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Symmetry based approach to triplet correlation functions

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Two related approaches to the theory of inhomogeneous classical systems are introduced, both yielding analytic forms for triplet and higher-order direct correlation functions in the homogeneous limit. The present theories lead to results that exactly obey the known sum rule relating the triplet direct correlation function to the derivative of the Ornstein-Zernike function. The resulting triplet direct correlation functions are then found to be simple products in both reciprocal and real space. Agreement with simulation results for the triplet direct correlation function in the hard sphere fluid is generally found to be very good; even the simpler version of the theory agrees well with the results of the more computationally intensive weighted density approximation. [S1063-651X(99)10402-1]

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I. INTRODUCTION

A primary aim of the density-functional theory of classical inhomogeneous fluids [1] is to accurately model the generally unknown excess Helmholtz free energy $F_{\mathrm{ex}}[\rho(\mathbf{r})]$ of a system of interacting particles. The latter may be expressed as a functional Taylor series expansion about the homogeneous state, namely,

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

where $\Delta\rho(\mathbf{r})=\rho(\mathbf{r})-\rho$ and $f(\rho)$ is the excess free energy per particle of a homogeneous system. Here $\rho(\mathbf{r})=\langle\Sigma_i\delta(\mathbf{r}-\mathbf{r}_i)\rangle$ is the one-particle density of the inhomogeneous system, with $\rho=N/V$, the average density of the uniform counterpart. The functions forming the coefficients of the expansion are the hierarchy of direct correlation functions (DCFs) for which the excess free energy is the generating functional; they are defined by

$$c_0^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n;\rho)=-\beta\frac{\delta^n F_{\mathrm{ex}}[\rho]}{\delta\rho(\mathbf{r}_1)\cdots\delta\rho(\mathbf{r}_n)}, \qquad (2)$$

and they obey the real space sum rule,

$$\int d\mathbf{r}_n c_0^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n;\rho)=\frac{\partial}{\partial\rho}c_0^{(n-1)}(\mathbf{r}_1,\ldots,\mathbf{r}_{n-1};\rho), \qquad (3)$$

which can be written in Fourier space as the algebraic relation,

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

It has been shown for hard-sphere systems that when approximate functionals are constructed to reproduce the functional expansion to *third order* in the homogeneous limit [2,3], there is a tendency for improvement in results for melting parameters, trends also seen in the phase behavior of softer potential systems [4]. It is at this order that nonlocal corrections to weighted-density and related approximations to density-functional theory first make an appearance, and accordingly the study of the DCFs, beyond second order is of fundamental interest to the density-functional theory of melting; this is a major motivation behind the present paper [5]. For homogeneous systems themselves, knowledge of higher-order DCFs can also lead to improved closure relations for the distribution functions. For example, the third-order DCF provides the lowest-order correction to the bridge function [6], leading in principle to an improved closure statement beyond the hypernetted chain approximation. In the next section we briefly review some extant approximations to the third-order direct correlation functions, and in Sec. III we introduce the symmetry based arguments for the approximations proposed here. Section IV takes up the application of two separate symmetry based approximations for $c^{(3)}$ to the hard-sphere fluid where the results are shown to illustrate the important emerging role of nonlocality, which is further emphasized in the discussion of Sec. V.

II. THIRD-ORDER DIRECT CORRELATION FUNCTIONS; APPROXIMATIONS

Some time ago, Barrat, Hansen, and Pastore (BHP) [7] introduced an elegant approach to the modeling of the triplet direct correlation function particularly notable in what follows for its symmetric structure. The rotational and translational invariance of the homogeneous liquid as well as the lowest order h-bond expansion of the triplet DCF led them to consider the product form $c_0^{(3)}(\mathbf{r}_1,\mathbf{r}_2;\rho)=t(\mathbf{r}_1)t(\mathbf{r}_2)t(\mathbf{r}_3)$, where $\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3$ are relative coordinate vectors between three points in a plane, which satisfy $\mathbf{r}_1+\mathbf{r}_2+\mathbf{r}_3=\mathbf{0}$. A unique specification of the function $t(\vec{\mathbf{r}})$ then follows from an application of Eq. (3) at third order ($n=3$); it is subsequently determined from numerical solution of an integral

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equation. However, the more demanding task computationally, an issue addressed in part here, is to find the Fourier transform of the triple product [8]. The BHP theory gives good results for long-range potentials such as the Coulomb system, and indeed agrees well with molecular dynamics simulations of the soft sphere model near freezing [7]. Nevertheless, it does not predict a freezing transition in the hard-sphere system within the context of the extended modified weighted density approximation (WDA) [2], although no study has been performed to date to ascertain whether third-order extensions of local mappings such as the WDA [9] or the hybrid weighted density approximation (HWDA) [10] also reach the same conclusion. Further, it has also proven difficult so far to extend the BHP method to the calculation of higher-order DCFs [7]; again, this is an issue to be addressed in what follows.

Soon after the work of BHP, it was observed [11] that the WDA could also be used to directly calculate the third-order and higher-order DCF's but in a manner that *automatically* satisfies Eq. (3). In the WDA, the excess free energy per particle is given by $F_{\mathrm{ex}}[\rho]=\int d\mathbf{r}\,\rho(\mathbf{r})f(\overline{\rho}(\mathbf{r}))$, which is a mapping of the local excess free energy per particle onto a new system at a coarse-grained density, self-consistently determined by $\overline{\rho}(\mathbf{r})\equiv\int d\mathbf{r}'\rho(\mathbf{r}')W(\mathbf{r}-\mathbf{r}';\overline{\rho}(\mathbf{r}))$. The weight function $W(\mathbf{r}-\mathbf{r}';\overline{\rho}(\mathbf{r}))$, clearly taken here as *local*, is uniquely determined by requiring the functional to reproduce Eq. (1) at second order, and the resulting third-order DCF is then found from repeated functional differentiation of $F_{\mathrm{ex}}[\rho]$ [11,12]. The weight function is not known *a priori* and must be determined by the solution of a nonlinear differential equation [9]. Further, because W has about the same range as the second-order DCF, the corresponding triplet DCF tends to be too small at larger wave vectors. This problem is not shared by the BHP approach, which is based on a real space convolution.

The HWDA was proposed recently by Leidl and Wagner [10], who pointed out that the numerical calculation of the weight function in the WDA might actually be circumvented if the density argument of the weight function is replaced by a homogeneous (constant) effective density $\hat{\rho}$, itself consistently defined through the weight function. The latter is then specified by the solution of a simple quadratic. Again, the resulting triplet DCF exactly obeys Eq. (3), but $c_0^{(3)}(\mathbf{q},\mathbf{q}')$ is found to be *discontinuous* at $\mathbf{q}'=\mathbf{0}$ [10]. Consequently a considerable discrepancy can arise between the true triplet DCF and the approximate counterpart at wave vectors just beyond those satisfying the sum rule. We also note that Denton and Ashcroft [13] have proposed an analytic form for the triplet DCF by modeling the first-order DCF instead of the excess free energy as achieved by the HWDA and the WDA. Using the mapping $c^{(1)}(\mathbf{r};[\rho])=c_0^{(1)}(\overline{\rho}(\mathbf{r}))$ and with $\overline{\rho}(\mathbf{r})$ defined as in the WDA above, they found an *analytic* expression for the triplet DCF in Fourier space. But once again the resulting DCF does not satisfy Eq. (3).

III. SYMMETRY BASED APPROXIMATIONS

With this as background, we now present a *symmetry based* ansatz for triplet DCF's (applicable to higher-order DCFs as well) with the dual aims of requiring that the known sum rule on the third-order DCF be satisfied, but at the same time avoiding significant numerical impediments. As we shall see, even the simpler of the two applications of this approach yields DCFs that are already similar to the more computationally intensive WDA calculation, and as will also be seen, the triplet DCFs introduced below exactly satisfy the sum rule, Eq. (3), but with no discontinuities as found in the HWDA. In what follows we present two versions of triplet DCF theories based on analytical weight functions; for notational convenience, they are referred to as AT1 and AT2, and we compare their predictions to Monte-Carlo simulations.

In attempting to formulate a relatively simple theory of triplet correlations, the chief difficulty in directly applying the BHP form arises from the triple product of real-space functions and the complexity that arises from an integral equation that subsequently results from enforcing the sum rule of Eq. (3) in real space. However, we may observe that the sum rule condition is nevertheless a simple *algebraic* relation in Fourier space and we are, therefore, likewise motivated to introduce a *symmetric* algebraic ansatz for $c_0^{(3)}$ in Fourier space *directly*. An elementary example (actually one of the many possible suggestions) is the doublet form

$$3c_0^{(3)}(\mathbf{q}_1,\mathbf{q}_2)=A(\rho)[W(\mathbf{q}_1)W(\mathbf{q}_2)+W(\mathbf{q}_2)W(\mathbf{q}_3)+W(\mathbf{q}_3)W(\mathbf{q}_1)], \tag{5}$$

which we refer to as AT1. Imposition of the sum rule ($\mathbf{q}_3=\mathbf{0}$, $|\mathbf{q}_2|=|\mathbf{q}_3|\equiv\mathbf{q}$) leads to $A(\rho)=c_0^{(2)\prime}(\mathbf{q}=0)$ from the $\mathbf{q}=\mathbf{0}$ condition and then immediately to the elementary quadratic relation

$$W^2(\mathbf{q})+2W(\mathbf{q})-3C'(\mathbf{q};\rho)=0 \tag{6}$$

with the physically acceptable solution

$$W(\mathbf{q};\rho)=-1+\sqrt{1+3C'(\mathbf{q};\rho)}, \tag{7}$$

where we define the function $C'(\mathbf{q};\rho)=c_0^{(2)\prime}(\mathbf{q};\rho)/c_0^{(2)\prime}(0;\rho)$ and where the weight function W satisfies the normalization $W(\mathbf{q}\to\mathbf{0};\rho)=1$. The result here is relatively simple because the triplet DCF is taken to be directly proportional to a product of known weight functions. Note that the resulting triplet DCF obeys Eq. (3) *exactly* and following arguments similar to those given by BHP [7], it is also exact to second order (as are both of the forms we propose here) in a wave-number expansion about $\mathbf{q},\mathbf{q}'=\mathbf{0}$. Note also that for all densities, the density derivative of $c^{(2)}$ displays damped oscillatory behavior progressing to zero at large wave vector. Accordingly, C' is a function with a maximum value of unity (at $\mathbf{q}=0$) and for all densities it also decays to zero in an oscillatory fashion as wave vector increases. The quadratic solution in Eq. (7) is, therefore, well-defined for the hard-sphere system. Finally, for large $\mathbf{q}$, $C'(\mathbf{q})$ is small and the weight function therefore decays as $\frac{3}{2}C'(\mathbf{q})$ (for all ρ).

As a second and perhaps more interesting example, we introduce an analytic theory that now goes considerably beyond previous approaches by approximating the second-order DCF in an inhomogeneous system through the statement $c^{(2)}(\mathbf{r},\mathbf{r}';[\rho])=[c_0^{(2)}(\mathbf{r}-\mathbf{r}';\overline{\rho}(\mathbf{r}))+c_0^{(2)}(\mathbf{r}$

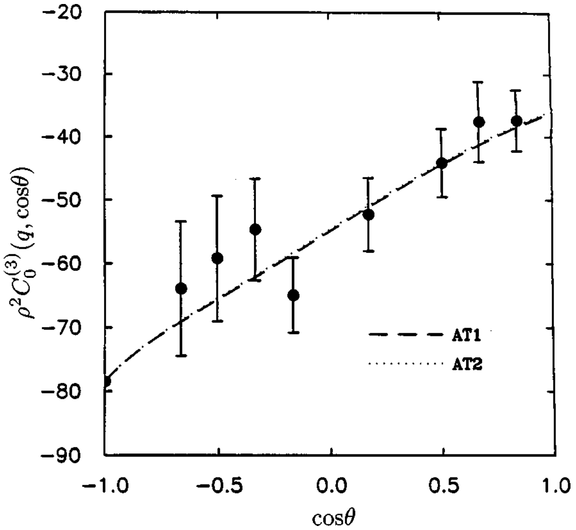

FIG. 1. Triplet direct correlation functions $c_0^{(3)}(\mathbf{q},\cos\theta;\rho)$ for isosceles triangle configurations $|\mathbf{q}_1|=|\mathbf{q}_2|\equiv\mathbf{q}=2.3045$ and packing fraction $\eta=0.45$, $\cos\theta$ being the angle between $\mathbf{q}_1$ and $\mathbf{q}_2$. Solid circles are simulation results with two standard deviation error bars [14]. The dashed and dotted curves are, respectively, the analytic theories AT1 and AT2.

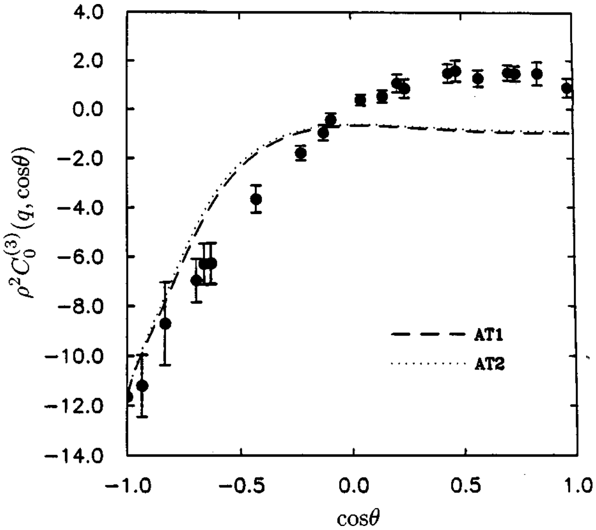

FIG. 3. As in Fig. 1, but for $\mathbf{q}=5.153$.

$-\mathbf{r}';\overline{\rho}(\mathbf{r}'))]/2$. Note that this form incorporates the physically important aspect of nonlocality, at least on an approximate basis. By taking the functional derivative, and by defining $\delta\overline{\rho}(\mathbf{r})/\delta\rho(\mathbf{r}')\equiv W(\mathbf{r}-\mathbf{r}')$, we obtain $c_0^{(3)}(\mathbf{r}-\mathbf{r}',\mathbf{r}-\mathbf{r}'';\rho)=c_0^{(2)\prime}(\mathbf{r}-\mathbf{r}')[W(\mathbf{r}-\mathbf{r}'')+W(\mathbf{r}'-\mathbf{r}'')]/2$. Further, given three points $\mathbf{r}$, $\mathbf{r}'$, $\mathbf{r}''$ and the definition of relative coordinates $\mathbf{r}_1=\mathbf{r}'-\mathbf{r}''$, $\mathbf{r}_2=\mathbf{r}-\mathbf{r}'$, $\mathbf{r}_3=\mathbf{r}''-\mathbf{r}$, a *symmetrized* ansatz for the triplet DCF in real space, becomes

$$\begin{aligned}6c_0^{(3)}(\mathbf{r}_1,\mathbf{r}_2;\rho)=&\,c_0^{(2)\prime}(\mathbf{r}_1)[W(\mathbf{r}_2)+W(\mathbf{r}_3)]\\&+c_0^{(2)\prime}(\mathbf{r}_2)[W(\mathbf{r}_3)+W(\mathbf{r}_1)]\\&+c_0^{(2)\prime}(\mathbf{r}_3)[W(\mathbf{r}_1)+W(\mathbf{r}_2)],\end{aligned}\tag{8}$$

and this we shall call AT2. This direct product form in real space is particularly notable because it *remains* a direct product in Fourier space; indeed, direct transformation yields

$$\begin{aligned}6c_0^{(3)}(\mathbf{q}_1,\mathbf{q}_2;\rho)=&\,W(\mathbf{q}_1)[c_0^{(2)\prime}(\mathbf{q}_2)+c_0^{(2)\prime}(\mathbf{q}_3)]\\&+W(\mathbf{q}_2)[c_0^{(2)\prime}(\mathbf{q}_3)+c_0^{(2)\prime}(\mathbf{q}_1)]\\&+W(\mathbf{q}_3)[c_0^{(2)\prime}(\mathbf{q}_1)+c_0^{(2)\prime}(\mathbf{q}_2)],\end{aligned}\tag{9}$$

where $\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3=0$. Taking the $|\mathbf{q}_1|=|\mathbf{q}_2|\equiv\mathbf{q}$, $\mathbf{q}_3=\mathbf{0}$ limit as before, and solving for the weight function, we obtain

$$W(\mathbf{q};\rho)=\frac{2c_0^{(2)\prime}(\mathbf{q};\rho)}{c_0^{(2)\prime}(\mathbf{q};\rho)+c_0^{(2)\prime}(\mathbf{q}=0;\rho)},\tag{10}$$

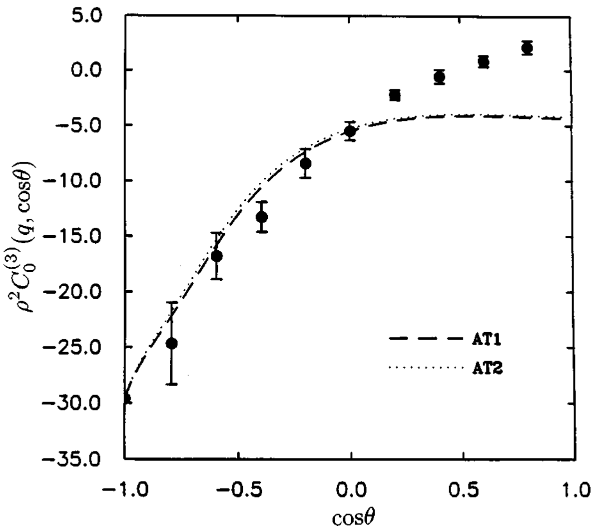

FIG. 2. As in Fig. 1, but for $\mathbf{q}=4.2074$.

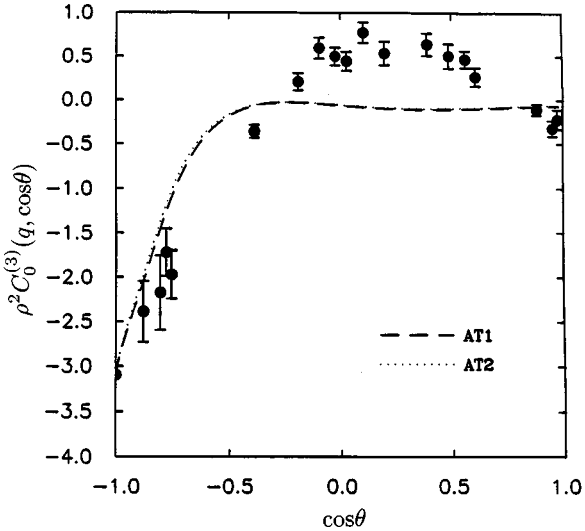

FIG. 4. As in Fig. 1 but for $\mathbf{q}=6.024$.

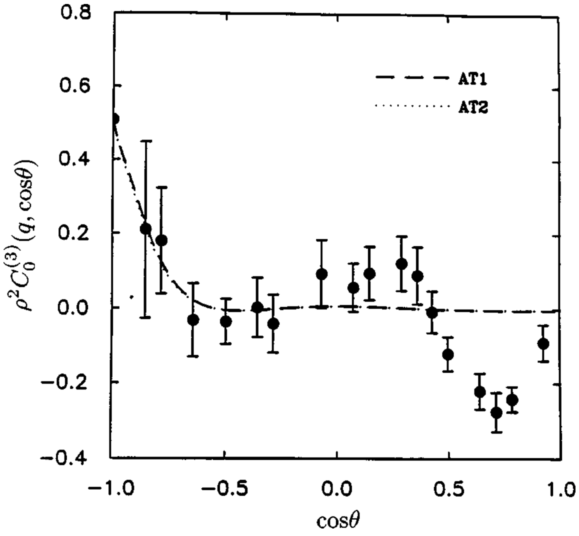

FIG. 5. As in Fig. 1 but for $\mathbf{q}=7.0404$.

where again W satisfies the normalization $W(\mathbf{q}\rightarrow\mathbf{0};\rho)=1$.

This second form also obeys the sum rule by definition of the weight function and, as noted, retains its simple product form in both real and Fourier space. The emerging form for $c^{(3)}$ is clearly a consequence of a local density approximation.

IV. APPLICATION TO THE HARD-SPHERE FLUID

By way of application we invoke these two approximations for the dense, hard-sphere fluid. In Figs. 1–5 we plot the triplet DCFs resulting from the two analytic forms for isosceles triangle configurations with various choices of wave-vector magnitudes, and at a packing fraction of $\eta=0.45$. Also shown are the results of Monte Carlo simulations of the hard-sphere system with two standard deviation error bars [14]. All of the calculations use the Verlet-Weiss direct correlation function based on the Carnahan-Starling expression for the excess free energy of a homogeneous liquid [15]. Consequently, the data point for $\cos\theta=-1$ ($\cos\theta$ is the angle between wave vectors $\mathbf{q}_1$ and $\mathbf{q}_2$) is necessarily exact, and as noted above, both of our approaches are also exact at this point. For the smallest wave vector considered, $|\mathbf{q}\sigma|=2.3045$ (here $|\mathbf{q}_1|=|\mathbf{q}_2|\equiv|\mathbf{q}|$), both yield excellent results, and they are seen to be well within the two standard deviation error bars of the simulation data. For larger wave vectors, we also observe that the two theories continue to give generally accurate results for configurations satisfying $\cos\theta<0$, only lacking the detailed structure of the true DCF for $\cos\theta>0$. In general, the two DCFs tend to exhibit very similar behavior, even though one is based on a simple symmetry ansatz, while the other is based on a local density approximation to the second-order DCF. The results given here are similar to those obtained from the more computationally demanding WDA [9], and the reason for this is traced to the fact that much of the information inherent in the weighted density is actually *lost* when the homogeneous limit is taken. An important consequence is that the weight function of the WDA is quite strongly constrained both by normalization and by the form of the second-order DCF. Lack of detailed structure for $\cos\theta>0$ can now be readily understood from the observation that for large wave vectors, the contribution to the DCF at, say, $\cos\theta=1$ arises from terms of the form $W(\vec{\mathbf{q}})c_0^{(2)\prime}(2\vec{\mathbf{q}})$ and permutations. For the hard-sphere system the second-order DCF is short ranged and its density derivative is quite small, thereby making the contribution to the triplet DCF almost negligible for large wave vectors. The results embodied in Fig. 5, therefore, give important insight on the emerging role of nonlocality.

We may observe that the two forms just presented can be extended very simply to direct correlation functions beyond third order. A straightforward approach is to propose Fourier space forms involving a single weight function and then by a subsequent appeal to the $\mathbf{q}=\mathbf{0}$ limit, invoking Eq. (4) until a relation between the weight function and the derivative of the second-order DCF is reached. Again we see that the result must be a quadratic equation for the weight function. On the other hand, if accurate representations of higher-order DCFs are already known, the DCF at the next higher level may then be found by introducing more than a single weight function into the factorization ansatz.

V. DISCUSSION

By way of summary, we have introduced two simple analytic models leading to triplet (and higher-order) DCFs that obey a principal sum rule, but at the same time, remain simple to calculate in both real and Fourier space. Results are generally in good agreement with simulation; for larger wave vectors they tend to lack some small structure for $\cos\theta>0$ geometries but this is now understood to arise from the loss of information resulting from the role of nonlocality and the imposition of a homogenous limit in the determination of the weight function. It has been verified that the direct correlation functions introduced here give rise to a freezing transition in short-range systems [5] when used in conjunction with recent extensions of the modified weighted density approximation. More generally, the use of the single integral condition on an approximate form of triplet DCF appears quite insufficient to specify the general behavior of the true DCF and we may therefore expect that further developments will also need to take into account additional sum rules or scaling relations obeyed by the true triplet DCF. Finally, though the connection is not immediate in the numerical sense, it is nevertheless evident that a proposition for a form of the direct correlation function $c^{(3)}$ also implies a form for a corresponding total correlation function (for example, $g^{(3)}$). Since the latter has been investigated by simulation methods for the hard-sphere system [16], a comparison can, therefore, be sought and this is under investigation.

ACKNOWLEDGMENTS

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