High-order direct correlation functions of uniform classical liquids

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Analytic approximations for the third- and higher-order direct correlation functions of uniform classical liquids are presented. These are derived from a weighted-density approximation for the one-particle direct correlation function of a *nonuniform* liquid which requires as input only the two-particle function of the corresponding *uniform* liquid. The three-particle result is shown to have the same accuracy as two recently proposed approximations, but has a much simpler form. The four- and five-particle results are new, and in principle can be tested by simulation methods.

INTRODUCTION

In the density-functional formalism of nonuniform classical liquids[1] the n-particle direct correlation functions (DCF's) $c^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n; [\rho])$ are defined as functional derivatives of the excess Helmholtz free energy $F_{\text{ex}}[\rho]$ with respect to the one-particle density $\rho(\mathbf{r})$:

$$c^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n; [\rho]) = -\beta \frac{\delta^n F_{\text{ex}}[\rho]}{\delta\rho(\mathbf{r}_1) \cdots \delta\rho(\mathbf{r}_n)}, \qquad (1)$$

where $\beta \equiv 1/k_B T$. These quantities are of direct relevance to those theories of nonuniform liquids that are based on expansions of thermodynamic potentials in $\Delta\rho(\mathbf{r}) \equiv \rho(\mathbf{r}) - \rho_l$, the departure of the density from the density ρ_l of a uniform reference liquid. Thus, in the density-functional theory of freezing due to Ramakrishnan and Yussouff[2]—and its later reformulation by Haymet and Oxtoby[3]—the reference liquid DCF's $c_0^{(n)}$ appear as coefficients in a functional Taylor-series expansion of the crystalline F_{ex} of the form

$$\beta F_{\text{ex}}[\rho] = \beta F_{\text{ex}}(\rho_l) - \sum_{n=1}^{\infty} \frac{1}{n!} \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_n c_0^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n; \rho_l) \Delta\rho(\mathbf{r}_1) \cdots \Delta\rho(\mathbf{r}_n) . \qquad (2)$$

In most applications of the theory to date the expansion has been truncated at second order, succeeding terms involving $c_0^{(3)}, c_0^{(4)}$, etc. being ignored entirely. For highly nonuniform systems—the crystalline phase in studies of the freezing transition being a prime example—there is no apparent *a priori* justification for such a severe truncation,[4] which is usually made because of a lack of reliable approximations for the higher-order DCF's. Nevertheless, for the hard-sphere liquid the second-order theory predicts freezing parameters which are generally in reasonable agreement with computer simulation (the Lindemann parameter and the latent heat being, however, notable exceptions). In applications to systems characterized by other pair potentials the second-order theory has proven less adequate. In fact, a recent study[5] of the freezing of "soft-sphere" liquids, characterized by pair potentials $v(r) \sim r^{-n}$, has concluded that the theory consistently overestimates the stability of the liquid phase, the disagreement with simulation worsening as the steepness of the potential n decreases. In applications to the one-component plasma[6,7] (an assembly of identical point charges in a neutralizing background) the second-order theory actually fails to predict a freezing transition at all. This record of mixed success points to the need for a careful examination of the truncation approximation on which the second-order density-functional theory is founded, and raises the issue of the form and behavior of the higher-order DCF that reside in the omitted terms.

The purpose of this work, therefore, is to describe a simple scheme for approximating the $c_0^{(n)}$ of uniform classical liquids which yields *analytic* approximations for the three-, four-, and five-particle DCF's (and, in principle, all higher-order functions). These approximations may then prove useful in future assessments of the relative importance of the higher-order contributions to the free energy expansion of Eq. (2) which are ignored in the second-order theory. Our scheme may be compared with two recently proposed approximations[8,9] for the three-particle DCF that have been used to study the effects of the neglected third-order terms on the predicted freezing parameters of hard-sphere[10] and soft-sphere[11] liquids. In the first, Barrat, Hansen, and Pastore[8] (BHP) have suggested an approximation for $c_0^{(3)}$ based on a factorization *ansatz*

$$c_0^{(3)}(\mathbf{r}, \mathbf{r}') = t(r)t(r')t(|\mathbf{r}-\mathbf{r}'|) , \qquad (3)$$

with the function $t(r)$ determined by requiring that in Fourier space $c_0^{(3)}$ satisfy the exact relation (for $n=3$)

$$c_0^{(n)}(\mathbf{k}_1, \ldots, \mathbf{k}_{n-1}, 0; \rho_0) = \frac{\partial}{\partial\rho_0} c_0^{(n-1)}(\mathbf{k}_1, \ldots, \mathbf{k}_{n-1}; \rho_0) . \qquad (4)$$

They have also determined $c_0^{(3)}$ directly from a molecular dynamics (MD) simulation of a soft-sphere $[v(r) \sim r^{-12}]$

liquid near freezing and have found good agreement with their approximation. In the second, Curtin and Ashcroft[9] (CA) have pointed out that an approximation for $c_0^{(3)}$ (and, in principle, all higher-order DCF's), also satisfying Eq. (4), is implicit in their weighted-density-functional theory of nonuniform liquids.[12] They showed, furthermore, that their approximation is in close agreement with both the BHP approximation and the MD data.

APPROXIMATION SCHEME

Our approximation scheme is close in spirit[13] to that of Ref. 9. In essence, we make a weighted-density approximation (WDA) for the one-particle DCF $c^{(1)}(\mathbf{r};[\rho])$ of a *nonuniform* liquid and then, as prescribed by Eq. (1), take functional derivatives with respect to the density to generate approximations for the higher-order DCF's in the limit of a *uniform* liquid. Explicitly, we approximate $c^{(1)}(\mathbf{r};[\rho])$ by

$$c_{\text{WDA}}^{(1)}(\mathbf{r};[\rho]) = c_0^{(1)}(\bar{\rho}(\mathbf{r})) , \qquad (5)$$

where $c_0^{(1)}(\bar{\rho}(\mathbf{r}))$ is the one-particle DCF of an *effective uniform liquid* of density $\bar{\rho}(\mathbf{r})$, with $\bar{\rho}(\mathbf{r})$ defined as a *weighted average* of the physical density $\rho(\mathbf{r})$ according to

$$\bar{\rho}(\mathbf{r}) = \int d\mathbf{r}'\rho(\mathbf{r}')w(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}(\mathbf{r})) . \qquad (6)$$

The self-consistency with respect to $\bar{\rho}(\mathbf{r})$ in this definition is a crucial feature of the WDA, a point emphasized in Refs. 9 and 12. For completeness, we note that, from Eq. (1), the quantity $c_0^{(1)}(\rho_0)$ is related to the excess chemical potential μ_{ex} of a uniform liquid by

$$c_0^{(1)}(\rho_0) = -\beta\mu_{\text{ex}} \equiv -\beta(\mu-\mu_{\text{id}}) = -\beta\mu + \ln(\rho_0\lambda^3) , \qquad (7)$$

where μ is the total chemical potential, μ_{id} is the chemical potential of an ideal gas, and λ is the thermal de Broglie wavelength.

To ensure that Eq. (5) is exact in the uniform liquid limit $[\rho(\mathbf{r}) \to \rho_0]$, the "weight function" w is required to satisfy the normalization condition

$$\int d\mathbf{r}'w(|\mathbf{r}-\mathbf{r}'|;\rho_0) = 1 . \qquad (8)$$

A *unique* specification of w now follows by imposing the requirement that the relationship between $c^{(1)}$ and $c^{(2)}$, which is implicit in Eq. (1), is satisfied *exactly* in the uniform liquid limit; that is,

$$\lim_{\rho(\mathbf{r}) \to \rho_0} \left[\frac{\delta}{\delta\rho(\mathbf{r}')} c_{\text{WDA}}^{(1)}(\mathbf{r};[\rho]) \right] = c_0^{(2)}(|\mathbf{r}-\mathbf{r}'|;\rho_0) . \qquad (9)$$

Equation (9), together with Eqs. (5), (6), and (8), now implies the following simple form for the weight function:[14]

$$w(r;\rho_0) = \frac{c_0^{(2)}(r;\rho_0)}{c_0^{(1)\prime}(\rho_0)} , \qquad (10)$$

where the prime denotes a derivative with respect to density. Equations (5)–(10) constitute our approximation for $c^{(1)}(\mathbf{r};[\rho])$. In passing, we note that this approximation can serve as the basis of an alternative weighted-density-functional theory of nonuniform liquids.

THREE-PARTICLE DIRECT CORRELATION FUNCTION

We can now proceed to generate approximations for the higher-order DCF's $c_0^{(n)}$ by taking the required successive functional derivatives of Eq. (5) and then proceeding to the uniform liquid limit. Thus, by taking two functional derivatives, we obtain for the three-particle DCF the approximation[15] (in Fourier space)

$$c_0^{(3)}(k,k') = \frac{1}{c_0^{(1)\prime}}[c_0^{(2)}(k)c_0^{(2)\prime}(k') + c_0^{(2)}(k')c_0^{(2)\prime}(k)]$$

$$- \frac{c_0^{(1)\prime\prime}}{[c_0^{(1)\prime}]^2}c_0^{(2)}(k)c_0^{(2)}(k') . \qquad (11)$$

Compared with the previous approximations (Refs. 8 and 9), the approximation in Eq. (11) is similar in two important respects. First, it requires as input only the two-particle function $c_0^{(2)}$ [since $c_0^{(1)\prime} = c_0^{(2)}(k=0)$]. Second, it satisfies Eq. (4) exactly for $k=0$ or $k'=0$ (though, in contrast to the previous approaches, only approximately for $\mathbf{k}' = -\mathbf{k}$). This second feature is a direct and crucial consequence of the self-consistency built into the definition of the weighted density $\bar{\rho}(\mathbf{r})$ [Eq. (6)]. A significant *practical* difference is that, whereas the previous approaches involve demanding numerical procedures, the approach presented here leads to an *analytic* expression for $c_0^{(3)}$ (and, as shown below, also for higher-order DCF's) which is trivially evaluated.

We have computed the approximation $c_0^{(3)}$ of Eq. (11) for the hard-sphere liquid, using the Percus-Yevick approximation for $c_0^{(2)}$ as input. It is plotted in Fig. 1 versus ka, where $a = (3/4\pi\rho_0)^{1/3}$, for the special case of wave vectors of equal magnitude. Also shown for com-
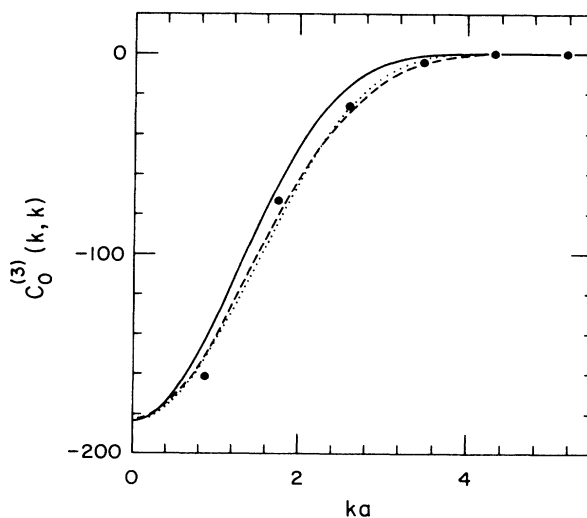

FIG. 1. Three-particle DCF $c_0^{(3)}$ vs ka for wave vectors all of equal magnitude. The solid curve is our approximation for hard spheres; the dashed curve is the CA approximation for hard spheres; the dotted curve is the BHP approximation for soft spheres; and the dots are the MD data of BHP for soft spheres.

parison are (i) the CA approximation[9] for hard spheres, (ii) the BHP approximation[8] for soft spheres, and (iii) the MD data,[8] also for soft spheres. The density $\rho_0\sigma^3 = 0.871$, at which our hard-sphere $c_0^{(3)}$ was computed, was chosen to enforce agreement with the BHP soft-sphere approximation at $k=0$. Using the same criterion, the CA approximation requires the same density. The dependence on wave-vector magnitude of our approximate $c_0^{(3)}$ is clearly in close quantitative agreement with the BHP and CA approximations, and all three approximations are together in close agreement with the MD data, to within statistical uncertainty in the data.

An obvious *deficiency* of our approximation is the lack of any dependence of $c_0^{(3)}$ on the angle between the wave vectors $\mathbf{k}$ and $\mathbf{k}'$, an absence which can be traced to the fact that we began with an approximation for $c^{(1)}(\mathbf{r};[\rho])$ rather than for $F_{ex}[\rho]$. The expected angular dependence can easily be introduced by imposing a simple symmetry requirement on Eq. (11) of the form

$$c_0^{(3)}(\mathbf{k},\mathbf{k}') = \tfrac{1}{3}[c_0^{(3)}(k,k') + c_0^{(3)}(k,|\mathbf{k}+\mathbf{k}'|)$$

$$+ c_0^{(3)}(k',|\mathbf{k}+\mathbf{k}'|)] , \qquad (12)$$

but this symmetry is obtained at a cost, for the symmetric $c_0^{(3)}(\mathbf{k},\mathbf{k}')$ now satisfies Eq. (4) exactly *only* for $k=k'=0$. It should be noted that the BHP and CA approximations naturally contain angular dependence and satisfy Eq. (4) for $k=0$, $k'=0$, or $\mathbf{k}'=-\mathbf{k}$, and not only for $k=k'=0$. We have compared the angular dependence of the *ad hoc* symmetrized form in Eq. (12) with that reported in Ref. 8 and, though it is not in quantitative agreement, the scale of variation is identical. Since our results pertain to hard spheres, whereas those of Ref. 8 pertain to soft spheres, the significance of this discrepancy, and the utility of the symmetrization approach, is difficult to interpret at this time. With this proviso, it should be noted that compared with the CA approximation, the angular variation of our symmetrized approximation is qualitatively the same, though somewhat smaller in magnitude.[16]

HIGHER-ORDER DIRECT CORRELATION FUNCTIONS

By taking additional functional derivatives of Eq. (5), we have also obtained approximations for the four- and five-particle DCF's. The four-particle result is

$$c_0^{(4)}(k,k',k'') = c_0^{(1)\prime\prime\prime\prime}w(k)w(k')w(k'') + 2c_0^{(1)\prime\prime\prime}[w'(k)w(k')w(k'') + \mathcal{P}w'(k)w(k')w(k'')]$$

$$+ c_0^{(1)\prime\prime}\{2[w'(k)w'(k')w(k'') + \mathcal{P}w'(k)w'(k')w(k'')] + [w''(k)w(k')w(k'') + \mathcal{P}w''(k)w(k')w(k'')]\} ,$$

$$(13)$$

where, from Eq. (10), $w(k) = c_0^{(2)}(k)/c_0^{(1)\prime\prime}$, and $\mathcal{P}$ denotes permutations of k, k', and k''. It is straightforward to show that this approximation for $c_0^{(4)}$ satisfies Eq. (4) exactly when at least one of k,k',k'' is zero. Furthermore, although it cannot be shown yet that Eq. (4) holds for all orders in our approximation scheme, it is easily verified that it also holds for $n=5$, and there is no reason to suppose that it should fail at higher orders. The evident lack of angular dependence in Eq. (13) can be remedied, as in the case of $c_0^{(3)}$, by imposing a symmetry requirement analogous to Eq. (12). For the special case of wave vectors all of equal magnitude, Eq. (13) reduces to

$$c_0^{(4)}(k,k,k) = c_0^{(1)\prime\prime\prime\prime}w(k)^3 + 6c_0^{(1)\prime\prime\prime}w(k)^2w'(k) + 3c_0^{(1)\prime\prime}w(k)[2w'(k)^2 + w''(k)w(k)] . \qquad (14)$$

The *five*-particle result, also for the case of wave vectors all of equal magnitude, is

$$c_0^{(5)}(k,k,k,k) = c_0^{(1)\prime\prime\prime\prime\prime}w(k)^4 + 12c_0^{(1)\prime\prime\prime\prime}w(k)^3w'(k) + 12c_0^{(1)\prime\prime\prime}w(k)^2[2w'(k)^2 + w''(k)w(k)]$$

$$+ 4c_0^{(1)\prime\prime}w(k)[w'''(k)w(k)^2 + 9w''(k)\omega'(k)w(k) + 6w'(k)^3] . \qquad (15)$$

The four- and five-particle results of Eqs. (14) and (15) are plotted in Fig. 2 versus ka for the hard-sphere liquid (at the density $\rho_0\sigma^3 = 0.871$). Also shown for comparison is the three-particle result of Eq. (11). The inset shows the behavior at large k (i.e., $ka>4$). There are two observations worth noting concerning these results. First, with each increment in the order of the function n, the magnitude at $k=0$ increases markedly—by roughly a factor of 5. With the Percus-Yevick form for $c_0^{(2)}$ that we have used, this is an exact result that follows directly from Eq. (4). Second, the higher the order of the function, the more rapid is the decrease in the magnitude of $c_0^{(n)}(k)$ with increasing k. This is illustrated more clearly in Fig.

3 where the normalized functions, from $c_0^{(2)}$ up to $c_0^{(5)}$, are compared.

As noted previously, the approximations presented here for the $c_0^{(n)}$ can, in principle, be used to study the rate of convergence of the crystalline free-energy expansion in Eq. (2) for various pair potentials. In practice, however, the issue can be decided only by explicitly evaluating higher-order terms in the expansion, taking into account the effects of the symmetry of the lattice, the form of $\rho(\mathbf{r})$ and the combinatorial factor.[4] Of course, the $c_0^{(n)}$ are also of interest in their own right.

In summary, we have presented here a simple approximation scheme which generates *analytic* expressions for
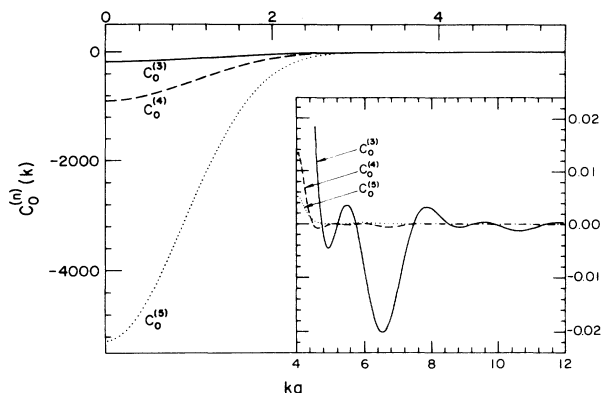
FIG. 2. Approximate four- and five-particle DCF's vs ka for wave vectors all of equal magnitude. The three-particle function is also shown for comparison. Note the difference in scale compared with Fig. 1. The inset displays the large-k behavior.

FIG. 3. Normalized approximate DCF's for wave vectors all of equal magnitude, illustrating the increasingly rapid decrease with increasing k of the higher-order functions.

the many-particle DCF's of uniform classical liquids, and which requires as input only the two-particle function. We have given explicit expressions for the three-, four-, and five-particle functions and shown that the three-particle approximation is in good agreement with two recent approximations and MD data. It is hoped that the simplicity of this scheme will make it of practical value in future applications of density-functional theory to nonuniform systems, and will stimulate further simulation work, directed especially towards the DCF's of uniform liquids.
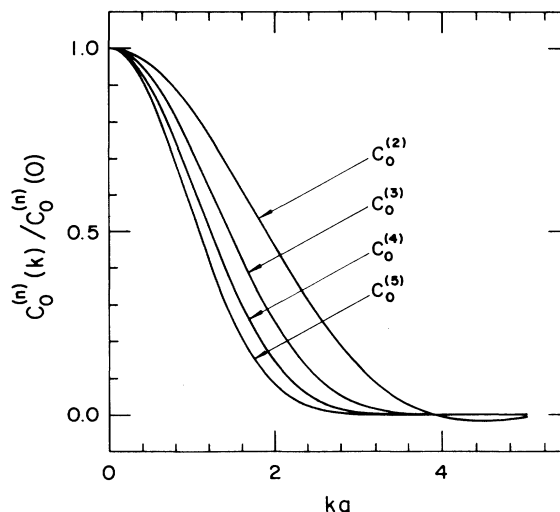
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[4] Note that for highly nonuniform systems, such as solids, $\Delta\rho(\mathbf{r})/p_l \gg 1$ for some values of $\mathbf{r}$. By itself, this observation does not rule out convergence of the expansion in Eq. (2) since it is the integrated effect of $\rho(\mathbf{r})$ which must be considered. The $c_0^{(n)}$ appear as weights in the integrals, however, and their form then becomes of crucial importance in determining whether rapid convergence is possible *a priori*. This issue can be decided, in principle, by using the approximate forms for $c_0^{(n)}$ derived in this paper. A recent calculation of the third-order contribution to the expansion for the hard-sphere liquid, based on the approximation for $c_0^{(3)}$ of Ref. 9, indicates questionable convergence (see Ref. 10).

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[13] This approach differs slightly from that of Refs. 9, 10, and 12, where a weighted-density approximation is made, not on $c^{(1)}$, but on f, the excess Helmholtz free energy per particle. The relationship between f and $c^{(1)}$ is

$$f(\mathbf{r};[\rho]) = -\beta^{-1} \int_0^1 d\alpha\, c^{(1)}(\mathbf{r};[\alpha\rho]) \ .$$

[14] The simple analytic form of the weight function in Eq. (10) may be compared with the weight function of Refs. 9, 10, and 12, which is obtained only by numerical solution of the nonlinear differential equation

$$-\beta^{-1} c_0^{(2)}(k) = 2f_0' w(k) + \rho_0 f_0'' w(k)^2 + 2\rho_0 f_0' w(k) w'(k) \ ,$$

where f_0 is the uniform liquid limit of the excess Helmholtz free energy per particle.

[15] In deriving Eq. (11), we have made use of the fact that, from Eq. (8), $w'(k=0) = 0$.

[16] W. A. Curtin (private communication).