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Abstract

C The triplet correlation function for high density fluid argon was calculated by the Monte Carlo method with a truncated cube as the basic box. This new box provides us a longer range for the triplet function than the conventional cubic box using the same number of particles; it also provides us better statistics for the same computing time. The MC $g^{(3)}$ at $\rho^* = .80$ was found to be very different from the SA prediction. Upon substituting both MC $g^{(2)}$ and SA $g^{(2)}$ into the Born-Green equation, it is found that the result is fair for MC $g^{(3)}$ but very poor for the SA one. We conclude that the Superposition Assumption is poor at high density.

I. Introduction

Recently, several experimental studies¹⁻³ of the triplet correlation function were published. They all concluded that the true triplet function is quite different from the prediction of the Superposition Assumption. These conclusions are in agreement with the theoretical computer calculations by either the molecular dynamics⁴ or the Monte Carlo⁵ method.

In previous calculations with either method, the basic box has always been chosen to be a cube. N particles were then placed randomly inside, and the periodical boundary conditions were added so that the extended system could simulate the liquid state. The advantage of the cubic shape is that the process of locating the eight images of a certain particle inside a simple cubic boundary takes very little computing time. But one pays a price in evaluating the triplet function, in that the cubic shape provides a very low percentage of 'useful' triplets. This can be understood as follows. Suppose we use a cube of size S ; then the range* of the pair function is $S/2$, which is the radius of the largest sphere that can be fitted into the cube. Thus among the N particles that are inside the cube, only those

* Here we shall disregard the boundary effect reported in our earlier paper⁵. This boundary effect reduces the range of the triplet function to about $S/3$, but does not seem to change the range of $g(r)$.

52.4% which are also inside that sphere contribute toward the evaluation of $g(r)$, and the others that are in the eight corners of the cube are of no use for this purpose. In the case of the triplet function this problem is triply compounded because for a triplet to be 'useful' all three sides must be less than $S/2$. Thus only 14.4% of all possible triplets in a given computed configuration can be accepted.

This percentage of useful triplets can be increased to about 40% if a truncated dodecahedron (TDH) shaped box is used as the basic box. This TDH box has the same shape as the Wigner-Seitz cell of a fcc lattice. Besides the advantage of increasing the percentage of useful triplets, a TDH box having the same volume as a cube can enclose a larger sphere, whose radius is $2^{1/6}$ times greater than that of the cubic one. In other words, the ranges of $g(r)$ or $g^{(3)}$ using a TDH box with N particles are the same as those using a cube with $N\sqrt{2}$ particles. There is only one disadvantage associated with the TDH box-- whenever one particle moves out of the box, one of its images will move in through the opposite surface. The process of looking for this particular image is very simple for a cube because of its x, y, z symmetry. But for a TDH box not only has the number of images been increased to 12, but we also lose this simple symmetry. This difficulty can be alleviated somewhat by restricting ourselves to the three images in the positive x -,

y-, z-direction whenever we only need the magnitude of the relative distances. The final program runs two times slower than the cubic version, but each configuration now provides three times more useful triplets. This represents a net gain of about 50%. Thus by using the TDH box, we not only extend the range of $G(r)$ and $g^{(3)}$ using the same number of particles, but also count more triplets in a given length of computing time.

II. Results

The triplet correlation function $g^{(3)}$ for argon has been previously obtained by molecular dynamics method⁴ at $\rho^* = .807$ and $T^* = .79$ and by the Monte Carlo method⁵ at $\rho^* = .45$ and $T^* = 1.552, 1.194, .776$ respectively. In all of these calculations a Lennard-Jones type potential with the usual argon parameters ($\epsilon/k = 119.8$ K, $\sigma = 3.405$ Å) were used. Our present calculation is at $\rho^* = .80$ and $T^* = .719$, very close to the conditions set in reference 4. 160 particles were placed randomly inside a TDH box, and a chain of 77000 configurations were generated in 46 minutes on the CDC-6600 at the Courant Institute of Mathematics, New York University.

A relatively short run was made to check the boundary effect to see whether it would be the same for the TDH box as for the previous cubic box. The resultant $g(r)$ and the cubic root of the symmetric triplets $(g^{(3)}(r,r,r))^{1/3}$ are listed in Table 1. It is found that the distance r_B , i.e.,

the maximum range of $g^{(3)}$, is roughly $(2/3) S$, similar to the cubic case.

The values of the triplet function $g^{(3)}(r,s,t)$ for r , s , and t less than r_B are listed in Table 2. Values of the Monte Carlo $g(r)$ and the cube roots of the symmetric triplet $g^{(3)}(r,r,r)$ are listed in the second and third column, respectively. A few asymmetric triplets are listed in column 4 to 6, and the ratios of these to the SA are listed in the last three columns. By comparison with our previous work⁵, it is observed that the SA is less adequate at high density than at low density. At high density the SA predictions for the triplet function differ from the MC results by as much as 70%. For triplets (r,s,t) , for which r , s , and t are all less than 1.2σ , the SA always overestimates the frequency of their occurrence in agreement with Rahman's result⁴; but for these with at least one side greater than 1.2σ this is not always true (first neighbor distance is about 1.1σ in present case). Note that at low density the above conclusions are not true⁵.

The MC $g^{(3)}$ and the SA $g^{(3)}$ constructed from the MC $g(r)$ are substituted into the Born-Green equation⁶ together with the Lennard-Jones potential to see whether they satisfy the BG equation identically. Previously we observed⁶ excellent agreement for the MC $g^{(3)}$ and poor agreement for the SA at low density. Now at high density the agreement for the MC $g^{(3)}$ is only fair but for the SA one it is disastrous, as

shown in Table 3. The reason is the following. At high density the oscillation in the correlation functions are more pronounced and extend to a farther distance than at low density. With a system of 160 particles at $\rho^* = .80$, the function $g^{(3)}$ can be obtained only for all r 's less than $r_B = 2.212\sigma$. But at this value of r both $g(r)$ and $g^{(3)}$ are still oscillating strongly ($g(r) = 1.137$ at $r = r_B$). Thus we can not expect the MC $g^{(3)}$ with such a finite range to satisfy the BG equation as well as the low density MC $g^{(3)}$ did. For comparison, at low density $\rho^* = .45$, $g(r)$ is a few percent from unity at the boundary.

Since we would expect the finite range r_B to have similar influence on both the MC $g^{(3)}$ and the SA $g^{(3)}$, it is clear that the disastrous SA results can not be blamed on the finite range alone. If we recall that the SA deviates from the MC $g^{(3)}$ systematically at small r , and that the derivative of the pair potential is very large there, we clearly see why the SA values and the MC values for the BG integral are so much different. Thus we believe one should not use the Superposition Assumption at high densities.

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Table 1. Test for r_B $\rho^* = .80$, $T^* = .719$

r/σ	$g(r)$	$[g^{(3)}(r, r, r)]^{1/3}$
.948	.148	0.
1.022	1.784	1.543
1.097	2.792	2.719
1.171	2.160	2.174
1.245	1.472	1.526
1.319	1.027	1.045
1.393	.830	.910
1.467	.629	.605
1.541	.601	.544
1.615	.611	.536
1.689	.695	.734
1.763	.785	.784
1.837	.948	1.069
1.911	1.112	1.184
1.985	1.202	1.239
2.059	1.280	1.269
2.134	1.249	1.222
$r_B \rightarrow$ 2.208	1.140	1.171
2.282	1.016	1.108
2.356	.925	1.053
2.430	.869	1.059
2.504	.841	1.033
2.578	.867	1.115
2.653	.900	1.162
2.727	.957	1.296
2.801	.994	1.404
2.875	1.045	1.482
2.949	1.079	1.580
3.023	1.074	1.600
3.097	1.042	1.562
3.171	1.011	1.583
3.245	.972	1.551

Table 2. Symmetric and asymmetric triplets for argon at $\rho^* = .80$, $T^* = .719$

r/σ	$g(r)$	$(g^{(3)})^1/3$	$R_s(r) = \frac{g^{(3)}(s,s,r)}{g(s)^2}$			$\frac{R_s(r)}{g(r)} = \frac{g^{(3)}(s,s,r)}{SA}$		
			$s/\sigma = .987$	$s/\sigma = 1.108$	$s/\sigma = 1.272$	$s/\sigma = .987$	$s/\sigma = 1.108$	$s/\sigma = 1.272$
.946	.090	.0	.026	.075	.081	.291	.836	.908
.987	.730	.596	.397	.617	.746	.544	.845	1.022
1.027	1.953	1.754	1.415	1.727	1.941	.725	.885	.994
1.068	2.737	2.555	1.657	2.408	2.933	.605	.880	1.072
1.108	2.821	2.752	1.968	2.620	2.848	.698	.929	1.010
1.149	2.424	2.409	2.229	2.238	2.509	.920	.923	1.035
1.190	1.951	1.969	1.753	1.929	2.176	.899	.989	1.116
1.231	1.570	1.686	1.574	1.578	1.736	1.003	1.005	1.106
1.272	1.253	1.317	1.087	1.270	1.455	.867	1.013	1.161
1.313	1.033	1.072	.915	1.086	1.179	.886	1.052	1.142
1.354	.866	.877	.823	.908	.999	.950	1.048	1.153
1.395	.752	.764	.785	.788	.797	1.045	1.049	1.061
1.436	.687	.729	.572	.719	.751	.832	1.046	1.092
1.477	.635	.659	.676	.679	.705	1.065	1.071	1.110
1.517	.617	.587	.836	.688	.650	1.355	1.115	1.054
1.558	.610	.666	.792	.670	.667	1.298	1.099	1.095
1.599	.610	.551	.793	.713	.576	1.301	1.169	.944
1.640	.644	.550	.750	.755	.605	1.164	1.173	.938
1.681	.689	.654	1.083	.826	.628	1.571	1.199	.912
1.722	.739	.696	1.216	.915	.678	1.646	1.238	.917
1.762	.810	.853	1.149	1.034	.772	1.418	1.276	.953
1.803	.896	.981	1.005	1.071	.858	1.122	1.196	.958
1.844	.970	1.081	.971	1.109	.885	1.001	1.144	.913
1.885	1.051	1.120	.849	1.184	1.020	.807	1.126	.970
1.925	1.117	1.169	.878	1.205	1.099	.786	1.079	.984

Table 2. ntinued

1.966	1.181	1.240	1.657	1.141	1.168	1.403	.967	.989
2.007	1.209	1.226	1.946	1.058	1.265	1.610	.875	1.046
2.048	1.244	1.248		.947	1.221		.761	.982
2.089	1.259	1.247		.901	1.197		.716	.951
2.130	1.246	1.258		.927	1.184		.743	.950
2.171	1.193	1.214		.967	1.057		.811	.886
2.212	1.137	1.186		1.037	.986		.912	.867

Table

The Born-Green integral $\frac{\pi \rho_0}{r^2} \int_0^\infty \frac{d\phi}{dt} \int \frac{g^{(3)}(r,s,t)}{g(r)} (s^2 - r^2 - t^2) s ds$ evaluated with

MC $g^{(3)}$ and SA $g^{(3)}$ for fluid argon at $\rho^* = .80$, $T^* = .719$, compared with the exact result of $\frac{d\phi}{dr} - \frac{dU}{dr}$.

BG integral by

r/σ	$g(r)$	$\frac{d\phi}{dr}$	$\frac{dU}{dr}$	Exact $(\frac{d\phi}{dr} - \frac{dU}{dr})$	BG integral by	
					SA	MC
.946	.090	-2230.	-1770.	-460.35	-51.48	-122.85
.987	.730	-1077.	- 955.4	-121.21	-56.24	-116.32
1.027	1.953	- 493.7	- 379.6	-114.14	-62.00	-108.54
1.068	2.737	- 185.3	- 105.7	- 79.55	-67.39	- 95.02
1.108	2.821	- 33.33	41.14	- 74.47	-71.83	- 86.87
1.149	2.424	41.78	128.39	- 86.61	-74.50	- 73.12
1.190	1.951	73.89	143.89	- 70.00	-73.49	- 61.21
1.231	1.570	83.83	135.32	- 51.49	-69.70	- 48.33
1.272	1.253	82.72	134.92	- 52.20	-62.88	- 36.30
1.313	1.033	76.52	111.20	- 34.67	-55.44	- 33.46
1.354	.866	68.36	100.10	- 31.74	-47.00	- 24.28
1.395	.752	59.85	72.89	- 13.04	-39.84	- 18.91
1.436	.687	51.77	47.15	4.61	-32.63	- 11.98
1.477	.635	44.46	30.46	14.00	-25.39	4.49
1.517	.617	38.18	9.13	29.05	-18.42	13.40
1.558	.610	32.60	2.76	29.84	-11.23	26.40
1.599	.610	27.81	- 12.64	40.46	- 4.07	30.79
1.640	.644	23.74	- 41.52	65.26	2.84	44.58
1.681	.689	20.29	- 43.43	63.72	10.07	58.22
1.722	.739	17.36	- 52.69	70.06	17.33	62.44
1.762	.810	14.94	- 61.62	76.56	24.52	69.63

Table 3. Continued

1.803	.896	12.84	-	58.03	70.87	32.18	70.61
1.844	.970	11.05	-	47.29	58.34	39.52	65.42
1.885	1.051	9.54	-	45.56	55.10	46.90	55.13
1.925	1.117	8.28	-	35.48	43.76	54.01	44.89
1.966	1.181	7.18	-	26.87	34.05	58.96	31.65
2.007	1.209	6.24	-	12.42	18.66	56.47	21.81
2.048	1.244	5.44	-	14.63	20.07	45.27	13.59
2.089	1.259	4.75	-	1.14	5.89	27.20	- 2.60
2.130	1.246	4.15		15.35	- 11.20	6.95	- 17.75
2.171	1.193	3.64		31.38	- 27.73	-10.76	- 24.62
2.212	1.137	3.20		24.51	- 21.31	-23.45	- 31.26