Monte Carlo simulation results for the full pair correlation function of the hard dumbell fluid

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An ultimate goal of the equilibrium statistical mechanical study of molecular fluids is the determination of the full pair correlation function \( g(R, \Omega) \), since this function provides complete information on the system. However, this is not a simple task, since \( g \) is a function of at least five variables (in the case of linear molecules) and it is therefore practically impossible to determine it completely, even by computer simulation.

There are, in principle, two ways of obtaining information on \( g(R, \Omega) \) from computer simulations. The most frequently used method is to compute coefficients of the spherical harmonic expansion of \( g \). However, it is known that this expansion is only slowly convergent and provides a poor means of reconstructing \( g \), in particular at small separations, especially for hard-body molecular fluids. Consequently, this approach is of limited value. The other method is to compute \( g \) for some fixed angular variables, \( g = g_\Omega \). This is not a trivial matter, especially at small separations, and only one simulation of this type for a hard body system has been reported: simulations of the hard spherocylinder fluid due to Nezbeda [1]. He found that for the crossed and T-shaped orientations, \( g_\Omega \) was monotonically decreasing for distances approaching the separation of closest approach, \( r \rightarrow r_c(\Omega) \). However, he reported some problems with the evaluation of \( g_\Omega \) for the parallel orientation, obtaining an apparent peak near contact. Resummation of the spherical harmonic expansion, both for hard spherocylinders and hard dumbells, yields a result for \( g_\Omega \) that exhibits a peak near contact for all orientations considered.

The only theoretical approach currently available for computing \( g_\Omega \) for hard body molecular fluids is by means of perturbation theory. The most successful
of these, the RAM theory proposed independently by Smith [2] and by Perram and White [3], predicts a monotonic rise of \( g_\Omega \) to its value at contact as \( r \to r_c(\Omega) \) for both the hard dumbell fluid and the hard spherocylinder fluid at these orientations.

It is the purpose of this note to investigate carefully the behaviour of \( g_\Omega \) for the hard dumbell fluid at a number of orientations by means of computer simulations, especially in the region \( r \to r_c(\Omega) \).

In the course of the simulation, the numbers of pairs of molecules, \( N_i \), at a given orientation are stored in radially spaced bins of small angular volume. One must consider a small angular volume element centred at the desired angular configuration and generate very long Monte Carlo (MC) chains in order to obtain reasonable statistics, especially at short distances.

The function \( g_\Omega \) is evaluated from the relation

\[
N_i = N \rho g_\Omega \Delta V_i, \tag{1}
\]

where \( N_i \) is the number of molecular pairs in the configurational volume element \( \Delta V_i \), \( N \) is the total number of particles in the system and \( \rho \) is the number density. \( \Delta V_i \) is given by

\[
\Delta V_i = \int \frac{d\mathbf{r}}{(V_\Omega)} \int d\mathbf{\omega}_1 \, d\mathbf{\omega}_2, \tag{2}
\]

where \( V_i \) and \( V_\Omega \) are translation and orientation elements, respectively, defining the slice through the total \( g(\mathbf{r}, \mathbf{\omega}_1, \mathbf{\omega}_2) \). More specifically, for linear molecules we have

\[
\Delta V_i = \frac{1}{2} \int dr \, r^2 \, d\Omega \\
= \frac{1}{2} \int_{r_i-\Delta r}^{r_i+\Delta r} \int_{\theta_i-\Delta \theta}^{\theta_i+\Delta \theta} \int_{\phi_i-\Delta \phi}^{\phi_i+\Delta \phi} \sin \nu_1 \, d\nu_1 \int_{\theta_i-\Delta \theta}^{\theta_i+\Delta \theta} \int_{\phi_i-\Delta \phi}^{\phi_i+\Delta \phi} \sin \nu_2 \, d\nu_2 \int d\phi. \tag{3}
\]

\( \theta_j \) is the polar angle of molecule \( j \) with respect to the line joining the molecular centres and \( \phi_{12} \) is the azimuthal angle. \( \Delta \theta \) and \( \Delta \phi \) are fixed angular intervals used in the simulation. For molecules not possessing a hard core, the evaluation of \( \Delta V_i \) from (3) is relatively straightforward. A problem exists in the hard core case, since the orientational volume element \( V_\Omega \) may depend on \( r_i \).

Due to the high cost of computer experiments of this type, we investigated the hard dumbell fluid at \( L/\sigma = 0.6 \) at one density only, \( \rho \sigma^3 = 0.5 \). Using the usual Monte Carlo method with 144 particles in the box and starting from the perfect crystalline structure, \( 1.8 \times 10^8 \) configurations were initially generated to melt and disorder the system thoroughly. In order to avoid problems with the bottle-neck effect [4], the random walks in orientation space were accomplished in the manner proposed recently by Nezbeda [1] (we refer to this paper for further technical details of the simulation). Finally, eighteen million \( (18 \times 10^8) \) configurations were generated, with statistics obtained over each 500 configurations.

The quantities \( N_i \) in equation (1) for the crossed \( (\theta_j = \phi_{12} = \pi/2) \), parallel \( (\theta_j = \pi/2, \phi_{12} = 0 \text{ or } \phi_{12} = \pi) \) and T-shaped \( (\theta_1 = \pi/2, \theta_2 = 0) \) orientations, respectively, were computed. The fixed angular intervals were set to \( \Delta \theta = \Delta \phi = \pi/18 \). The counts in the radial bins for the evaluation of \( g_\Omega \) were the order of \( 10^8 \) to \( 10^4 \). The smallest value was about 600, corresponding to the bin at the smallest separation. These numbers guarantee an overall accuracy of about 5 per cent for small \( r \).
At large separations, the appropriate volume element obtained from equation (3) is
\[ \Delta V_i = \frac{S}{2} r_i^2 \Delta r \Delta \phi \prod_{j=1}^{2} \left[ \frac{1}{2} (\Delta \theta)^2 \cos \theta_j + \Delta \theta \sin \theta_j \right], \] (4)
where \( S \) is the symmetry number. However, at smaller separations, the volume element decreases, due to the fact that the molecules may overlap within the volume element given by equation (4). The actual accessible volume may be computed from
\[ \Delta V_i = \int_{r_i - \Delta r}^{r_i + \Delta r} dr \int \sin \theta \frac{dv_1}{r} \exp \left\{ -\beta u(r, \theta_1, \theta_2, \phi_{12}) \right\} \int_{\phi_1 - \Delta \phi}^{\phi_1 + \Delta \phi} \sin \phi_2 \frac{dv_2}{r} \int_{\phi_2 - \Delta \phi}^{\phi_2 + \Delta \phi} d\phi, \] (5)
where \( \exp \left\{ -\beta u \right\} \) is the Boltzmann factor, which is zero when the molecules overlap and unity when they do not. As \( r_i \) decreases towards its contact value, \( \Delta V_i \) approaches zero, since the molecules are 'locked' at this distance, which occurs in the crossed orientation. We have computed \( \Delta V_i \) numerically from equation (5) using an adaptive product Simpson rule quadrature routine.

We show our results in figures 1–3. The crosses show the (incorrect) results obtained from equation (1) using the volume element giving by equation (4). These numbers underestimate the correct results at small \( r \), since the volume element \( \Delta V_i \) is too large. The dashed curves show the results of resumming the spherical harmonic expansion coefficients of Streett and Tildesley [5]. It is seen that these lie close to the incorrect results discussed above at small separations. These results should be expected to be rather poor at small distances, since

Figure 1. Radial slice through the full pair correlation function \( g(R, \Omega) \) surface of hard dumbbells in the crossed orientation. Full circles and crosses are the computer simulation results with volumes evaluated from equations (5) and (4), respectively. The dashed line is the resummation of the spherical harmonic expansion.
$g_{n_{1,2,3}}(r)$ approaches zero exactly as $r$ approaches its contact value in the crossed orientation. The poor behaviour of the expansion is a result of the fact that $g(R, \Omega)$ has an angular dependent step function discontinuity.

For all three orientations considered, $g_{n}$ rises monotonically to its contact value at small distances. This is in agreement with the corresponding results for hard spherocylinders [1] at the T-shaped and crossed orientations. For the parallel configuration, the rise is still monotonic, but apparently passes through an inflection point before finally rising to its contact value. Re-examination of the hard spherocylinder results in this configuration (using the correct volume element $\Delta V_i$ obtained from equation (5)) indicates a roughly similar behaviour. Thus, for both fluid models, the behaviour is qualitatively similar at small separations. This is in agreement with the predictions of the RAM theory [6, 7].

The contact values for $g_{n}$ in the parallel and T-shaped orientation are roughly similar in magnitude, whereas the corresponding value for the crossed orientation is much larger. The general tendency for the contact configuration to be severely restricted in angular movement (to be locked) increases in the order parallel, T-shaped, and crossed. The contact values for $g_{n}$ increase in the same order. The crossed orientation, which is the most severely restricted in the above sense, exhibits much larger values near contact than do the other two orientations. However, inspection of figures 1–3 show that over the range of distances common
to the parallel and crossed orientations \((r > 1)\), the \(g_\Omega\) values appear to be roughly similar. This indicates that \(g_\Omega\) does not depend strongly on the azimuthal angle, at least for \(\theta_\parallel \approx \pi/2\).

We have resolved the difficult problem of calculating the pair correlation function of hard non-spherical molecular fluids at short distances. In the course of our simulations, we also calculated the site-site correlation function and several spherical harmonic coefficients of \(g(R, \Omega)\). Tables of our results are available upon request from the second or third author.

We believe that our results are very accurate, especially in the case of \(g_\Omega\) at short distances, and they should hence provide unambiguous tests of any proposed theories.

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References