Factorization of the Triplet Direct Correlation Function in Dense Fluids

Jean-Louis Barrat, Jean-Pierre Hansen, and Giorgo Pastore[(a)]
Laboratoire de Physique Théorique des Liquides, Université Pierre et Marie Curie, 75252 Paris, Cedex 05, France

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A factorization *Ansatz* for the three-particle direct correlation function $c^{(3)}$ is combined with the exact relation between $c^{(3)}$ and the pair function $c^{(2)}$ to derive a simple and tractable approximation for $c^{(3)}$ in dense, classical fluids. The predictions compare favorably with "exact" molecular-dynamics results for the "soft-sphere" fluid near freezing.

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The n-particle direct correlation functions (DCF) $c^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)$ are key ingredients in the density-functional theory of inhomogeneous classical fluids[1,2] and of freezing.[3] They are the functional derivatives of the excess (nonideal) part of the Helmholtz free energy $F_{\mathrm{ex}}[\rho^{(1)}]$ (the generating functional), with respect to the one-particle density $\rho^{(1)}(\mathbf{r})$, according to

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

where $\beta=1/k_{\mathrm{B}}T$. Expansions of inhomogeneous fluid or crystal properties around a uniform reference state are almost invariably limited to second order, involving the well-known uniform Ornstein-Zernike DCF $c^{(2)}(\mathbf{r})$ ($\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2$), because very little is known about higher-order DCF's $c^{(n)}$ ($n\geq 3$), in particular about the triplet function $c^{(3)}(\mathbf{r},\mathbf{r}')$ of a uniform fluid. The purpose of this Letter is to present a new, systematic procedure for the calculation of $c^{(3)}$, and to compare the predictions of this theory with the results of extensive molecular-dynamics (MD) simulations.

The standard approximation schemes for triplet correlations in dense fluids generally focus on the three-particle distribution function $g^{(3)}(\mathbf{r},\mathbf{r}')$, rather than on $c^{(3)}$. The Kirkwood superposition approximation[4,5] amounts to setting

$$g^{(3)}(\mathbf{r},\mathbf{r}')=g^{(2)}(r)g^{(2)}(r')g^{(2)}(|\mathbf{r}-\mathbf{r}'|),\tag{2}$$

where $g^{(2)}$ denotes the usual pair distribution function. The convolution approximation[6] assumes a similar factorization, but in k space, i.e.,

$$S^{(3)}(\mathbf{k},\mathbf{k}')=S^{(2)}(k)S^{(2)}(k')S^{(2)}(|\mathbf{k}+\mathbf{k}'|),\tag{3}$$

where the two- and three-particle structure factors $S^{(2)}(k)$ and $S^{(3)}(\mathbf{k},\mathbf{k}')$ are Fourier transforms of the distribution functions $g^{(2)}$ and $g^{(3)}$. The superposition approximation (2) and its improvements[7] are not well adapted to derivation of transparent expressions for the DCF $c^{(3)}$. The Fourier transform $\hat{c}^{(3)}(\mathbf{k},\mathbf{k}')$ of the latter is related to the structure factor $S^{(3)}$ by the triplet Ornstein-Zernike relation[8,9]

$$S^{(3)}(\mathbf{k},\mathbf{k}')=S^{(2)}(k)S^{(2)}(k')S^{(2)}(|\mathbf{k}+\mathbf{k}'|)[1+\rho^2\hat{c}(\mathbf{k},\mathbf{k}')],\tag{4}$$

where ρ is the number density. Comparison with Eq. (3) immediately shows that within the convolution approximation, $c^{(3)}\equiv 0$. The first correction to the convolution result, in an $h^{(2)}$-bond [where $h^{(2)}=g^{(2)}-1$] expansion of $c^{(3)}$, is given by[9]

$$c^{(3)}(\mathbf{r},\mathbf{r}')=h^{(2)}(r)h^{(2)}(r')h^{(2)}(|\mathbf{r}-\mathbf{r}'|).\tag{5}$$

This approximate expression has in fact been recently used to evaluate the third-order contributions to the free energy of the crystal phase in a density-functional calculation of freezing of the classical one-component plasma.[10] Equation (5) has the undesirable property that it leads to $c^{(3)}(\mathbf{r},\mathbf{r}')\simeq -1$, independently of density, for all triangles such that r, r', and $|\mathbf{r}-\mathbf{r}'|$ are less than the range σ of the repulsion between atoms, where $h(r)\simeq -1$.

We have maintained the factorization assumption, corresponding to a procedure of separation of variables (r, r', and $|\mathbf{r}-\mathbf{r}'|$) which satisfies the obvious symmetry properties of $c^{(3)}$. However, we replace $h^{(2)}$ in Eq. (5) by an arbitrary function $t(r)$, so that our basic expression for $c^{(3)}$ now reads

$$c^{(3)}(\mathbf{r},\mathbf{r}')=t(r)t(r')t(|\mathbf{r}-\mathbf{r}'|).\tag{6}$$

Once the factorized form (6) has been assumed, the optimum choice for $t(r)$ is made by our requiring that it satisfy the exact relation between $c^{(2)}$ and $c^{(3)}$, which follows immediately from Eq. (1) in the limit of a homogeneous fluid[11] [$\rho^{(1)}(\mathbf{r})=\rho$]:

$$\frac{\partial c^{(2)}(r)}{\partial\rho}=\int d^3r'\,c(\mathbf{r},\mathbf{r}')=t(r)\int d^3\mathbf{r}'\,t(r')t(|\mathbf{r}-\mathbf{r}'|).\tag{7}$$

Given a means of calculating the Ornstein-Zernike DCF $c^{(2)}$ and its variation with density, Eq. (7) uniquely determines $t(r)$ and hence $c^{(3)}$ from Eq. (6). The nature of the constraint (7) is more transparent in Fourier space where it reads

$$\partial c^{(2)}(k)/\partial\rho=\hat c^{(3)}(\mathbf{k},\mathbf{k}'=0) \tag{8}$$

This shows that the factorization (6) together with Eq. (7) ensures that the resulting $\hat c^{(3)}(\mathbf{k},\mathbf{k}')$ is exact whenever one of the two wave vectors vanishes. For arbitrary wave vectors $\mathbf{k}$ and $\mathbf{k}'$, $\hat c^{(3)}$ is given by

$$\hat c^{(3)}(\mathbf{k},\mathbf{k}') = \frac{1}{(2\pi)^3}\int d^3k''\,\hat t(k'')\hat t(|\mathbf{k}-\mathbf{k}''|)\hat t(|\mathbf{k}'+\mathbf{k}''|), \tag{9}$$

which can be evaluated by a standard expansion in Legendre polynomials.[7] In practical applications, $c^{(2)}(r)$ may be calculated with a high degree of accuracy, for a given interatomic pair potential $v(r)$, from one of the self-consistent integral equations recently proposed in the literature.[12-14] These integral equations supplement the two-particle Ornstein-Zernike relation

$$S^{(2)}(k)=[1-\rho\hat c^{(2)}(k)]^{-1} \tag{10}$$

by an appropriate closure relation between $g^{(2)}(r)$, $c^{(2)}(r)$, and $v(r)$; they can be solved simultaneously, by numerical iteration, for the functions $c^{(2)}(r)$, $h^{(2)}(r)$, and their density derivatives $C_\rho(r)=\partial c^{(2)}(r)/\partial\rho$ and $H_\rho(r)=\partial h^{(2)}(r)/\partial\rho$. The resulting $C_\rho(r)$ is substituted in Eq. (7) which is then solved numerically. The straightforward iterative Picard method,

$$t_{n+1}(r)=c_\rho(r)/(t_n * t_n)(r), \tag{11}$$

where the asterisk denotes a convolution product, leads to difficulties whenever the convolution of the nth iteration estimate t_n has zeros. Instead we have used a crude, but efficient, "steepest-descent" method which amounts to minimizing the functional

$$A[t]=\int d^3r\,[t(r)(t*t)(r)-c_\rho(r)]^2 \tag{12}$$

with respect to $t(r)$.

We have applied our method to the simple "soft-sphere" model, made up of atoms interacting via the pair potential

$$V(r)=\epsilon(\sigma/r)^{12}. \tag{13}$$

Like all inverse-power potentials, the soft-sphere model has a trivial scaling property, according to which its reduced equilibrium properties (excess thermodynamics as well as correlation functions) depend on a single dimensionless coupling parameter—in this case $\gamma=(\rho\sigma^3)\times(k_BT/\epsilon)^{-1/4}$. These properties are accurately known over a wide range of γ values from computer simulations[15] and are well reproduced by the self-consistent integral equation of Rogers and Young (RY).[13] We have used this equation to compute $C_\rho(r)$; then Eq. (7) was solved by the steepest-descent method to obtain $t(r)$. This function is compared to $h^{(2)}(r)$ for $\gamma=1.15$ (a thermodynamic state of the fluid near freezing[15]) in Fig. 1. The two functions are seen to differ considerably at all distances r. In particular $t(r)$ is much more negative inside the core region, and oscillates more rapidly, than $h^{(2)}(r)$. Figure 1 also shows the function $t(r)$ computed for the one-component plasma near freezing [i.e., for $\Gamma=e^2/ak_BT=178$,[16] where e is the charge and $a=(3/4\pi\rho)^{1/3}$ is the ion-sphere radius]. It is remarkably similar to the result for soft spheres under comparable conditions; this close agreement reflects the similarity of the density derivatives $C_\rho(r)$ in both models.

Once $t(r)$ has been computed, the triplet DCF $c^{(3)}$ and its Fourier transform $\hat c^{(3)}$ follow directly from Eqs. (6) and (9). To test our approximation scheme, we have carried out extensive MD simulations on a system of $N=256$ soft spheres in a periodically repeated cubic cell, using the standard Verlet finite-difference algorithm.[17] With the unit of time[17] $\tau=(m\sigma^2/\epsilon)^{1/2}$, the first run extended over 10^5 time steps $\Delta t=0.008\tau$, for a thermodynamic state $\gamma=1.13$, i.e., just before freezing. In the second run, 1.8×10^5 time steps were generated, with $\Delta t=0.01\tau$, and $\gamma=1.17$, corresponding to a slightly supercooled fluid state. The simulations yield directly the pair triplet structure factors, for wave vectors $\mathbf{k}$ and $\mathbf{k}'$ compatible with the periodic boundary conditions, according to the definitions

$$S^{(2)}(k)=N^{-1}\langle\rho_{\mathbf{k}}\rho_{-\mathbf{k}}\rangle, \tag{14a}$$

$$S^{(3)}(\mathbf{k},\mathbf{k}')=N^{-1}\langle\rho_{\mathbf{k}}\rho_{\mathbf{k}'}\rho_{-\mathbf{k}-\mathbf{k}'}\rangle, \tag{14b}$$

$$\rho_{\mathbf{k}}=\sum_{i=1}^{N}\exp(i\mathbf{k}\cdot\mathbf{r}_i).$$

$\hat c^{(3)}(\mathbf{k},\mathbf{k}')$ is finally derived from the Ornstein-Zernike

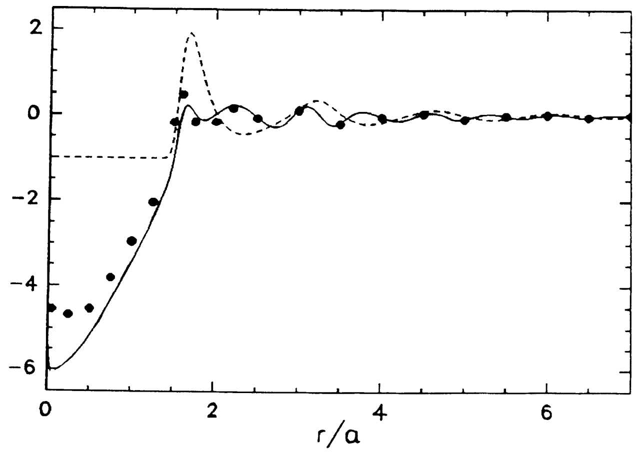

FIG. 1. Comparison of the functions $h^{(2)}(r)$ (dashed curve) and $t(r)$, as determined from Eq. (7) (full curve), vs distance, in units of $a=(3/4\pi\rho)^{1/3}$, for soft spheres near freezing ($\gamma=1.15$). The function $t(r)$ for the one-component plasma near freezing ($\Gamma=178$) is represented by dots.

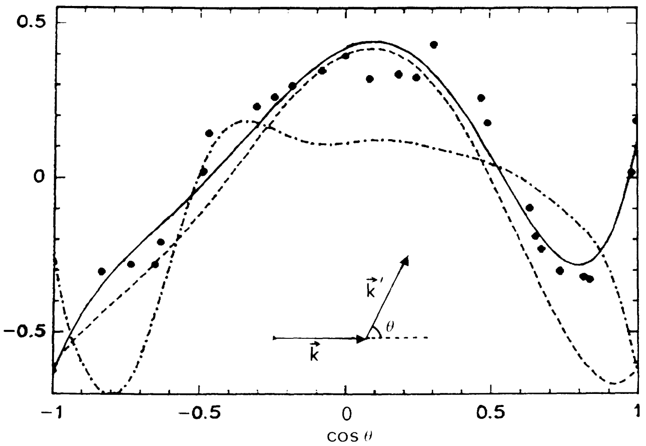

FIG. 2. Triplet DCF $\hat{c}^{(3)}(\mathbf{k},\mathbf{k}')$ of soft spheres for isosceles triangles, vs cosθ (the geometry is shown schematically) for $ka=k'a=4.3$ and $\gamma=1.17$. Dashed curve, approximation (6) [with $t(r)$ determined from Eq. (7)]; dash-dotted curve, approximation (5); dots, MD data; the full curve is a least-squares polynomial fit to the data, drawn for visual guidance.

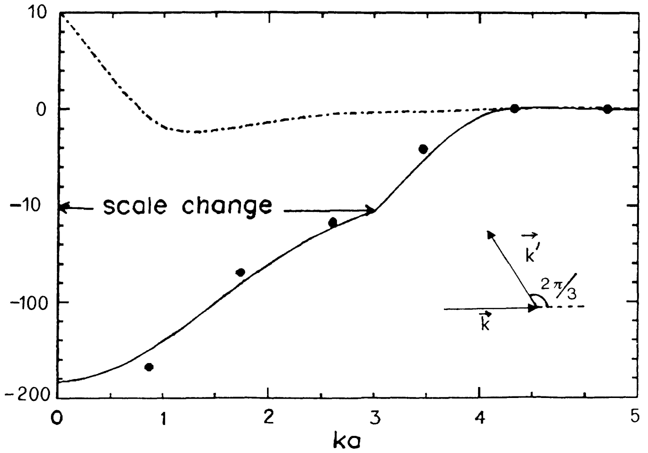

FIG. 3. Triplet DCF $\hat{c}^{(3)}(k,k,k)$ of soft spheres vs ka (equilateral triangles). Dash-dotted curve, approximation (5); full curve, approximation (6); dots, MD results; note the change of scale around $ka \simeq 3$.

relation (4). The statistical uncertainty on $S^{(3)}(\mathbf{k},\mathbf{k}')$ is estimated to be of the order of (3–5)% on the basis of the average values obtained for the imaginary part of $S^{(3)}$, which should vanish identically. The error on $\hat{c}^{(3)}$ is correspondingly larger, since this quantity, as determined from Eq. (4), represents a correction to the convolution approximation (3) which is the dominant contribution at intermediate wave numbers $k \simeq k' \simeq k_{\max}$ [where $k_{\max}$ is the position of the main peak in the structure factor $S^{(2)}(k)$]. For significantly smaller wave numbers, $S^{(3)}(\mathbf{k},\mathbf{k})$ is small, and the relative errors on $S^{(3)}$ and $\hat{c}^{(3)}$ increase rapidly. For these reasons very long MD runs are needed to obtain significant results for $\hat{c}^{(3)}$. An earlier attempt to compute $\hat{c}^{(3)}$ for a Lennard-Jones fluid did not lead to conclusive results, because of insufficient statistics.[18]

$S^{(3)}(\mathbf{k},\mathbf{k}')$ and $\hat{c}^{(3)}(\mathbf{k},\mathbf{k}')$ were computed for two particular geometries: (a) Isosceles triangles with $k=k'=k_{\max}$ and various angles θ, such that $0 \le |\mathbf{k}+\mathbf{k}'| \le 2k_{\max}$; (b) equilateral triangles with various side lengths. The MD results for geometry (a) are compared in Fig. 2 to the DCF's $\hat{c}^{(3)}$ calculated from Eqs. (5) and (6). Because of the large statistical scatter of the MD results we show a least-squares polynomial fit to the data for visual clarity. Note that according to Eq. (8), the result of approximation (6) is exact for $\theta=\pi$. Figure 2 shows that our approximation for $\hat{c}^{(3)}$ correctly reproduces the general shape of the "exact" $\hat{c}^{(3)}$, although quantitative discrepancies remain, especially for small angles θ. Approximation (5) leads to qualitatively wrong results, especially near $\theta=0$ and $\theta=\pi$.

The comparison between MD and approximate results for equilateral triangles [geometry (b)] is made in Fig. 3, as a function of the side length k. The MD result is not very reliable for the smallest wave number ($ka \simeq S^{(3)}$ is very small). The $\hat{c}^{(3)}$ calculated from approximations (5) and (6) differ dramatically for $ka \lesssim 4$; the predictions of our theory are in fair agreement with the MD data, and are again exact in the limit $k \to 0$. Approximation (5) is qualitatively and quantitatively wrong for equilateral geometry. For $ka \gtrsim 4$, $\hat{c}^{(3)}(k,k,k)$ remains very small and appears to oscillate around zero.

In summary, we have proposed a simple and efficient approximation for the triplet DCF in dense fluids which is similar in spirit to an earlier *Ansatz* for the triplet distribution function $g^{(3)}$.[19] Comparison with the results of long MD simulations shows that our approximation is vastly superior to the standard factorization (5). The new factorization (6), with $t(r)$ determined by Eq. (7), opens up the possibility of deriving a new type of simultaneous integral equation for the pair and triplet correlation functions. The latter will allow a quantitative study of angular correlations in dense fluids, and in supercooled liquids close to the glass transition. We are presently examining in more detail the influence of the pair potential on triplet correlations.

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(a)Permanent address: International School for Advanced Studies, Strada Costiera 11, 34014 Trieste, Italy.

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