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Structure of Interfaces from Uniformity of the Chemical Potential

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It is shown that a generalized chemical potential suggested by the potential-distribution theory is uniform even in a nonuniform fluid. Leng, Rowlinson, and Thompson had already observed its uniformity through the liquid–vapor interface in the penetrable-sphere model, in mean-field approximation. Following those authors, we exploit the uniformity of that generalized chemical potential to obtain unified and transparent derivations of the results of Ono and Kondo and of van der Waals on the liquid–vapor interfaces in the lattice-gas model and in the model of attracting hard spheres, respectively, both in mean-field approximation.

KEY WORDS: Surfaces; interfaces; nonuniform fluids; density profile; lattice gas; attracting hard spheres; van der Waals theory.

1. INTRODUCTION

Leng *et al.*(1) found the density profile of the liquid–vapor interface of the penetrable-sphere model(2) in a mean-field approximation. They also calculated the local thermodynamic activity (or, equivalently, chemical potential) as defined by the prescription of the potential-distribution theory,(3–5) and found that it is uniform through the interface, where it has the same value as it does in the bulk phases. In the theory of Leng *et al.*, uniformity of the activity implies an integral equation for the density profile. Their observation amounted to verifying that the profile they had derived satisfied that integral equation; but they could equally well have asserted uniformity of the activity from the start, and then taken the resulting integral equation to determine the profile.(6) That idea for determining interfacial density profiles has been used before,(7,8) but with different expressions for the local activity.

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In Section 2 we show that the activity defined by the potential-distribution theory is indeed uniform even in an otherwise nonuniform fluid. The methods of Leng *et al.* may therefore be adapted to find the interfacial profile in mean-field approximation for any model fluid. In Section 3 this is done for the lattice gas and in Section 4 for a continuum fluid of attracting hard spheres. For the former, the resulting equation for the density profile is that previously obtained for the same model by Ono and Kondo;(9),[2] it is also that of the van der Waals,(11) Cahn–Hilliard(12) theory, with a second difference in place of a second derivative, as is appropriate to a discrete space. For the model continuum fluid the resulting equation for the density profile is nonlocal in a way proposed by recent authors; in the further approximation that the density gradient is small, it reduces to the conventional theory with a characteristic length determined by the second moment of the attractive component of the intermolecular potential.

These results are not new; it is the transparency of their derivation that justifies this account.

2. CHEMICAL POTENTIAL IN A NONUNIFORM FLUID

We follow the original derivation of the formulas of the potential-distribution theory,(3,4) but now allowing the fluid to be nonuniform. The nonuniformity may arise from the interfaces between phases, from the walls of the containing vessel, from external fields, or from any combination of these.

We suppose such a fluid of N molecules to be in equilibrium at a uniform temperature T in a vessel of volume V. From the Boltzmann distribution law, the probability of finding the molecules $1,\ldots, N$ in the respective elements of volume $d\tau_1,\ldots, d\tau_N$ centered at $\mathbf{r}_1,\ldots, \mathbf{r}_N$ is

$$Q_N^{-1} \exp[-W_N(\mathbf{r}_1,\ldots, \mathbf{r}_N)/kT]\, d\tau_1 \cdots d\tau_N \tag{1}$$

where k is Boltzmann's constant; W_N is the potential energy of the system in the configuration $\mathbf{r}_1,\ldots, \mathbf{r}_N$, including the energies of interaction of the molecules with the walls of the vessel, with any external fields, and with each other; and Q_N is the configuration integral,

$$Q_N = \int_V \cdots \int_V \exp[-W_N(\mathbf{r}_1,\ldots, \mathbf{r}_N)/kT]\, d\tau_1 \cdots d\tau_N \tag{2}$$

the integrations extending throughout the volume V. Then the mean density $\rho(\mathbf{r})$ at the position $\mathbf{r}$ in the vessel is

$$\rho(\mathbf{r}) = NQ_N^{-1} \int_V \cdots \int_V \exp[-W_N(\mathbf{r}_1,\ldots, \mathbf{r}_{N-1}, \mathbf{r})/kT]\, d\tau_1 \cdots d\tau_{N-1} \tag{3}$$

[2] The density profile for this model was obtained in higher (quasichemical) approximation by Parlange.(10)

When an Nth molecule is added at $\mathbf{r}$ to a system of $N - 1$ molecules in the configuration $\mathbf{r}_1,..., \mathbf{r}_{N-1}$, the potential energy of the system increases by

$$\Psi(\mathbf{r}_1,..., \mathbf{r}_{N-1}, \mathbf{r}) = W_N(\mathbf{r}_1,..., \mathbf{r}_{N-1}, \mathbf{r}) - W_{N-1}(\mathbf{r}_1,..., \mathbf{r}_{N-1}) \tag{4}$$

This includes the interaction of the added particle with the walls, with any external fields, and with the other particles. In terms of this Ψ, Eq. (3) becomes

$$\rho(\mathbf{r}) = (NQ_{N-1}/Q_N)\langle\exp(-\Psi/kT)\rangle_{\mathbf{r}} \tag{5}$$

where

$$\langle\exp(-\Psi/kT)\rangle_{\mathbf{r}} = Q_{N-1}^{-1} \int_V \cdots \int_V \exp\{-[\Psi(\mathbf{r}_1,..., \mathbf{r}_{N-1}, \mathbf{r}) + W_{N-1}(\mathbf{r}_1,..., \mathbf{r}_{N-1})]/kT\}\, d\tau_1 \cdots d\tau_{N-1} \tag{6}$$

is the mean value of the function $\exp[-\Psi(\mathbf{r}_1,..., \mathbf{r}_{N-1}, \mathbf{r})/kT]$ at the position $\mathbf{r}$ in a fluid of $N - 1$ particles (at the variable positions $\mathbf{r}_1,..., \mathbf{r}_{N-1}$) that is at equilibrium in the volume V at the temperature T. When N and V are both large, the N-particle and $(N - 1)$-particle fluids are negligibly different, so the $\rho(\mathbf{r})$ in Eq. (5) is then the local density in the same equilibrium fluid as that in which $\langle\exp(-\Psi/kT)\rangle_{\mathbf{r}}$ is evaluated.

Though $\rho(\mathbf{r})$ and $\langle\exp(-\Psi/kT)\rangle_{\mathbf{r}}$ are separately $\mathbf{r}$-dependent, their ratio, according to Eq. (5), is just NQ_{N-1}/Q_N, which is independent of $\mathbf{r}$. This uniform value of $\rho(\mathbf{r})/\langle\exp(-\Psi/kT)\rangle_{\mathbf{r}}$ may now be called the activity λ, for that is what it is when the fluid is uniform; that is, when ρ and $\langle\exp(-\Psi/kT)\rangle$ are separately $\mathbf{r}$-independent. Thus,

$$\rho(\mathbf{r})/\langle\exp(-\Psi/kT)\rangle_{\mathbf{r}} = NQ_{N-1}/Q_N = \lambda, \quad \text{independent of } \mathbf{r} \tag{7}$$

Likewise, the (configurational) chemical potential μ defined by $\mu = kT \ln[\rho(\mathbf{r})/\langle\exp(-\Psi/kT)\rangle_{\mathbf{r}}]$ is uniform, its uniform value being $kT \ln \lambda$.

Other definitions of chemical potential or activity in a nonuniform fluid are possible,(7–9,13–17) all reducing to the conventional thermodynamic chemical potential or activity when the fluid is uniform. According to how it is defined or identified, such an activity may or may not be uniform in a nonuniform fluid; when it is, it then may (but need not) be equivalent to that in Eq. (7). It is the present $\rho(\mathbf{r})/\langle\exp(-\Psi/kT)\rangle_{\mathbf{r}}$ that Leng *et al.*(1) called the local activity, and they verified its uniformity through the liquid–vapor interface of the penetrable-sphere model, in the mean-field approximation.

The idea is now to express $\langle\exp(-\Psi/kT)\rangle_{\mathbf{r}}$ as a functional of $\rho(\mathbf{r})$, whereupon Eq. (7), with λ independent of $\mathbf{r}$, becomes a functional equation for $\rho(\mathbf{r})$. In the following sections we do this for two different models in mean-field approximation, following Leng *et al.*, and we thereby determine the density profiles of the liquid–vapor interfaces in those models.

3. DENSITY PROFILE OF THE LIQUID–VAPOR INTERFACE OF THE LATTICE GAS IN THE MEAN-FIELD APPROXIMATION

There are N molecules in a volume V. The volume is divided into V/v cells, each of volume v. Each cell has c faces, and shares each one with one of c neighboring cells. The energy of interaction of the molecules is the sum of the energies of interaction of pairs: when the two molecules of the pair are in the same cell, that energy is infinite; when they are in neighboring cells, it is $-\epsilon$ ($\epsilon > 0$); and when they are neither in the same cell nor in neighboring cells, it is zero.

We shall first see how to obtain the equation of state of the homogeneous lattice gas, in the mean-field approximation, from Eq. (7), by taking ρ and $\langle \exp(-\Psi/kT)\rangle$ to be independent of $\mathbf{r}$, and it will then be clear how to apply Eq. (7) to obtain the density profile through the liquid–vapor interface in the same mean-field approximation.

In the lattice gas, $\exp(-\Psi/kT)$, whose mean value appears in Eq. (7), is zero in every occupied cell, and is $\exp(m\epsilon/kT)$ in every empty cell that has m occupied and $c - m$ unoccupied neighboring cells. The mean-field (Bragg–Williams) approximation is that in which the molecules are taken to occupy the cells at random, subject only to the restrictions that no cell be occupied by more than one molecule and that the average number of molecules per cell be some prescribed $v\rho = vN/V < 1$. Random occupancy implies that the probability p_m that m of the c neighbors of any cell are occupied and $c - m$ are empty is

$$p_m = \frac{c!}{m!\,(c-m)!}(v\rho)^m(1 - v\rho)^{c-m} \tag{8}$$

and that, independently of the state of occupancy of its neighbors, the probability that any cell is empty is $1 - v\rho$. Then from Eqs. (7) and (8),

$$\begin{aligned}\rho/\lambda &= \langle e^{-\Psi/kT}\rangle \\ &= (1 - v\rho)\sum_{m=0}^{c} p_m e^{m\epsilon/kT} \qquad (9)\\ &= (1 - v\rho)[1 + (e^{\epsilon/kT} - 1)v\rho]^c \qquad (10)\end{aligned}$$

But the mean-field approximation is in the first place only accurate when each molecule has many neighbors and interacts weakly with any one of them;(18–21) i.e., in the limit $\epsilon/kT \to 0$, $c \to \infty$, $c\epsilon/kT$ fixed. Therefore, to the degree that it is accurate at all, Eq. (10) is equivalent to

$$\lambda = [\rho/(1 - v\rho)]e^{-c\epsilon v\rho/kT} \tag{11}$$

The sum $\sum p_m \exp(m\epsilon/kT)$ in Eq. (9) is the mean value of $\exp(-\Psi/kT)$ over the empty cells alone, $\langle\exp(-\Psi/kT)\rangle$ being its mean value over all the cells and $1 - v\rho$ the probability that a cell is empty. Having replaced $\{1 + [\exp(\epsilon/kT) - 1]v\rho\}^c$ by $\exp(c\epsilon v\rho/kT)$ in going from Eq. (10) to Eq. (11) amounts to having replaced $\sum p_m \exp(m\epsilon/kT)$ by $\exp[(\epsilon/kT)\sum mp_m]$; i.e., to having approximated the average of the exponential of $-\Psi/kT$, over the empty cells, by the exponential of the average.

Though with $c\epsilon/kT$ of order 1, the λ given by Eq. (10) differs only by terms of the order of the small quantity ϵ/kT from that given by Eq. (11), it is the latter that is the canonical expression for λ in the mean-field approximation; for if $\lambda(\rho)$ is the activity as a function of the density ρ at fixed temperature, then it is an exact symmetry property of the lattice gas that(22)

$$v^2\lambda(\rho)\lambda(1/v - \rho) = e^{-c\epsilon/kT} \tag{12}$$

which Eq. (11) satisfies exactly, but Eq. (10) only approximately. This is the analog of an earlier observation about the mean-field approximation to the penetrable-sphere model.(2)

We turn now to the determination of the density profile through the liquid–vapor interface in this same lattice-gas model, still in mean-field approximation. The cells are imagined arranged in layers at positions indexed by $z = ..., -2, -1, 0, 1, 2,...$ (Fig. 1). A cell in the layer at z has c' of its neighbors in the adjacent layer at $z + 1$; c' in the adjacent layer at $z - 1$; and the remaining $c - 2c'$ of its neighbors in the same layer with itself, at z. In the illustration in Fig. 1, $c = 6$ and $c' = 1$. Liquid and vapor phases are present in equilibrium, with $z \to \infty$ in the bulk liquid, say, and $z \to -\infty$ in the bulk vapor. The number density ρ is now z-dependent: $\rho = \rho(z)$, with $\rho(\infty) = \rho_l$ and $\rho(-\infty) = \rho_g$, the densities of the bulk liquid and vapor phases, respectively.

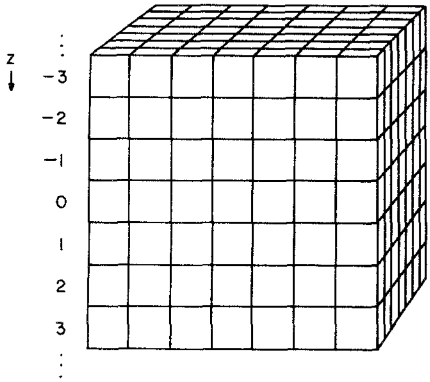

Fig. 1. Cells in layers indexed by z. In this illustration the cells are cubical and the array is simple cubic, with $c = 6$, $c' = 1$.

In the mean-field approximation to this inhomogeneous lattice gas we again take the molecules to occupy the cells at random, subject to the restriction that no cell be occupied by more than one molecule; but now, instead of additionally prescribing merely the overall average density N/V, we prescribe the (as yet unknown) local density $\rho(z)$ at each z.

For a cell at z, the probability p_{lmn} that exactly l (not more and not fewer) of its c' neighbors at $z+1$, that m of its $c-2c'$ neighbors at z, and that n of its c' neighbors at $z-1$, are occupied, is, by the approximation of random occupancy,

$$\begin{aligned} p_{lmn} = {} & \frac{c'!}{l!\,(c'-l)!}[v\rho(z+1)]^{l}[1-v\rho(z+1)]^{c'-l} \\ & \times \frac{(c-2c')!}{m!\,(c-2c'-m)!}[v\rho(z)]^{m}[1-v\rho(z)]^{c-2c'-m} \\ & \times \frac{c'!}{n!\,(c'-n)!}[v\rho(z-1)]^{n}[1-v\rho(z-1)]^{c'-n} \end{aligned} \tag{13}$$

By that same approximation, the probability that a cell at z is empty is $1-v\rho(z)$, independently of the states of occupancy of its neighbors. Therefore, from Eqs. (7) and (13),

$$\begin{aligned} \rho(z)/\lambda &= \langle e^{-\Psi/kT}\rangle_z \\ &= [1-v\rho(z)]\sum_{l=0}^{c'}\sum_{m=0}^{c-2c'}\sum_{n=0}^{c'} p_{lmn}e^{(l+m+n)\epsilon/kT} \qquad (14) \\ &= [1-v\rho(z)][1+(e^{\epsilon/kT}-1)v\rho(z+1)]^{c'} \\ &\quad \times [1+(e^{\epsilon/kT}-1)v\rho(z)]^{c-2c'}[1+(e^{\epsilon/kT}-1)v\rho(z-1)]^{c'} \qquad (15) \end{aligned}$$

with λ the uniform value of the activity. The latter is known from the hole–particle symmetry of the lattice gas to be[(22)]

$$\lambda = v^{-1}e^{-c\epsilon/2kT} \tag{16}$$

Equations (14) and (15) are generalizations of Eqs. (9) and (10). With λ independent of z, Eq. (15) is a second-order difference equation for the density profile $\rho(z)$.

If we take the limit $\epsilon/kT \to 0$, c and $c' \to \infty$, with $c\epsilon/kT$ and $c'\epsilon/kT$ fixed, Eq. (15) becomes

$$\rho(z)/[1-v\rho(z)]\lambda = \exp\{[c\rho(z) + c'\Delta^2\rho(z)]v\epsilon/kT\} \tag{17}$$

where Δ^2 means the second difference: $\Delta^2\rho(z) = \rho(z+1) + \rho(z-1) - 2\rho(z)$. Equation (17) is a generalization of Eq. (11) and reduces to it when the fluid is uniform; i.e., when $\rho(z)$ is independent of z. Having gone from Eq. (15) to

Eq. (17) amounts to having replaced $\sum\sum\sum p_{lmn} \exp[(l+m+n)\epsilon/kT]$ in Eq. (14) by $\exp[(\epsilon/kT)\sum\sum\sum(l+m+n)p_{lmn}]$; i.e., to having approximated the average of the exponential of $-\Psi/kT$, over the empty cells, by the exponential of the average, just as before in going from Eq. (10) to Eq. (11). The analogous step was taken by Leng *et al.* in their mean-field theory of the density profile in the penetrable-sphere model.(1)

By the hole–particle symmetry of the lattice gas,(22) the density profile $\rho(z)$ must be antisymmetric about $\rho = 1/2v$; that is to say, there is a function $R(z)$ of the continuous variable z, such that

$$R(-z) + R(z) = 1 \tag{18}$$

for all z, and a fraction z' $(0 \leqslant z' < 1)$ such that

$$v\rho(z) = R(z - z') \tag{19}$$

for all integer z. The relation(22) $\rho_g + \rho_l = 1/v$ between the densities of the bulk phases is the special case $|z| = \infty$ of Eqs. (18)–(19). We may determine the function $R(z)$ from Eq. (17), but not the number z', which is determined by accidental, nonthermodynamic factors, such as the precise integer numbers N and V/v of molecules and cells, and the shape of the container. When account is taken of Eq. (16), it is seen that the required antisymmetry expressed by Eqs. (18)–(19) would be satisfied exactly by the solution of Eq. (17) but only approximately by the solution of Eq. (15); just as in the homogeneous fluid the symmetry expressed by Eq. (12) is satisfied exactly by the λ of Eq. (11) but only approximately by that of Eq. (10).

From Eqs. (16) and (17),

$$c'v\,\Delta^2\rho = c(\tfrac{1}{2} - v\rho) + (kT/\epsilon)\ln[v\rho/(1 - v\rho)] \tag{20}$$

which is the difference equation for $\rho(z)$ in the form in which it was obtained previously by Ono and Kondo.(9),[3] They explained how to solve it numerically and gave sample profiles. The functions $R(z)$ of Eqs. (18)–(19) for two such profiles are shown in Fig. 2.

Let the right-hand side of Eq. (11) be called $\Lambda(\rho)$:

$$\Lambda(\rho) = [\rho/(1 - v\rho)]e^{-c\epsilon v\rho/kT} \tag{21}$$

It is the activity of a homogeneous lattice gas of density ρ, as a function of ρ at fixed temperature, in the mean-field approximation. In terms of this function, Eq. (20), with Eq. (16), becomes

$$(vc'\epsilon/kT)\,\Delta^2\rho = \ln[\Lambda(\rho)/\lambda] \tag{22}$$

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[3] The second-difference operator Δ^2 of Ono and Kondo is slightly different from the one used here. If we call theirs Δ^2_{OK} and still call the present one Δ^2, then $\Delta^2_{\mathrm{OK}}\rho(z-1) = \Delta^2\rho(z)$.

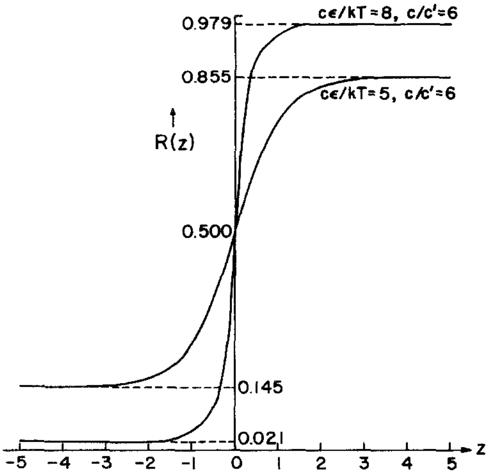

Fig. 2. The function $R(z)$ of Eqs. (18)–(19) for two sample density profiles. The profiles $v\rho(z)$ are identical to $R(z)$ except for an indeterminate shift of the z scale.

or, equivalently, in terms of the (configurational) chemical potential $M(\rho) = kT \ln \Lambda(\rho)$ and its uniform value $\mu = kT \ln \lambda$, the difference equation for $\rho(z)$ becomes

$$vc'\epsilon\, \Delta^2 \rho = M(\rho) - \mu \tag{23}$$

This has the form of the fundamental equation of the van der Waals,(11) Cahn–Hilliard(12) theory, but with a second difference in place of a second derivative, as appropriate to a discrete space. Finite differences, unlike derivatives, are nonlocal; the occurrence here of $\Delta^2\rho$ is a foreshadowing of the nonlocality we shall find when this same line of argument is applied to a continuum fluid, in the next section.

4. DENSITY PROFILE OF THE LIQUID–VAPOR INTERFACE OF A MODEL CONTINUUM FLUID IN THE MEAN-FIELD APPROXIMATION

We again imagine a fluid in which the total energy of interaction of the molecules is the sum of the energies of interaction of all pairs, but now we take the interaction of a pair to be that of attracting hard spheres. Let the fluid consist of a liquid and a vapor phase, and let z measure distance in the direction perpendicular to the interface, with the bulk liquid at $z = \infty$ and the bulk vapor at $z = -\infty$. This is as before, except that now z is a continuous distance, whereas before it was a discrete, dimensionless index.

Let q_z be the probability that if another hard-sphere molecule identical to those in the fluid is inserted in the equilibrium fluid while the configuration of the latter remains fixed, and if the inserted molecule is centered at a randomly chosen point in the plane at z, then the newly added hard sphere will be found to fit among those of the fluid that are already there. Then from Eq. (7),

$$\rho(z)/\lambda = \langle \exp(-\Psi/kT) \rangle_z = q_z \langle \exp(-\Psi_{\text{attr}}/kT) \rangle_z \tag{24}$$

where Ψ_{attr} is the potential energy of attraction between the added test molecule and the other molecules of the fluid. Equation (24) is analogous to Eq. (14) in the lattice-gas model, with what we here call q_z equal there to $1 - v\rho(z)$, and with the present $\langle \exp(-\Psi_{\text{attr}}/kT) \rangle_z$ given there by

$$\sum \sum \sum p_{lmn} \exp[(l + m + n)\epsilon/kT]$$

We again treat the attractions in mean-field approximation, and so, as before, replace[(23)] $\langle \exp(-\Psi_{\text{attr}}/kT) \rangle_z$ by $\exp(-\langle \Psi_{\text{attr}} \rangle_z/kT)$. The conditions under which this approximation is accurate are also those in which the equilibrium configuration of the fluid is identical to that of a fluid in which the molecules interact only as hard spheres, with no additional interaction;[(24)] so we also replace q_z by $\rho(z)/\lambda_{\text{hs}}[\rho(z)]$, where $\lambda_{\text{hs}}(\rho)$ is the activity of an equilibrium fluid of such nonattracting hard spheres, of density ρ. [A small-gradient approximation is also implicit here: only if $\rho(z)$ varies little over a distance equal to the sphere diameter can the arrangement of the molecules of the fluid about a test particle at z be sensibly the same as that about a test particle in a homogeneous fluid of nonattracting hard spheres of uniform density equal to $\rho(z)$.] Then Eq. (24) becomes

$$\lambda_{\text{hs}}[\rho(z)] \exp(\langle \Psi_{\text{attr}} \rangle_z/kT) = \lambda \tag{25}$$

Now let $\phi_{\text{attr}}(r)$, a function of the distance r between molecular centers, be the potential energy of attraction that is superimposed on the hard-sphere repulsions. Then

$$\langle \Psi_{\text{attr}} \rangle_z = \int \phi_{\text{attr}}(r) \rho(z + \zeta)\, d\tau \tag{26}$$

where r is here the distance between a point that is fixed in the plane at z and a variable point P with z coordinate $z + \zeta$ (so that r and ζ vary with the location of P); $d\tau$ is an element of volume centered at P; and the integration is over all points P of space. But when the model fluid is homogeneous, of density ρ, its activity $\Lambda(\rho)$ as a function of ρ at fixed temperature, in this mean-field approximation, is[(24)]

$$\Lambda(\rho) = \lambda_{\text{hs}}(\rho) e^{-2a\rho/kT} \tag{27}$$

where

$$a = -\tfrac{1}{2}\int \phi_{\mathrm{attr}}(r)\,d\tau \tag{28}$$

is van der Waals' a parameter.(25) Then from Eqs. (25)–(28) we obtain an integral equation for the density profile $\rho(z)$,

$$-\int \phi_{\mathrm{attr}}(r)[\rho(z+\zeta)-\rho(z)]\,d\tau = kT\ln\{\Lambda[\rho(z)]/\lambda\} \tag{29}$$

or, equivalently, in terms of the (configurational) chemical potential $M(\rho) = kT\ln\Lambda(\rho)$ and its uniform value $\mu = kT\ln\lambda$,

$$-\int \phi_{\mathrm{attr}}(r)[\rho(z+\zeta)-\rho(z)]\,d\tau = M[\rho(z)] - \mu \tag{30}$$

This was in essence derived by van der Waals.(11) It is the analog of Eq. (23) for the lattice gas, with the nonlocality now manifest.

When $\rho(z)$ is much more slowly varying than $\phi_{\mathrm{attr}}(r)$, Eq. (30) becomes the differential equation

$$m\,d^2\rho/dz^2 = M(\rho) - \mu \tag{31}$$

where in d dimensions

$$m = -(1/2d)\int r^2\phi_{\mathrm{attr}}(r)\,d\tau \tag{32}$$

The coefficient m in Eq. (31) is, by Eq. (32), a measure of the second moment of the attractive component of the intermolecular potential; and $m > 0$ because $\phi_{\mathrm{attr}} < 0$. Equation (31) is even more obviously analogous to Eq. (23) than is Eq. (30). Equations (31) and (32) are also due to van der Waals;(11) Eq. (31) is the basic equation of the van der Waals,(11) Cahn–Hilliard(12) theory.

If $\phi_{\mathrm{attr}}(r)$ is interpreted more generally as(26) $-kTc(r)$, with $c(r)$ the direct correlation function, then Eq. (32) for the coefficient of $d^2\rho/dz^2$ in Eq. (31) becomes

$$m = (kT/2d)\int r^2 c(r)\,d\tau \tag{33}$$

familiar in another context.(17)

There are many known generalizations of these formulas, including improved approximations,(8,27–30) and formally exact generalizations of Eq. (30) that are nonlocal in the manner of Eq. (30) and that contain direct correlation functions in place of intermolecular interaction potentials.(31–39)

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