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Three-particle equilibrium correlations in dense hard-sphere fluids

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We performed molecular-dynamics simulation experiments for a hard-sphere fluid at four high densities and determined the spatial Fourier transform of the three-particle equilibrium correlation function with two of the three particles at contact.

Recent studies[1-5] of the viscosity η and the diffusivity D of dense noble-gas and hard-sphere fluids in equilibrium have shown that the experimentally observed divergence[6-10] of η and D^{-1} near solidification may be understood on the basis of the extended mode-coupling theory.[4,11] Theoretical calculations have been performed for hard-sphere systems in particular, but the results are relevant also for real fluids, if one uses effective hard-sphere diameters for these fluids.[3] In these explicit hard sphere calculations[1-5] one needs the equilibrium pair correlation function $g(r)$ and the three-particle correlation function $g_3(\mathbf{r},\mathbf{r}',\mathbf{r}'')$ of three particles,[12] two of which are at contact. In fact one needs their spatial Fourier transforms, i.e., the static structure factor

$$S(k)=1+n\int d\mathbf{r}\exp(-i\mathbf{k}\cdot\mathbf{r})[g(r)-1]$$

and

$$G(k,\phi)=\int d\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}}\left[g_3\left[\frac{\boldsymbol{\sigma}}{2},-\frac{\boldsymbol{\sigma}}{2},\mathbf{r}\right]-g(\sigma)\right] . \tag{1}$$

Here $n=N/V$ is the number density of a hard sphere fluid of N hard spheres with diameter σ in a volume V, $\mathbf{r}$, $\mathbf{k}$, and $\boldsymbol{\sigma}$ are vectors with lengths r, k, and σ, respectively, and $\cos\phi=\mathbf{k}\cdot\boldsymbol{\sigma}/(k\sigma)$, so that ϕ is the angle between the wave vector $\mathbf{k}$ and the vector $\boldsymbol{\sigma}$ which gives the relative position of two colliding hard spheres in the fluid.

While pair correlations for hard spheres have been studied extensively[12,13] by means of molecular dynamics (MD) experiments both through $g(r)$ as well as through $S(k)$, three-particle correlations have been studied sparsely[14-16] and through $g_3(\mathbf{r},\mathbf{r}',\mathbf{r}'')$ only. In fact, the presently available MD data for $g_3(\boldsymbol{\sigma}/2,-\boldsymbol{\sigma}/2,\mathbf{r})$ cover a range of vectors $\boldsymbol{\sigma}$ and $\mathbf{r}$ that is too coarsely spaced for determining $G(k,\phi)$ from Eq. (1). Therefore, to obtain $G(k,\phi)$, which is the function needed in the extended mode-coupling-theory calculations, use has been made so far of theoretical approximations expressing $G(k,\phi)$ in terms of the well-known pair correlation functions $g(r)$ and $S(k)$.

In this note we present new MD results for $G(k,\phi)$ at four reduced densities $n^*=n\sigma^3=0.812$, 0.860, 0.884, and 0.900, respectively, as a function of ϕ for 30 values of the wave number k. In addition we study two theoretical approximations for $G(k,\phi)$ which have been used in mode-coupling-theory calculations.

At each of the four densities n^* we consider a system of $N=256$ hard spheres in equilibrium in a cubic volume V and use the relations

$$S(k)=\left\langle N^{-1}\sum_{j=1}^{N}\sum_{l=1}^{N}e^{i\mathbf{k}(\mathbf{r}_j-\mathbf{r}_l)}\right\rangle , \tag{2}$$

$$G(k,\phi)=n^{-1}g(\sigma)\left\langle\!\left\langle \sum_{\substack{j=1\\ j\neq i^*,j^*}}^{N}\cos\left[\mathbf{k}\cdot\left[\mathbf{r}_j-\frac{\mathbf{r}_{i^*}+\mathbf{r}_{j^*}}{2}\right]\right]\right\rangle\!\right\rangle , \tag{3}$$

both valid for $k\neq0$, with

$$\cos\phi=\mathbf{k}\cdot(\mathbf{r}_{i^*}-\mathbf{r}_{j^*})/(k\sigma) . \tag{4}$$

Here $\mathbf{r}_j$ is the position of particle j, the single brackets in Eq. (2) denote the (usual) equilibrium canonical ensemble average, and the double brackets in Eq. (3) denote the equilibrium average over those states only in which two of the N particles (i^* and j^*, respectively) are at contact.

In our MD experiments we calculated at each n^* the positions $\mathbf{r}_j$ and velocities $\mathbf{v}_j$ of the N particles over a time range so long as to include 800.000 single binary collisions between the hard spheres. From these MD data we first determined the four $g(\sigma)$ from the observed collision rates.[17] The results agree with those calculated from the hard-sphere equation of state,[18] i.e., $g(\sigma)=4.13$, 4.64, 4.92, and 5.12 for $n^*=0.812$, 0.860, 0.884, and 0.900, respectively. Second, for 3×30 wave vectors $\mathbf{k}$ taken from the reciprocal lattice of the cubic volume V along the three orthogonal main axes we calculated the quantity within brackets on the right-hand side of Eq. (2) for a series of times separated by equal intervals. By averaging these results, we determined $S(k)$ and its uncertainty for 30 values of the wave number k and four reduced densities n^*. The uncertainty in $S(k)$ is about 2% of the largest $S(k)$ value obtained at each density. Within this uncertainty, we find that $S(k)$ can be described by the theoretical Percus-Yevick approximation[12] for all four densities and all k. Finally, for the same 90 wave vectors $\mathbf{k}$ and for those states of the fluid for which two hard spheres collide, we calculated the quantity with double brackets on the right-hand side of Eq. (3) for 11 small ranges of ϕ values [cf. Eq. (4)] given by $|\cos\phi| \le 0.03$; $|\cos\phi| = 0.1 \pm 0.015$; $|\cos\phi| = 0.2 \pm 0.015$; ...; $|\cos\phi| = 0.9 \pm 0.015$, and $|\cos\phi| \ge 0.97$. By averaging the results [cf. Eq. (3)] obtained in each of these 11 ranges of ϕ values we determined $G(k,\phi)$ and its uncertainty as a function of ϕ, k, and n^*. We find that the absolute uncertainty in $nG(k,\phi)$ is about 0.5 for all ϕ, k, and n^*. Here we discuss our MD results in terms of the direct three-particle correlation function $H(k,\phi)$ rather than in terms of $G(k,\phi)$ since $H(k,\phi)$ is the more useful function is extended mode-coupling-theory calculations. $H(k,\phi)$ is related to $G(k,\phi)$ by[1]

$$H(k,\phi) = \frac{1}{nS(k)}\{nG(k,\phi) - 2g(\sigma)[S(k)-1] \times \cos(\tfrac{1}{2}k\sigma\cos\phi)\} . \tag{5}$$

We find that more than 90% of the MD values for $H(k,\phi)$ vanish for $k\sigma > 15$ and for all four n^*. Through a least-squares fitting procedure we find that all MD data with $k\sigma < 15$ can be represented in very good approximation by

$$nH(k,\phi) = \sum_{l=0,2,\cdots}^{10} \sum_{i=l}^{10} X_{il}(n^*) P_l(\cos\phi) j_i(k\sigma) \tag{6}$$

with l and i even, and

$$X_{il}(n^*) = a_{il} + b_{il}(n^* - 0.884) , \tag{7}$$

where a_{il} and b_{il} are given in Table I. In Eq. (6) the $P_j(x)$ are Legendre polynomials,[19] i.e., $P_0(x)=1$, $P_2(x) = (3x^2-1)/2, \ldots$, and $j_i(x)$ is the spherical Bessel function of order i (Ref. 19). To illustrate the agreement, we show in Fig. 1 the MD results for $nH(k,\phi)$ and its parametrization given by Eq. (6) for $n^*=0.884$ as a function of $\cos\phi$ for the smallest 12 values of $k\sigma$.

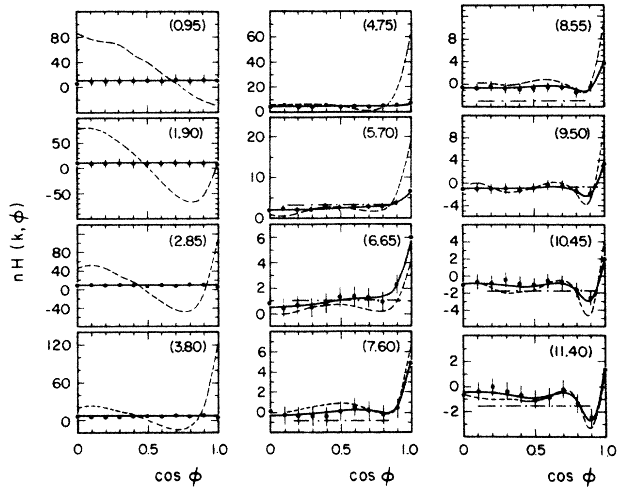

FIG. 1. Reduced direct correlation functions $nH(k,\phi)$ (closed circles with error bars) obtained from MD for a hard-sphere fluid at $n^*=0.884$ as a function of $\cos\phi$ for 12 reduced wave numbers $k\sigma$, given in parentheses ( ) in each subfigure. Also shown are the best fits to $nH(k,\phi)$, given by Eqs. (6), (7), and Table I (solid curves); the approximation $nH_{\mathrm{KSA}}(k,\phi)$, cf. Eqs. (5) and (8) (dashed curves); and the approximation $nH(k)$, Eq. (12) (dashed-dotted curves). For $0.95 \le k\sigma \le 4.75$, the solid and dashed-dotted curves overlap and are indistinguishable.

The first theoretical approximation we have studied is Kirkwood's superposition approximation (KSA), i.e.,

$$g_3(\mathbf{r},\mathbf{r}',\mathbf{r}'') = g(|\mathbf{r}-\mathbf{r}'|)g(|\mathbf{r}-\mathbf{r}''|)g(|\mathbf{r}'-\mathbf{r}''|) .$$

Thus with Eq. (1)

$$G_{\mathrm{KSA}}(k,\phi) = 2n^{-1}g(\sigma)[S(k)-1]\cos(\tfrac{1}{2}k\sigma\cos\phi) + \frac{g(\sigma)}{2\pi^2 n^2}\int_0^\infty dk'\,k'^2 \int_0^1 dx\, J_0(\kappa_1)\cos(\kappa_2)[S(\kappa_3)-1][S(\kappa_4)-1] , \tag{8}$$

where $J_0(x)$ is the (normal) Bessel function of order zero,

$$\kappa_1 = k'\sigma(1-x^2)^{1/2}\sin\phi ,$$

$$\kappa_2 = k'\sigma x\cos\phi ,$$

$$\kappa_3 = (k^2/4 + k'^2 + kk'x)^{1/2} ,$$

and

$$\kappa_4 = (k^2/4 + k'^2 - kk'x)^{1/2} .$$

We have calculated $G_{\mathrm{KSA}}(k,\phi)$ from Eq. (8) using the (analytical) Percus-Yevick expression for $S(k)$. We find for all four densities that $H_{\mathrm{KSA}}(k,\phi)$, obtained from $G_{\mathrm{KSA}}(k,\phi)$ via Eq. (5), describes $H(k,\phi)$ very poorly for $k\sigma < 5$ and reasonably well for $k\sigma > 5$. This is illustrated for $n^*=0.884$ in Fig. 1, where also the $H_{\mathrm{KSA}}(k,\phi)$ are shown.

For the second theoretical approximation to $H(k,\phi)$ we need the Bogoliubov-Born-Green-Kirkwood-Yvon-hierarchy equation which relates $g(r)$ exactly to $g_3(\mathbf{r},\mathbf{r}',\mathbf{r}'')$, i.e.,[20]

$$\frac{d}{dr}g(r) = g(\sigma)\delta(r-\sigma) + n\sigma^2 \int d\hat{\sigma}\,\hat{\sigma}\cdot\hat{\mathbf{a}}\, g_3\left(\frac{\sigma\hat{\sigma}}{2}, \frac{-\sigma\hat{\sigma}}{2}, \frac{\sigma\hat{\sigma}}{2} - r\hat{\mathbf{a}}\right) , \tag{9}$$

where $\hat{\sigma}$ and $\hat{\mathbf{a}}$ are unit vectors. Then from the spatial Fourier transform of this equation and Eqs. (1) and (5), one finds straightforwardly that

$$H(k)=\int_0^{\pi/2} d\phi\, w(k,\phi)H(k,\phi) \ , \tag{10}$$

with

$$w(k,\phi)=\frac{-8\pi\sigma^2}{kf(k/2)}\sin\phi\cos\phi\sin\left[\frac{k\sigma}{2}\cos\phi\right] , \tag{11}$$

$$H(k)=2\frac{[1-ng(\sigma)f(k)]S(k)-1}{n^2 f(k/2)S(k)} , \tag{12}$$

and

$$f(k)=-4\pi\sigma^2 j_1(k\sigma)/k \ , \tag{13}$$

so that $H(k)$ is expressed in terms of pair correlation functions only. Since

$$\int_0^{\pi/2} d\phi\, w(k,\phi)=1 \ , \tag{14}$$

for all k, it follows from Eq. (10) that $H(k,\phi)\simeq H(k)$ when $H(k,\phi)$ depends very weakly on ϕ. This is the second approximation we study, i.e., $H(k,\phi)=H(k)$ for all k and ϕ. We find for all four densities that $H(k)$ describes $H(k,\phi)$ excellently for $k\sigma<5$, reasonably well for $5<k\sigma<7$, and poorly for $k\sigma>7$. This is illustrated for $n^*=0.884$ in Fig. 1, where also the $H(k)$ are shown.

We conclude from the foregoing that at high densities $H(k,\phi)$ can be represented perfectly by $H(k)$ for $k\sigma<5$, reasonably well both by $H(k)$ and $H_{\mathrm{KSA}}(k,\phi)$ for $5<k\sigma<7$, and reasonably well by $H_{\mathrm{KSA}}(k,\phi)$ for $k\sigma>7$. We remark that the region $5<k\sigma<7$ is the relevant k region in the extended mode-coupling-theory calculations. Therefore, the conclusions which have been drawn on the basis of the approximation $H(k,\phi)\simeq H(k)$ (Ref. 1) and on the basis of the approximation $H(k,\phi)\simeq H_{\mathrm{KSA}}(k,\phi)$ (Refs. 2 and 5) are both supported by the present MD simulation results.

TABLE I. The coefficients a_{il} and b_{il} in Eq. (7) for $X_{il}(n^*)$ obtained from Eq. (6) for $H(k,\phi)$ by a least-squares fitting procedure.

l	i	a_{il}	b_{il}
0	0	10.90	43.8
0	2	24.45	128.2
0	4	13.18	30.21
0	6	16.23	150.7
0	8	−24.01	−225.4
0	10	17.70	192.6
2	2	−1.28	−29.75
2	4	8.22	10.79
2	6	−0.71	−13.66
2	8	15.21	104.9
2	10	−21.44	−129.3
4	4	2.64	44.6
4	6	3.90	−74.2
4	8	6.11	139.3
4	10	−5.23	−180.4
6	6	8.51	61.2
6	8	2.39	−41.9
6	10	6.40	95.8
8	8	12.58	89.6
8	10	4.97	33.4
10	10	10.47	70.1

Finally, we note that $H(k,\phi)$ could also have been determined by Monte Carlo (MC) computer simulations, fixing two particles at contact with each other, rather than by MD simulations as was done here. Although explicit MC simulations are simpler to perform than MD simulations we estimated that the actual computer time is about the same for both cases when one requires equal accuracy.

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