$. Furthermore, we introduce μ and its inverse $1/\mu$, which are the matrices $\mu(\rho(x_1))\,\delta(x_1 - x_2)$ and $[1/\mu(\rho(x_1))]\,\delta(x_1 - x_2)$, respectively. In this way Eq. (23) may be written as

$$\tilde{C} = 1/\mu - \tilde{v} \tag{64}$$

Instead of $\tilde{H}$ we find it convenient to introduce the quantity $\tilde{K}$ closely related to $\tilde{H}$ by

$$\tilde{H} = \mu + \mu * \tilde{K} * \mu \tag{65}$$

With $\tilde{K}$ known, the evaluation of $\tilde{H}$ will be trivial. Insertion of Eqs. (64) and (65) in (63) yields

$$\tilde{K} = \tilde{v} + \tilde{v} * \mu * \tilde{K} \tag{66}$$

When $\chi(x)$ is an exponential, $v(r)$ will be of Yukawa form

$$v(r) = \alpha \frac{\lambda^2}{4\pi} \frac{e^{-\lambda r}}{r} \tag{67}$$

Its Fourier transform with respect to $\mathbf{r}$ is $\alpha\lambda^2/(\lambda^2 + k^2 + k_x^2)$ (where $k^2 = k_y^2 + k_z^2$). Transforming back to the x coordinate, we find

$$\tilde{v}(x, \mathbf{k}) = \frac{\alpha\lambda^2}{2(\lambda^2 + k^2)^{1/2}} \exp[-(\lambda^2 + k^2)^{1/2}\,|x|] \tag{68}$$

$$\chi(x) = \tilde{v}(x, 0) = \tfrac{1}{2}\alpha\lambda \exp(-\lambda\,|x|) \tag{69}$$

which is the exponential form used in the Sullivan model. We now note that

$$(-\nabla^2 + \lambda^2)\,v(r) = \alpha\lambda^2\delta(\mathbf{r}) \tag{70}$$

or

$$\left(-\frac{d^2}{dx_1^2} + k^2 + \lambda^2\right)\tilde{v} = \alpha\lambda^2 I \tag{71}$$

The operator acting on $\tilde{v}$ in this equation may now be applied to Eq. (66). Use of (71) then yields the following equation for $\tilde{K}$:

$$\left[\frac{1}{\alpha\lambda^2}\left(-\frac{d^2}{dx_1^2} + k^2 + \lambda^2\right) - \mu(\rho(x_1))\right]\tilde{K}(12, k) = \delta(x_1 - x_2) \tag{72}$$

This equation shows that $\tilde{K}$ is nothing but the Green's function of a one-dimensional Schrödinger equation. Like Eq. (41), the $\tilde{K}$ may be expanded in the eigenfunctions of the operator on the left-hand side of Eq. (72). A simplifying feature in the present case is that these eigenfunctions are independent of k, as is obvious from Eq. (72). Again for small k only the smallest eigenvalue will be of interest. This is obviously clearer in the present case, since a one-dimensional quantum problem with attractive interaction has a bond ground state with eigenvalue separated from other eigenvalues (the μ has a maximum at the interface). The eigenvalue and eigenfunction of this bond state we again find from Eq. (16) for the equilibrium profile. This leads to Eq. (29), which we now differentiate twice with respect to x. We notice that with use of (69)

$$\frac{d^2}{dx^2}\chi(x-x')=\lambda^2\chi(x-x')-\alpha\lambda^2\delta(x-x') \tag{73}$$

In the resulting equation the $\chi(x-x')$ can again be eliminated by use of (29), and we obtain, after division by $\alpha\lambda^2$,

$$\left[\frac{1}{\alpha\lambda^2}\left(-\frac{d^2}{dx^2}+\lambda^2\right)-\mu(\rho(x))\right]\psi_0(x)=\frac{1}{\alpha}\beta gM \tag{74}$$

where

$$\psi_0(x)=\frac{1}{\mu(\rho(x))}\rho'(x)=\frac{d\beta g_0(\rho(x))}{dx} \tag{75}$$

using definition (20) for μ.

Clearly for $g=0$ the ψ_0 is an eigenfunction of (74) with eigenvalue $\lambda_0=0$. For $g\neq 0$ the $\psi_0(x)$ will be an approximate eigenfunction to (74) and expansions like (32) may again be performed. This time, instead of (35) we find the eigenvalue to be

$$\lambda_0=\frac{1}{N}\frac{1}{\alpha}\beta gM\,\Delta(\beta g_0) \tag{76}$$

where

$$N=\int[\psi_0(x)]^2\,dx \tag{77}$$

and $\Delta(\beta g_0)$ is the difference in βg_0 between the two phases. This difference is found by means of Eq. (16) to be [with $g=0$, or $\rho(x)=\text{const}$]

$$\Delta(\beta g_0)=\alpha\,\Delta\rho \tag{78}$$

when $\chi(x)$ is given by (69). So (76) turns into

$$\lambda_0 = (1/N)\,\beta g M\,\Delta\rho \tag{79}$$

Clearly, the $\psi_0(x)$ is also an eigenfunction of the operator on the left-hand side of (72). However, the eigenvalue changes to

$$\lambda_0 = (\beta/N)(gM\,\Delta\rho + \gamma'' k^2) \tag{80}$$

with

$$\beta\gamma'' = \frac{N}{\alpha\lambda^2} = \frac{1}{\alpha\lambda^2}\int\left[\frac{d(\beta g_0)}{dx}\right]^2 dx \tag{81}$$

Thus altogether the small-k behavior of $\tilde{K}$ will be like expression (42) for $\tilde{H}$,

$$K(12, k) = [\psi_0(x_1)\,\psi_0(x_2)]/N\lambda_0 \tag{82}$$

since it is the Green's function of Eq. (72). With $\psi_0(x)$ given by (75) and λ_0 given by (80), this is the same as result (42) for $\tilde{H}$ provided $\gamma'' = \gamma'$. The $\tilde{K}$ and $\tilde{H}$ are related by Eq. (65).

Finally we show that $\gamma'' = \gamma'$. Inserting Eqs. (75) and (77) and utilizing Eq. (29) (with $g = 0$), we find

$$\begin{aligned}\beta\gamma'' &= \frac{1}{\alpha\lambda^2}\int\left[\frac{1}{\mu}\rho'(x)\right]^2 dx\\ &= \int \rho'(x_1)\,S(x_1 - x_2)\,\rho'(x_2)\,dx_1\,dx_2\end{aligned} \tag{83}$$

where

$$S(x_1 - x_2)\,\frac{1}{\alpha\lambda^2}\int \chi(x_1 - x_2)\,\chi(x_2 - x)\,dx \tag{84}$$

With $\chi(x)$ given by the exponential form (69), one finds by integration

$$S(x) = (\alpha/4\lambda)(1 + \lambda\,|x|)\,e^{-\lambda|x|} \tag{85}$$

Expression (83) with (85) inserted should be compared with expression (38) for γ'. The $\Delta\tilde{v}(12)$ for the present case is then needed. Equations (36) and (68) give

$$(1/k^2)\,\Delta v(12) \xrightarrow[k\to 0]{} S(x) \tag{86}$$

Thus, γ' and γ'' as given by (38) and (83), respectively, are equal.

8. AVERAGE DENSITY

The capillary waves cause the average density to be different from the intrinsic density of the van der Waals theory. Here we want to evaluate the leading contribution to the density beyond the van der Waals theory and compare it with capillary wave theory. Such a computation has been performed by Sullivan,$^{(9)}$ whose result indicates some kind of consistency with capillary waves, but the connection is unclear. The root of the problem is the divergences (when $g \rightarrow 0$) that wash out the average density profile. Theory is not quite able to cope with this problem. Capillary waves are harmonic oscillators of the positions of the intrinsic surface, but the oscillations of the local densities are not harmonic for large amplitudes, and the modes will couple. However, to avoid this difficulty, we may, as before, restrict ourselves to small amplitudes. Thus we may consider a large field of gravity to suppress oscillations or consider the contribution from single modes, i.e., we expand for small amplitudes. Capillary wave theory then yields for the average density

$$\langle \rho(x-A)\rangle = \rho(x) - \langle A\rangle\, \rho'(x) + \tfrac{1}{2}\langle A^2\rangle\, \rho''(x) + \cdots \tag{87}$$

Clearly, $\langle A\rangle = 0$. With $A_1 = A_2 = A$ and $y = z = 0$, Eq. (10) gives $\langle A^2\rangle = \frac{1}{4}a^2$ for a single mode. Adding the independent modes as in forming expression (11), we obtain, with a^2 given by (6),

$$\Delta\rho(x) = \langle \rho(x-A)\rangle - \rho(x) = \tfrac{1}{2}\rho''(x)J \tag{88}$$

where

$$J = \frac{1}{(2\pi)^2}\int \frac{d\mathbf{k}}{\beta\gamma k^2 + \beta g M\,\Delta\rho}$$

To prevent divergence this integral will need some large-k cutoff.

Change in average density can also be evaluated by going one step beyond the van der Waals theory in γ-ordering. Like Sullivan,$^{(9)}$ we will do so. The contribution to the free energy is then given by the sum of the ring graphs with potential bonds.$^{(9)}$ In the notation of Section 6 this contribution ΔF to be added to expression (13) is given by

$$-\frac{\beta\,\Delta F}{A} = -\frac{1}{2}\frac{1}{(2\pi)^d}\,\mathrm{Tr}\int \ln(1 - \mu * \tilde{v})\, d\mathbf{k} \tag{89}$$

where the asterisk denotes matrix multiplication, and Tr means trace with respect to the x coordinate. [To be correct, a term $-\frac{1}{2}v(0)\int \rho(x)\, dx$ should be included in (89), but it can be dropped, since it contributes only a constant to the chemical potential and has no physical significance.] The change Δg in chemical potential to be added to the right-hand side of Eq. (16) is then

$$\Delta g = \frac{\delta(\Delta F/A)}{\delta \rho(x)} \tag{90}$$

or

$$\beta\, \Delta g = -\frac{1}{2}\frac{1}{(2\pi)^d}\frac{d\mu(\rho(x))}{d\rho(x)} \int \tilde{K}(11, k)\, d\mathbf{k} \tag{91}$$

where, from (66),

$$\tilde{K} = \tilde{v}/(1 - \tilde{v} * \mu) \tag{92}$$

and $\tilde{K}(11, k)$ means $\tilde{K}$ with $x_1 = x_2 = x$. From the small-k expression (82) we obtain

$$\frac{1}{(2\pi)^d} \int \tilde{K}(11, \mathbf{k})\, dk = [\rho'(x)/\mu]^2 J \tag{93}$$

when $\psi_0(x)$ and $N\lambda_0$ are substituted by expressions (75) and (80), respectively. The J is the integral given by (88) ($\gamma'' = \gamma$). (Note that these expressions are not restricted to the Sullivan model considered in Section 7.) Furthermore, with the help of Eq. (20) we have

$$\frac{\partial^2(\beta g_0)}{\partial \rho^2} = \frac{\partial}{\partial \rho}\left(\frac{1}{\mu}\right) = -\frac{1}{\mu^2}\frac{\partial \mu}{\partial \rho} \tag{94}$$

Thus, insertion of Eqs. (93) and (94) in (91) yields

$$\beta\, \Delta g = \frac{1}{2}\frac{\partial^2(\beta g_0)}{\partial \rho^2} [\rho'(x)]^2 J \tag{95}$$

We add this to (16) and expand around the intrinsic profile $\rho(x)$ to obtain

$$0 = \frac{\partial(\beta g_0)}{\partial \rho} \Delta\rho(x) - \int \chi(x - x')\, \Delta\rho(x')\, dx' + \beta\, \Delta g \tag{96}$$

which determines the change $\Delta\rho(x)$ in average density. The solution of this integral equation does not seem obvious. However, in the spirit of the capillary wave result (88) and expression (95), we differentiate (16) twice to obtain

$$0 = \frac{\partial^2(\beta g_0)}{\partial \rho^2} [\rho'(x)]^2 + \frac{\partial(\beta g_0)}{\partial \rho} \rho''(x) - \int \chi(x - x')\, \rho''(x')\, dx' \tag{97}$$

when partial integration has been done in the last term. Clearly the first term of (97) is proportional to (95). Thus, comparing Eqs. (96) and (97), it follows that the solution $\Delta\rho(x)$ must be proportional to $\rho''(x)$, upon which these equations become identical. One finds the solution

$$\Delta\rho(x) = \tfrac{1}{2}\rho''(x)J \qquad (98)$$

This is precisely the capillary wave result (88). Thus, the leading γ-ordered perturbation of van der Waals theory corresponds to capillary waves when amplitudes are regarded as small.

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