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On the Relationship Between the Density Functional Formalism and the Potential Distribution Theory for Nonuniform Fluids

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It is shown that the variational principle for the grand potential of a nonuniform fluid as a functional of the singlet density yields the potential distribution theory for the equilibrium density. We derive the explicit form that the functional takes for a system of hard rods, and propose an approximate one for hard spheres. Attractive interactions are also considered in mean-field approximation. In all cases the pair direct correlation function of the nonuniform system is obtained and the density gradient expansion of the free energy is investigated.

KEY WORDS: Density functionals; potential distribution theory; nonuniform fluids.

1. INTRODUCTION

Many recent studies on the structure and thermodynamics of nonuniform systems, involving applications to fluid–fluid interfaces in pure(1,2) and multicomponent fluids,(3,4) fluid-to-wall density profiles,(5) solidification,(6) nucleation(7) and spinodal decomposition,(8) etc., have been developed along one of two theoretical frameworks. One of these is the density functional formalism,(9) in which a variational principle for the grand potential determines the equilibrium number density or singlet distribution function. The second approach is that of the potential distribution theory,(2) which provides an expression relating the thermodynamic activity of the system to the equilibrium density. This expression follows from the consideration of a canonical average involving the difference in configurational energy that arises when a molecule is added at $\mathbf{x}$ to a system of N other molecules.

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Although it is to be expected that the potential distribution theory expressions must follow from the variational principle for the grand potential, no explicit link between the two formalisms has been presented. An exception is the case of the well-studied van der Waals, Cahn–Hilliard approximation(1,9) for the liquid–vapor interface, where the equations that determine the density profile and the surface tension are readily obtained upon imposition of slowly varying conditions on either approach.(2,9) Here, we consider an expression for the grand potential functional $\Omega[f_N]$, where f_N is a probability density in the N-particle phase space (or equivalently, $\Omega[\rho]$, where ρ is the singlet distribution function), from which one obtains, upon variation, the potential distribution formula. Subsequently, we exploit this expression to derive the explicit form of $\Omega[\rho]$ for a system of hard rods, and propose an approximate one for the case of hard disks and spheres. We also consider attractive interactions superimposed to the infinite repulsions and treat them within the mean-field approximation. In all cases we derive the potential distribution formulas and obtain the pair direct correlation function $c(\mathbf{x}, \mathbf{y}; [\rho])$.

The most important feature in the expressions obtained for $\Omega[\rho]$, or equivalently, the Helmoltz free energy $\mathcal{F}[\rho]$, is their nonlinear and nonlocal character. Both properties, relevant when far from slowly varying conditions, are of utmost importance in the description of the nonuniformities encountered in fluid–fluid interfaces away from the critical temperature,(2,9) as well as nucleation and spinodal decomposition in its intermediate and later stages.(7) To date,(9) all treatments of these problems have employed a square-gradient van der Waals, Cahn–Hilliard expression for this functional, which is applicable only in the slowly varying regime for ρ. The nonlocality that we found suggests that the inclusion of higher terms in a gradient expansion might not be the appropriate way of improving the existing treatments. Furthermore, some nonuniform systems, as represented, for example, by a hard-sphere fluid against a hard wall, have no slowly varying density regime. We hope that the approach presented here to obtain free energy functionals opens new opportunities to further progress in some of these problems.

2. THE FREE ENERGY FUNCTIONAL FOR A NONUNIFORM FLUID

The most direct approach to the fundamental variational principle for the grand potential Ω for a nonuniform classical system is that recently adopted by Evans.(9) This approach, which is analogous to that employed by Mermin(10) and by Hohenberg and Kohn(11) for the inhomogeneous electron gas, is more naturally expressed in the grand canonical ensemble language. Here, we resume the main argument, but, because of our purposes, choose instead to work with a canonical ensemble.

Thus, we first write the Helmholtz free energy functional as the average

$$\mathcal{F}[f_N] = \mathrm{tr}\left(f_N\left[H_N + \beta^{-1}\ln f_N\right]\right) \tag{1}$$

where f_N is a probability density in the phase space for a system of N classical particles in a volume V, tr is the classical trace

$$\mathrm{tr} = \left(h^{3N}N!\right)^{-1}\int dp^N dx^N \tag{2}$$

where p^N and x^N denote momentum and position variables, respectively; $\beta = 1/k_B T$, where k_B is Boltzmann's constant and T the temperature. H_N is the Hamiltonian

$$H_N = K_N + W_N = K_N + U_N + V_N \tag{3}$$

where K_N is the kinetic energy and W_N the interaction term. W_N is in turn divided into a particle interaction term U_N and an external field term V_N. Equation (1) merely furnishes the definition of the free energy as an internal energy plus a temperature–entropy term. $\mathcal{F}[f_N]$ has the property that for the equilibrium probability density

$$f_N^{\mathrm{eq}} = Q_N^{-1}\exp(-\beta H_N) \tag{4}$$

where Q_N is the partition function

$$Q_N = \mathrm{tr}\left[\exp(-\beta H_N)\right] \tag{5}$$

we obtain the usual relation

$$\mathcal{F}[f_N^{\mathrm{eq}}] = -\beta^{-1}\ln Q_N \tag{6}$$

Also, $\mathcal{F}[f_N]$ has the minimal property

$$\mathcal{F}[f_N] > \mathcal{F}[f_N^{\mathrm{eq}}], \qquad f_N \neq f_N^{\mathrm{eq}} \tag{7}$$

It can also be proved(9) that for a Hamiltonian with given interactions

$$U_N = U_N(\mathbf{x}_1, \ldots, \mathbf{x}_N) \tag{8a}$$

and

$$V_N = \sum_{i=1}^{N} v(\mathbf{x}_i) \tag{8b}$$

the probability density f_N is a unique functional of the singlet distribution function

$$\rho(\mathbf{x}) = \mathrm{tr}\left[f_N \sum_{i=1}^{N} \delta(\mathbf{x}-\mathbf{x}_i)\right] \tag{9}$$

and therefore $\mathcal{F}[f_N]$ is also a unique functional of $\rho(\mathbf{x})$, so that we denote it also by $\mathcal{F}[\rho(\mathbf{x})]$.

In establishing these results$^{(9)}$ it is important to note that, for a fixed interaction U_N, a given probability density f_N is the equilibrium density for an external potential V'_N; i.e., there exists a V'_N such that f_N is the equilibrium distribution for that problem. Thus we write f_N as

$$f_N = (\Lambda^N Z_N)^{-1} \exp[-\beta(K_N + U_N + V'_N)] \tag{10}$$

where $\Lambda = [h/2\pi m\beta^{-1}]^{3/2}$ is the de Broglie thermal length, and Z_N is the configurational integral

$$Z_N = \int dx^N \exp[-\beta(U_N + V'_N)] \tag{11}$$

Adopting from here on the above expression for f_N,[2] the trace in Eq. (1) can be partially performed to yield

$$\mathfrak{F}[\rho] = \int d\mathbf{x}\, \rho(\mathbf{x})[v(\mathbf{x}) - v'(\mathbf{x})] - \beta^{-1} \ln\left(\frac{\Lambda^N Z_N}{N!}\right) \tag{12}$$

and, $\rho(\mathbf{x})$ can be seen to be given by

$$\rho(\mathbf{x}) = N Z_N^{-1} \int dx^{N-1} \exp[-\beta(U_N + V'_N)] \tag{13}$$

It is from Eq. (12) for $\mathfrak{F}[\rho]$ that we shall obtain the formula of the potential distribution theory. To this purpose, we consider the variation on the grand potential[3]

$$\Omega = \mathfrak{F} - \mu N \tag{14}$$

that corresponds to adding a particle to a system of other N identical particles, with the constraint that the chemical potential μ is kept constant. This variation is

$$\delta\Omega = \int d\mathbf{x}\, \delta\rho(\mathbf{x})[v(\mathbf{x}) - v'(\mathbf{x})] + \beta^{-1} \ln\left[\frac{(N+1)Z_N}{\Lambda Z_{N+1}}\right] - \mu \tag{15}$$

At equilibrium, and in the thermodynamic limit, $\delta\Omega = 0$ implies the familiar relation

$$\beta\mu_c = \ln\left[\frac{(N+1)Z_N^{\text{eq}}}{Z_{N+1}^{\text{eq}}}\right] \tag{16}$$

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[2] $\mathfrak{F}$ depends on V_N through H_N and f_N. This can be made explicit by writing $\mathfrak{F}[f_N[V_N] \mid V_N]$. The statement above Eq. (10) can be expressed therefore by writing $\mathfrak{F}[f_N[V_N] \mid V_N] = \mathfrak{F}[f_N^{\text{eq}}[V'_N] \mid V_N]$, or alternatively, $\mathfrak{F}[\rho(x) \mid V_N]$, where $\rho(x) = \operatorname{tr}\{f_N^{\text{eq}}[V'_N] \sum_{i=1}^{N} \delta(\mathbf{x} - \mathbf{x}_i)\}$.

[3] Strictly speaking, the grand potential defined by Eq. (14) is not the same as that obtained, as is more often the case, from a grand canonical ensemble approach. The two of them however, become indistinguishable in the thermodynamic limit, just as for the more familiar uniform systems.

where μ_c is the configurational chemical potential

$$\mu_c \equiv \mu - \beta^{-1} \ln \Lambda \tag{17}$$

Now, from Eq. (13) we can rewrite the definition of $\rho^{\mathrm{eq}}(\mathbf{x})$ as

$$\begin{aligned} \rho^{\mathrm{eq}}(\mathbf{x}) &= \frac{(N+1)Z_N^{\mathrm{eq}}}{Z_{N+1}^{\mathrm{eq}}} \frac{\int dx^N e^{-\beta\psi(\mathbf{x})} e^{-\beta(U_N + V_N)}}{\int dx^N e^{-\beta(U_N + V_N)}} \\ &= \frac{(N+1)Z_N^{\mathrm{eq}}}{Z_{N+1}^{\mathrm{eq}}} \left\langle e^{-\beta\psi(\mathbf{x})} \right\rangle_N \end{aligned} \tag{18}$$

where

$$\psi(\mathbf{x}) = W_{N+1}(\mathbf{x}_1, \ldots, \mathbf{x}_N, \mathbf{x}) - W_N(\mathbf{x}_1, \ldots, \mathbf{x}_N) \tag{19}$$

is the difference in potential energy that arises when the $(N+1)$th particle is added at $\mathbf{x}$. This, together with Eq. (16), yields the potential distribution formula$^{(2)}$

$$\rho^{\mathrm{eq}}(\mathbf{x}) = e^{\beta\mu_c} \left\langle e^{-\beta\psi(\mathbf{x})} \right\rangle_N \tag{20}$$

This equation relates the equilibrium singlet distribution to the activity $\lambda = \exp(\beta\mu_c)$, and constitutes a functional relation that determines $\rho^{\mathrm{eq}}(\mathbf{x})$. Furthermore, since at equilibrium one has

$$\left.\frac{\delta\Omega}{\delta\rho(\mathbf{x})}\right|_{\mathrm{eq}} = \left.\frac{\delta\mathcal{F}}{\delta\rho(\mathbf{x})}\right|_{\mathrm{eq}} - \mu = 0 \tag{21}$$

the consideration of kinetic and configurational contributions to $\mathcal{F}[\rho]$, i.e.,

$$\mathcal{F}[\rho] = \mathcal{F}_k[\rho] + \mathcal{F}_c[\rho] \tag{22}$$

with

$$\mathcal{F}_k[\rho] = -\beta^{-1} N \ln \Lambda \tag{23a}$$

and

$$\mathcal{F}_c[\rho] = \int d\mathbf{x}\, \rho(v - v') - \beta^{-1} \ln\left(\frac{Z_N}{N!}\right) \tag{23b}$$

leads to the result

$$\left.\frac{\delta\mathcal{F}_c}{\delta\rho(\mathbf{x})}\right|_{\mathrm{eq}} = \ln\left[\rho^{\mathrm{eq}}(\mathbf{x})\right] \left\langle e^{-\beta\psi(\mathbf{x})} \right\rangle_N^{-1} \tag{24}$$

Potential distribution theory and the variational principle on the grand potential functional coincide, as they should, in indicating, as seen from Eqs. (20) and (21), that the equilibrium singlet density is that which ensures the uniformity of the chemical potential in the nonuniform fluid. What must be emphasized is that in exhibiting the relationship between the two formalisms we have provided Eq. (21) with an explicit prescription for $\delta\mathcal{F}/\delta\rho(r)$ in terms of the interaction potential function. One such prescription is required if the variational Eq. (21) is to be employed, either in the evaluation of the equilibrium density or in the determination of the free energy functional itself by functional integration. This way of constructing the free energy functional would be of value in the application of some statistical mechanical theories to relaxation phenomena such as nucleation, spinodal decomposition, and kinetics of phase change.(7,8) Finally, it must be noted that the potential distribution representation for $\delta\mathcal{F}/\delta\rho(r)$ given by Eq. (24) is only valid for systems in the thermodynamic limit.

3. SOME SPECIFIC EXAMPLES

We shall now proceed to illustrate how the free energy functional can be constructed from its definition, Eq. (12), for some specific model systems. As mentioned above, one could obtain $\mathcal{F}$ by functional integration of Eq. (24) provided the exact potential distribution formula for the system under consideration is known. In case only an approximate expression for Eq. (24) is available it is possible that this is not integrable. In any case we consider it preferable to follow the inverse procedure.

3.1. One-Dimensional Hard-Core Systems

In order to evaluate the configurational integral Z_N for a system of hard rods, we look first at its discrete space analogs. Let us consider a linear lattice gas of hard core particles of "length" m, i.e., a particle excludes $2m + 1$ contiguous sites from occupation by other particles. We denote by ρ_s the occupation number or probability of finding a particle at s. For the uniform system $\rho_s = \rho = N/M$ for all s, where M is the number of sites in the lattice.

The simplest situation is that of the uniform ideal lattice gas ($m = 0$ and $v_s' = v'$), for which we can write immediately

$$Z_N^{-1} e^{-\beta N v'} = \frac{1}{N!}\rho^N (1-\rho)^{M-N} = \frac{1}{N!}\left[\rho^\rho (1-\rho)^{1-\rho}\right]^M \tag{25}$$

In the equation above $Z_N^{-1}\exp(-\beta N v)$ represents the probability for a configuration of the fluid with uniform occupation number ρ. This probability is equal, after the correction factorial term for indistinguishable particles, to the probability of having the N particles in the lattice, ρ^N, multiplied by the probability of having $M - N$ empty sites, $(1-\rho)^{M-N}$, since multiple occupation is not allowed. If we now let the system be nonuniform, due to a site dependent external field v_s', the M factors in the last equality above are no longer equal and the probability for a configuration with number density ρ_s is now given by

$$Z_N^{-1}\exp\left(-\beta\sum_s \rho_s v_s'\right) = \frac{1}{N!}\prod_{s=0}^{M-1} \rho_s^{\rho_s}(1-\rho_s)^{1-\rho_s} \tag{26}$$

When the range of the hard core is extended the occupation of each site is no longer independent from that of its neighboring sites, but we can still write the probability of an allowed configuration as a site product as in Eq. (26). This product is made by "building up" the configuration taking as a starting point one end of the lattice and placing the particles in such a way that there are no overlaps of hard cores with those previously placed. For first neighbor exclusion ($m = 1$) we obtain (proceeding from $s = M - 1$ to $s = 0$)

$$Z_N^{-1}\exp\left(-\beta\sum_s \rho_s v_s'\right) = \frac{1}{N!}\prod_{s=0}^{M-1} \frac{\rho_s^{\rho_s}}{(1-\rho_{s-1})^{1-\rho_{s-1}}}(1-\rho_{s-1}-\rho_s)^{1-\rho_{s-1}-\rho_s} \tag{27}$$

where the factor $\rho_s^{\rho_s}(1-\rho_{s-1})^{-(1-\rho_{s-1})}$ above is the probability of finding a particle at s conditioned by the site $s-1$ being empty, whereas the second factor, $(1-\rho_{s-1}-\rho_s)^{1-\rho_{s-1}-\rho_s}$ is the probability of finding both sites s and $s-1$ empty.$^{(6)}$ The other allowed possibility for a configuration, around site s, that of finding site s empty and site $s-1$ occupied by a particle, is taken into account by the next factor in Eq. (27) (that for site $s-1$). In general, the result for mth neighbor exclusion is

$$Z_N^{-1}\exp\left(-\beta\sum_s \rho_s v_s'\right) = \frac{1}{N!}\prod_{s=0}^{M-1} \frac{\rho_s^{\rho_s}}{(1-t_{m-1})^{1-t_{m-1}}}(1-t_m)^{1-t_m} \tag{28}$$

where

$$t_m(s) = \sum_{l=0}^{m} \rho_{s-l} \tag{29}$$

is the probability of finding the set of m contiguous sites $\{s, s-1, \ldots, s-m\}$ empty.$^{(6)}$ The free energy functional for this system is therefore given by

$$\beta\mathcal{F}[\rho] = \sum_s \left\{\rho_s\left[\beta v_s + \ln\Lambda^{-1}\rho_s\right] + (1-t_m)\ln(1-t_m) - (1-t_{m-1})\ln(1-t_{m-1})\right\} \tag{30}$$

whereas the equilibrium density profile is determined from

$$\beta \frac{\delta \Omega}{\delta \rho_s}\bigg|_{\text{eq}} = \ln \rho_s - \beta(\mu_c - v_s) - \ln$$

$$\times \left\{ \prod_{k=0}^{m} \left[1 - t_m(s+k)\right] \Big/ \prod_{k=0}^{m-1} \left[1 - t_{m-1}(s+k)\right] \right\} = 0 \quad (31)$$

Equation (31) coincides, as it must, with that derived for this system directly from potential distribution theory.$^{(6)}$

To obtain $\mathscr{F}[\rho]$ for a system of hard rods we consider the limiting form of Eq. (30) for large m. Since

$$\frac{1}{N!} \rightarrow \prod_s \left(\frac{e}{N}\right)^{\rho_s}, \qquad \text{large } m \quad (32a)$$

and

$$\left[1 - \frac{\rho_s}{1 - t_m}\right]^{(1-t_m)/\rho_s} \rightarrow e, \qquad \text{large } m \quad (32b)$$

we have, from Eq. (28) that

$$Z_N^{-1} \exp\left(-\beta \sum_s \rho_s v_s'\right) = \prod_{s=0}^{M-1} \left[\frac{\rho_s}{N(1 - t_m)}\right]^{\rho_s} \quad (33)$$

Therefore, for the continuum-space system of hard rods of length σ, we obtain

$$\beta \mathscr{F}[\rho] = \int dx\, \rho(x) \left\{ \ln \Lambda^{-1} \rho(x) - 1 + \beta v(x) - \ln\left[1 - t(x)\right] \right\} \quad (34)$$

where

$$t(x) = \int_{x-\sigma}^{x} dy\, \rho(y)$$

Functional differentiation of Eq. (34) yields the following relation for the equilibrium density profile:

$$\beta \frac{\delta \Omega}{\delta \rho(x)}\bigg|_{\text{eq}} = \ln \rho(x) - \beta\left[\mu_c - v(x)\right] - \ln\left[1 - t(x)\right]$$

$$+ \int_x^{x+\sigma} dy\, \frac{\rho(x)}{1 - t(y)} = 0 \quad (35)$$

Equation (35) was originally derived by Percus$^{(12)}$ from the grand partition function for this system, and was later obtained$^{(6)}$ from potential distribution theory.

As can be observed, the most relevant properties of the exact free energy functionals derived above are their nonlinear and nonlocal dependence on the singlet density. In contrast with this situation, a truncated gradient expansion, such as that of Cahn and Hilliard and van der Waals, yields a functional that, although possibly nonlinear, is local in character. For illustrative purposes we show the gradient expansion of Eq. (34). The term $\ln(1 - t)$ in Eq. (34) can be expanded and integrated to yield

$$\beta\mathcal{F}[\rho] = \int dx\, \rho(x)\left\{\ln \frac{\Lambda^{-1}\rho(x)}{1 - \sigma\rho(x)} - 1 + \beta v(x) + \sum_{p=1}^{\infty} p^{-1}\left[\sum_{q=1}^{\infty} \frac{\sigma^q \rho^{(q)}(x)}{(q-1)!\left[1 - \sigma\rho(x)\right]}\right]^p\right\} \tag{36}$$

where $\rho^{(q)}$ denotes the qth derivative of ρ. From the first terms of Eq. (36) we have

$$\beta\mathcal{F}[\rho] = \int dx\, \rho(x)\left[\ln \frac{\Lambda^{-1}\rho(x)}{1 - \sigma\rho(x)} - 1 + \beta v(x)\right] + \frac{1}{24}\int dx\, \frac{4 - 3\sigma\rho(x)}{\left[1 - \sigma\rho(x)\right]^2}\left[\rho^{(1)}(x)\right]^2 + \cdots \tag{37}$$

where the terms $O(\rho^{(1)})$ and $O(\rho^{(3)})$ do not appear since they are exact differentials of ρ and hence only contribute by a constant to $\mathcal{F}$. The factor to the square gradient can be easily seen to be the second moment of the direct correlation function of the uniform system with the uniform ρ_u replaced by $\rho(x)$. The series in Eq. (36) converges uniformly for $0 \leqslant \sigma\rho(x) < 1$.

3.2. Hard-Disk and Hard-Sphere Systems

When considering higher-dimensional hard-core lattice gases we notice that it is no longer possible, unless one introduces an approximation, to express the configurational integral as a site product where each factor only involves a number of neighboring sites given by the range of the interactions. This is because in dimensions higher than 1 a hard-core particle, or an empty volume of equal extent, does not uncouple the space into separate regions as it does in one dimension.

Here we propose an approximate form for Z_N for a dimension d larger than 1. This is obtained by first writing Eq. (33) in a symmetrical form. We recall that the allowed configurations leading to Eq. (33) were "built" by performing the site product from large to small values of s. An alternative expression for Z_N is obtained by proceeding from small to large values of s.

Combining these two expressions one has, for $2n$th neighbor exclusion, n being a large number, the symmetrical form

$$Z_N^{-1}\exp\left(-\beta\sum_s \rho_s v_s'\right) = \prod_{s=0}^{M-1}\left(\frac{\rho_s}{N}\right)^{\rho_s}(1-\tau_n)^{-(\rho_{s-n}+\rho_{s+n})/2}, \qquad n \text{ large} \tag{38}$$

where

$$\tau_n(s) = \sum_{l=-n}^{n} \rho_{s+l} \tag{39}$$

Equation (38) suggests, for a $2n$th neighbor exclusion lattice gas with $d > 1$, the expression

$$Z_N^{-1}\exp\left(-\beta\sum_{\mathbf{s}} \rho_{\mathbf{s}} v_{\mathbf{s}}'\right) = \prod_{\mathbf{s}}\left(\frac{\rho_{\mathbf{s}}}{N}\right)^{\rho_{\mathbf{s}}}(1-\tau_n)^{-k^{-1}\sum_{\hat{s}}\rho_{\mathbf{s}+n\hat{s}}}, \qquad n \text{ large} \tag{40}$$

where

$$\tau_n(\mathbf{s}) = \sum_{\mathbf{l}=0} \rho_{\mathbf{s}+\mathbf{l}} \tag{41}$$

where **s** is the position vector for a site in the lattice, $\hat{s}$ is a unit vector in the direction of an nth neighbor of site **s**, k is the number of such neighbors, and the sum in Eq. (41) is over all sites around s up to its nth neighbors. Proceeding as before, we find that in the continuum-space limit the free energy functional is given by

$$\beta\mathcal{F}[\rho] = \int d\mathbf{x}\,\rho(\mathbf{x})\Big\{\ln\Lambda^{-1}\rho(\mathbf{x}) - 1 + \beta v(\mathbf{x}) - V^{-1}\int d\mathbf{x}'\,\delta$$
$$\times\left(|\mathbf{x}-\mathbf{x}'| - \frac{\sigma}{2}\right)\rho(\mathbf{x}')\ln\left[1-\tau(\mathbf{x})\right]\Big\} \tag{42}$$

where

$$\tau(\mathbf{x}) = \int d\mathbf{x}'\,\Delta(\mathbf{x}')\rho(\mathbf{x}+\mathbf{x}') \tag{43}$$

$$\Delta(\mathbf{x}) = \begin{cases} 1, & |\mathbf{x}| < \sigma/2 \\ 0, & |\mathbf{x}| > \sigma/2 \end{cases} \tag{44}$$

σ is the diameter of a hard sphere or disk and V is their volume or area. Equation (42) reduces to the exact result, Eq. (34) in one dimension. Functional differentiation of Eq. (42) leads to

$$\beta\frac{\delta\Omega}{\delta\rho(\mathbf{x})}\bigg|_{\mathrm{eq}} = \ln\rho(\mathbf{x}) - \beta[\mu_c - v(\mathbf{x})]$$
$$- V^{-1}\int d\mathbf{x}'\,\delta(|\mathbf{x}-\mathbf{x}'| - \sigma/2)\ln\left[1-\tau(\mathbf{x})\right]$$
$$+ V^{-1}\int d\mathbf{x}'\int d\mathbf{x}''\,\delta(|\mathbf{x}''| - \sigma/2)\Delta(\mathbf{x}-\mathbf{x}')\rho(\mathbf{x}''+\mathbf{x})$$
$$\times\left[1-\tau(\mathbf{x})\right]^{-1} = 0 \tag{45}$$

and

$$\begin{aligned} c(\mathbf{x},\mathbf{y}) &\equiv \frac{\delta}{\delta\rho(\mathbf{y})}\{\ln\rho(\mathbf{x}) - \beta[\mu_c - v(\mathbf{x})]\} \\ &= V^{-1}\int d\mathbf{x}'\,\delta(|\mathbf{x}-\mathbf{x}'| - \sigma/2)\Delta(\mathbf{y}-\mathbf{x}')[1-\tau(\mathbf{x}')]^{-1} \\ &\quad \times V^{-1}\int d\mathbf{x}'\,\delta(|\mathbf{y}-\mathbf{x}'| - \sigma/2)\Delta(\mathbf{x}-\mathbf{x}')[1-\tau(\mathbf{x}')]^{-1} \\ &\quad - V^{-1}\int d\mathbf{x}'\int d\mathbf{x}''\,\delta(|\mathbf{x}''| - \sigma/2)\Delta(\mathbf{x}-\mathbf{x}') \\ &\quad \times \Delta(\mathbf{y}-\mathbf{x}')\rho(\mathbf{x}'+\mathbf{x}'')[1+\tau(\mathbf{x}')]^{-2} \end{aligned} \tag{46}$$

Equation (45) determines the equilibrium singlet density for a given external potential $v(\mathbf{x})$, whereas Eq. (46) yields the pair direct correlation function $c(\mathbf{x},\mathbf{y})$ for the nonuniform fluid in terms of $\rho(\mathbf{x})$. We observe that $c(\mathbf{x},\mathbf{y})$, as given by the above expression, vanishes whenever $|\mathbf{x}-\mathbf{y}| > \sigma$, and thus it has the range of the hard-core interaction. Both Eqs. (45) and (46) reduce, of course, to the exact results$^{(6,12)}$ for the hard-rod system.

To gauge the approximation involved in our proposed expressions for $d > 1$, it is of interest to reduce Eq. (46) to the uniform fluid situation. In this case we obtain for $d = 2$

$$\begin{aligned} c(s) = &-(1-A\rho)^{-1}2\pi^{-1}\cos^{-1}\sigma^{-1}s \\ &- A\rho(1-A\rho)^{-2}2\pi^{-1}\left[\cos^{-1}\sigma^{-1}s - \sigma^{-2}s(\sigma^2 - s^2)^{1/2}\right], \quad s \leqslant \sigma \end{aligned} \tag{47a}$$

and for $d = 3$

$$\begin{aligned} c(s) = &-(1-V\rho)^{-1}(1-\sigma^{-1}s) \\ &- V\rho(1-V\rho)^{-2}(1 - 6\sigma^{-1}s + 32\sigma^{-3}s^3), \qquad s \leqslant \sigma \end{aligned} \tag{47b}$$

where $s = |\mathbf{x}-\mathbf{y}|$ and A and V are, respectively, the area and volume of a disk and a sphere. The s-dependent terms in brackets in Eq. (47a) constitute the arc and the area of intersection of two disks whose centers are separated by the distance s. Those in Eq. (47b) are the corresponding area and volume of intersection of two spheres. The cubic in s in this equation (with no quadratic term) has the same form as that obtained from the scaled-particle and the Percus–Yevick theories. This is because the volume of intersection of two spheres is a relevant quantity in all three approximations. We note that the density dependence in Eqs. (47) is like that of the one-dimensional system, and reflects the one-dimensional nature of our approximation. A better theory should yield higher inverse powers of $(1 - V\rho)$.$^{(13)}$

3.3. Attractive Interactions

We consider now attractive pair interactions superimposed to the hard-core repulsions, i.e., interactions of the form

$$\psi(|\mathbf{x}-\mathbf{y}|)=\begin{cases}\infty, & |\mathbf{x}-\mathbf{y}|<\sigma\\ \psi_{\text{attr}}(|x-y|), & |x-y|>\sigma\end{cases}\tag{48}$$

The additional term to the grand potential, Ω_{attr}, and its contributions to the potential distribution formula and to the direct correlation function, that are due to the attractive tail ψ_{attr}, are easily obtained in mean-field approximation. These are

$$\begin{aligned}\Omega_{\text{attr}}&=\int d\mathbf{x}\,\rho(\mathbf{x})v_{\text{eff}}(\mathbf{x})\\&=\frac{1}{2}\int d\mathbf{x}\int d\mathbf{x}'\,\rho(\mathbf{x})\psi_{\text{attr}}(|\mathbf{x}-\mathbf{x}'|)\rho(\mathbf{x}')\end{aligned}\tag{49a}$$

$$\frac{\delta\Omega_{\text{attr}}}{\delta\rho(\mathbf{y})}=\int d\mathbf{x}\,\rho(\mathbf{x})\psi_{\text{attr}}(|\mathbf{x}-\mathbf{y}|)\tag{49b}$$

and

$$\frac{\delta^2\Omega_{\text{attr}}}{\delta\rho(\mathbf{y})\delta\rho(\mathbf{z})}=\psi_{\text{attr}}(|\mathbf{z}-\mathbf{y}|)\tag{49c}$$

Thus, for the direct correlation function we have the usual mean-field result

$$c_{\text{attr}}(|\mathbf{z}-\mathbf{y}|)=-\beta\psi_{\text{attr}}(|\mathbf{z}-\mathbf{y}|)\tag{50}$$

The nonlocality of Ω_{attr} is responsible for the fact that its contribution to $c(\mathbf{z},\mathbf{y})$ is not a deltalike term like in the square-gradient approximation.(9) This is an important difference between the exact (mean-field, in this case) and the approximate van der Waals, Cahn–Hilliard, and related theories. Since stability criteria are often based on the behavior of $\delta^2\Omega/\delta\rho\delta\rho$ one may obtain qualitatively different predictions from both expressions. This may happen, for example, in the study of the response of the liquid–vapor interface to capillary wave fluctuations.(9,14) It is interesting to note, as shown in Ref. 4, that the equations for the density profiles that correspond to these two approaches are essentially the same near the critical point.

It is instructive to obtain the gradient expansion of Ω_{attr}. For slowly varying conditions, when $\rho(\mathbf{x})\simeq\rho_u+\delta\rho(\mathbf{x})$, $\delta\rho(x)$ small, we have

$$\begin{aligned}\Omega_{\text{attr}}\simeq&-\alpha\rho_u^2+\rho_u\int d\mathbf{x}\int d\mathbf{x}'\,\psi_{\text{attr}}(|\mathbf{x}-\mathbf{x}'|)\delta\rho(\mathbf{x}')\\&+\frac{1}{2}\int d\mathbf{x}\int d\mathbf{x}'\,\delta\rho(\mathbf{x})\psi_{\text{attr}}(|\mathbf{x}-\mathbf{x}'|)\delta\rho(\mathbf{x}')\end{aligned}\tag{51}$$

where

$$\alpha=-\frac{1}{2}\int d\mathbf{x}\,\psi_{\text{attr}}(|\mathbf{x}|)\tag{52}$$

The reference uniform density ρ_u can be chosen to make the term linear in $\delta\rho$ vanish, and by introducing the Fourier components

$$\psi_{\mathbf{q}} = \int d\mathbf{x}\, \psi_{\mathrm{attr}}(|\mathbf{x}|)\exp(i\mathbf{q}\cdot\mathbf{x}) \tag{53}$$

and

$$\rho_{\mathbf{q}} = \int d\mathbf{x}\, \delta\rho(\mathbf{x})\exp(i\mathbf{q}\cdot\mathbf{x}) \tag{54}$$

we have

$$\Omega_{\mathrm{attr}} \simeq -\alpha\rho_u^2 + (2V)^{-1}\sum_{\mathbf{q}} \psi_{\mathbf{q}}\rho_{\mathbf{q}}\rho_{-\mathbf{q}} \tag{55}$$

Considering the moment expansion of ψ_q,

$$\psi_q = a_0 + a_2 q^2 + a_4 q^4 + \cdots \tag{56}$$

where

$$a_{2n} = \frac{1}{2n!}\int d\mathbf{x}\, |\mathbf{x}|^{2n}\psi_{\mathrm{attr}}(|\mathbf{x}|) \tag{57}$$

we finally obtain

$$\begin{aligned}\Omega_{\mathrm{attr}} \simeq & -\alpha\rho_u^2 + a_0\int d\mathbf{x}\left[\delta\rho(\mathbf{x})\right]^2 \\ & + a_2\int d\mathbf{x}\, |\nabla\rho(\mathbf{x})|^2 + a_4\int d\mathbf{x}\, |\nabla\rho(\mathbf{x})|^4 + \cdots \end{aligned} \tag{58}$$

We note that the series above diverges if the interaction ψ_{attr} decays like a power law. This is the case, for example, of the Lennard–Jones potential. Thus, to have a meaningful density gradient expansion the interaction must decay at least as rapidly as an exponential.

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