MONTE CARLO SIMULATIONS OF THREE DIMENSIONAL HARD PARTICLE FLUIDS

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Abstract

Computer modeling is an important skill for engineering and science students to acquire. Monte Carlo simulations of three dimensional fluids provide an opportunity for students to develop their computer skills while deepening their knowledge of the behavior of materials. Using the Maple software package, students can easily create animations of particle movements.

Introduction

In previous publications in this journal, Lasky and Bishop [1] and Balady and Bishop [2] used Monte Carlo methods to simulate homogeneous, two dimensional hard disk fluids. Balady and Bishop [2] computed the equation of state from the pair correlation function [3]. Merriman and Bishop [4] and Havlicek and Bishop [5] investigated binary mixtures of disks for a variety of disk diameter ratios and compositions. In this work we examine homogenous fluids in three dimensions. Our results are compared to other simulations and theory.

A hard sphere system contains N particles, each with a diameter of σ, in a box with sides Lx , Ly and Lz. The number density, ρ, is given by

$$\rho = N / (Lx\ Ly\ Lz) \qquad (1)$$

In all the simulations, Lx = Ly = Lz. The systems are started in either a face-centered cubic lattice, fcc, or a cubic lattice [6]. A fcc lattice has 4 particles per unit cell so $N = 4n^3$ whereas a cubic lattice has 1 particle per unit cell and $N = n^3$. Here n is an integer. Figures 1A and 1B show the starting lattices when n = 2 (fcc) and n = 3 (cubic), respectively, when $\rho = 0.40$.

The equation of state [7] is given by the compressibility factor, $Z = P/\rho k_B T$, where P is the pressure, k_B is Boltzmann's constant and T is the absolute temperature. In an ideal gas the particles do not interact and then Z = 1. In the case of the homogeneous hard sphere fluid, Z is related [7] to the pair correlation function at contact by

$$Z = 1 + \rho\ (2\pi /3)\ \sigma^3 G(\sigma) \qquad (2)$$

Here, σ is the contact diameter, the separation between the centers of the particles when touching. The pair correlation function at contact is $G(\sigma)$. A pair correlation function [3], G(R**),** measures the relative distribution of particles at a distance |**R**| from the center of a reference particle.

Method

The details of our MC computer simulation are contained in the papers of Lasky and Bishop [1] and Merriman and Bishop [2]. The particles are started at positions in a lattice and then moved by the standard Metropolis Monte Carlo method [8-12] until a random, equilibrated state is achieved. A move is rejected whenever a particle overlaps another particle; e.g. the separation between their centers becomes less than σ. If the new position is not accepted, the test particle remains at its current location and the next particle is selected for a test move. Once all N particles have been tested a single pass (or MC step) is complete.

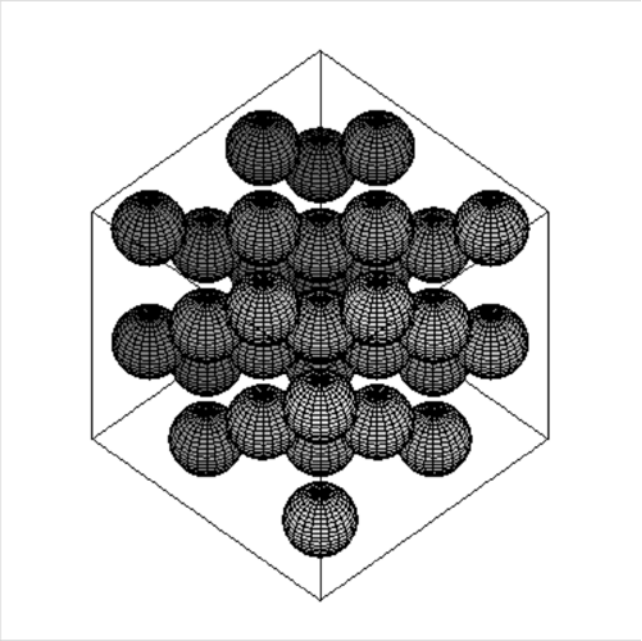

Figure 1A: FCC Lattice.

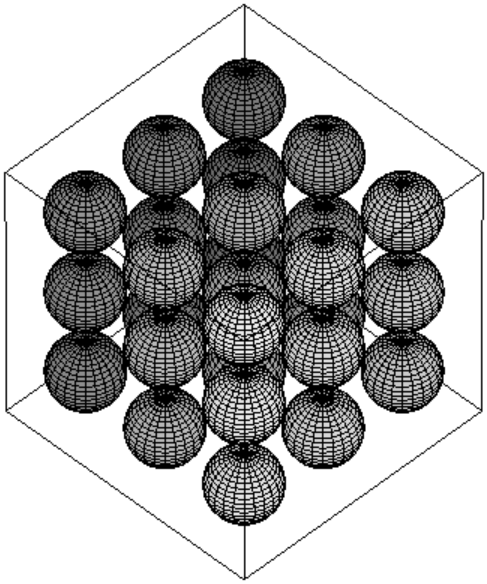

Figure 1B: Cubic Lattice.

The Maple software package allows one to easily create graphics snapshots indicating how the particles change their configuration. At the starting lattice stage and after every fixed interval of passes (a number specified by the user) a snapshot can be generated and written to a file. Using Farley and Tiffany's four step method [13], each snapshot can then be used to make an animation.

Results

The simulation has been developed by using the gnu C compiler on a PC with the Linux operating system. Production runs were generated for 12,000,000 MC steps and 2,000,000 steps were discarded. The sampling interval was set at 2,000 steps so that there were 5,000 equilibrated samples to average over.

The pair correlation function is computed by averaging over both the appropriate number of particles and the number of equilibrated samples. The details of the pair correlation function calculations are contained in the earlier paper by Lasky and Bishop [1]. Figure 2 presents G(R) for $\rho = 0.22$, 0.49 and 0.70 starting from a cubic lattice when N = 343. The pair correlation function for the lowest density, 0.22, displays no long range order but as the density is increased, a secondary peak develops which indicates the presence of long range order.

The equation of state has been obtained by finding the value of the pair correlation function at contact. This is determined by fitting a line to the first peak of the pair correlation functions and then extrapolating to the appropriate contact value, as illustrated in Havlicek and Bishop [5]. Once the contact value has been determined, the equation of state is found from Eq. 2. The Z values for all the systems studied are contained in the Table. Zcs are the theoretical values predicted by the Carnahan and Starling equation of state [14]:

$$Zsp = (1 + \eta + \eta^2 - \eta^3) / (1 - \eta)^3 \qquad (3)$$

Here η is the packing fraction, which in three dimensions is related to the number density by

$$\eta = \rho (\pi/6) \sigma^3 \qquad (4)$$

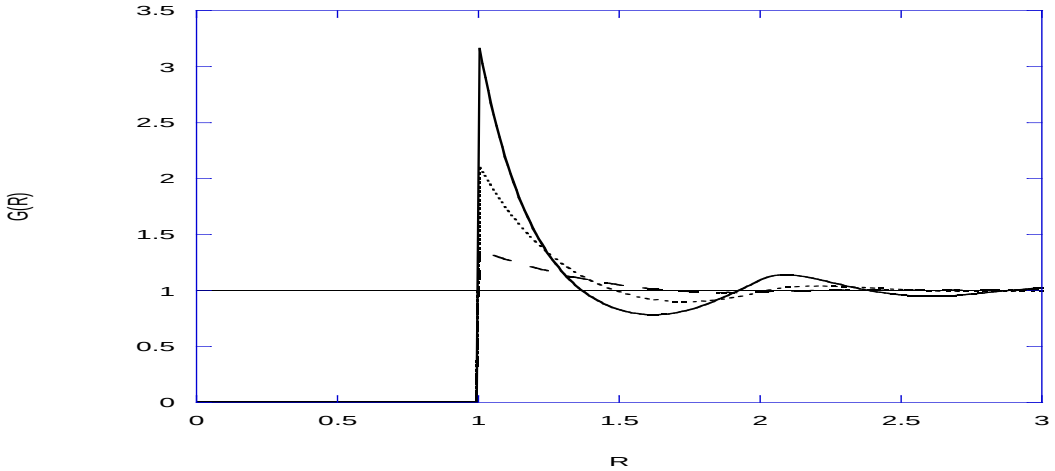

Figure 2: The pair correlation function for different densities:
$\rho = 0.22$ dashed line, $\rho = 0.49$ dotted line, and $\rho = 0.70$ solid line.

Table: Equation of State Data.

ρ	η	Zcs	Zws	Zblw	Zmc64	Zmc343	Zmc108
0.00	0.000	1.000					
0.04	0.021	1.088	1.089				
0.10	0.052	1.240	1.241	1.240			
0.13	0.068	1.325	1.329				
0.18	0.094	1.483					1.484
0.22	0.115	1.627	1.633		1.630	1.629	
0.25	0.131	1.745	1.753	1.750			
0.30	0.157	1.967		1.968	1.974		
0.37	0.194	2.335	2.343				
0.40	0.209	2.518	2.526	2.522			2.529
0.43	0.225	2.718	2.725				
0.45	0.236	2.862		2.867	2.884		
0.49	0.257	3.177	3.181		3.197	3.184	
0.51	0.267	3.350			3.381		
0.52	0.272	3.441	3.442				
0.57	0.298	3.942					3.954
0.60	0.314	4.283	4.295	4.295			
0.62	0.325	4.531			4.573		
0.65	0.340	4.936	4.949	4.950			
0.70	0.367	5.710	5.729	5.727	5.774	5.714	
0.72	0.377	6.061			6.112		
0.75	0.393	6.636	6.657	6.655			
0.80	0.419	7.750	7.766	7.770			
0.82	0.429	8.258					8.240

Also listed in the Table are Zws which are the values found by Wu and Sadus [15] for N = 500 or 1372 starting from an fcc lattice using Monte Carlo methods and Zblw which are the values determined by Bannerman, Lue and Woodcock [16] for N = 1098500 or 108000 starting from either an fcc or a cubic lattice using molecular dynamics, MD, methods. Zmc64 and Zmc343 are the new MC results when N=64 and N=343 starting from a cubic lattice and Zmc108 are the MC results for N=108 starting from a fcc lattice (see Figures 1A and 1B). In all cases the data are consistent with each other within 1%. Our new data are in agreement with the theoretical predictions for the equation of state. Figure 3 presents the equation of state, Z, as a function of density. All the data are in excellent agreement with the Carnahan Starling theoretical equation. The Table indicates that there is no significant difference between the cubic and fcc lattice MC results for the range of densities examined.

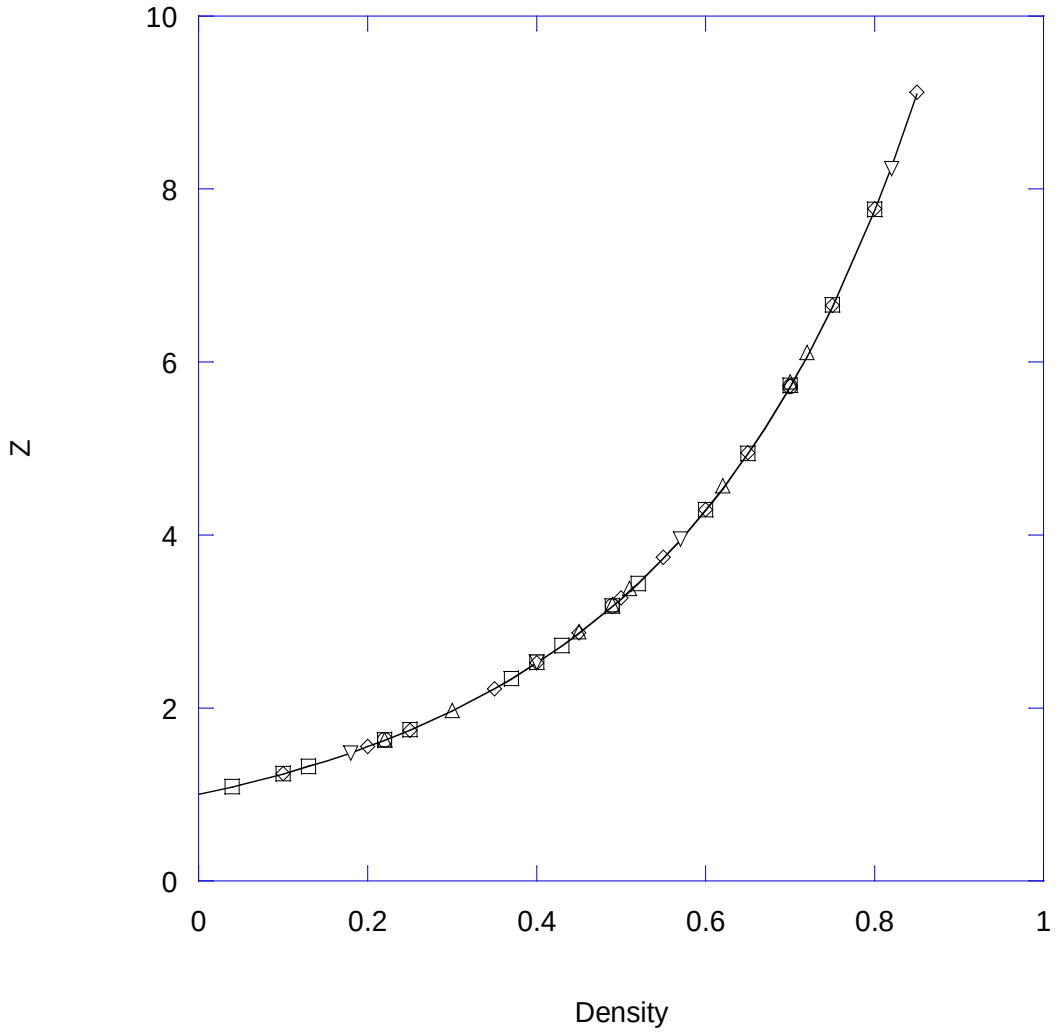

Figure 3: The equation of state, Z, as a function of the density. The solid line is the Carnahan and Starling theoretical equation (Eq. 3). The squares are the Wu and Sadus [15] MC data and the diamonds are the Bannerman, Lue and Woodcock [16] MD data. The up triangles and circles are the current MC data for N=64 and N=343 cubic lattice systems, respectively, and the down triangles are current MC data for N = 108 fcc lattice systems.

Conclusion

We have investigated three dimensional homogenous hard sphere systems by Monte Carlo simulations. The equation of state has been computed from the contact pair correlation function. The results are in excellent agreement with other simulations and theories. There is no significant difference between initializing the simulation from the cubic or fcc lattice. Animations can be used to indicate the nature of the equilibration. Modeling projects such as the one described here provide a clear demonstration of some aspects of the behavior of materials and thus strongly enhance student understanding and intuition.

Appendix: The Manhattan College Undergraduate Research Program

Manhattan College has a long tradition of involving undergraduates in research and was one of the original members of the Oberlin 50. This is a group of undergraduate institutions whose students have produced many PhDs in engineering and science. At Manhattan College, students can elect to take an independent study course for three credits during the academic year. In addition, the College provides grant support to the students for ten weeks of work during the summer. I have personally recruited the students from my junior level course in Systems Programming. Previously published articles in this journal by Manhattan College student co-authors are a very effective recruitment tool. The students have also presented their results at a variety of undergraduate research conferences including the Hudson River Undergraduate Mathematics Conference and the Spuyten Duyvil Undergraduate Mathematics Conference.

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Marvin Bishop is a Professor in the Departments of Computer Science and Mathematics at Manhattan College. He received his Ph.D. from Columbia University, his M.S. from New York University and his B.S. from the City College of New York. His research interests include simulation/modeling and parallel processing.