

MONTE CARLO STUDIES OF HARD SPHERE SOLIDS

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Abstract

Computer modeling is an important skill for engineering and science students to acquire. Monte Carlo simulations of three dimensional solids provide an opportunity for students to develop their computer skills while deepening their knowledge of the behavior of materials.

Introduction

In a previous publication in this journal, Balady and Bishop [1] used Monte Carlo, MC, methods to simulate homogeneous three dimensional hard sphere fluids. Balady and Bishop [1] computed the equation of state from the pair correlation function [2]. In this work their simulations are extended to investigate hard sphere solids. The results are compared to other simulations and theory.

A hard particle system is characterized by a few key parameters: the number of particles, N , the diameter of the particles, σ , and the system number density, ρ . The number density is given by

$$\rho = N / (L_x L_y L_z) \quad (1)$$

Here, L_x , L_y , and L_z are the lengths of the sides of the simulation box. In all the current simulations, $L_x = L_y = L_z = a$. The systems are started in a face-centered cubic lattice [3], fcc, which has 4 particles per unit cell so $N = 4n^3$. Here n is an integer. All of the current simulations employ 108 particles.

In three dimensions the packing fraction, η , is related to the number density, ρ , by

$$\eta = \rho(\pi/6)\sigma^3 \quad (2)$$

The equation of state [4] 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 hard particles, Z is related [4] to the pair correlation function at contact by

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

Here, σ is the contact diameter or the separation between the centers of particle i and particle j when touching. The pair correlation function at contact is $G(\sigma)$. A pair correlation function [2], $G(R)$, 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 [5] and Merriman and Bishop [6]. The particles are started at positions in an fcc lattice and then moved by the standard Metropolis Monte Carlo method [7-11] 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 for movement, a single pass (or MC step) is complete.

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 a total of 12,000,000 MC steps and the first 2,000,000 steps were discarded. The sampling interval was set at 2,000 steps so that there were 5,000 equilibrated samples for

averaging. The pair correlation function was computed by averaging over both the 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 [5].

Figure 1 presents the pair correlation function at a solid, 1.15, and a fluid, 0.80, density. These functions are very different; the higher density state displays distinct peaks which are characteristic of a solid whereas the lower density system has only a small second peak.

The integral of the pair correlation function, from $R = 0$ to R_{cut} , gives [4] the occupation number, ON , or the number of particles surrounding the reference one between $R = 0$ and R_{cut} .

$$ON = 4\pi\rho \int_0^{R_{cut}} G(R) R^2 dR \quad (4)$$

It is known [12] that an fcc crystal has 12 particles in its first shell, 6 in its second shell, and 24 in its third shell. Figure 2 presents the ON values obtained from the pair correlation functions shown in Figure 1. Numerical Simpson integration has been applied to perform the integral in Eq. 4. It is clear that the data at $\rho = 1.15$ have the distinct layers characteristic of a crystal. Moreover, the ON values correspond to those expected in an fcc crystal: 12, 18 and 42. In contrast, the data at $\rho = 0.80$ have no indication of any distinct packing layers.

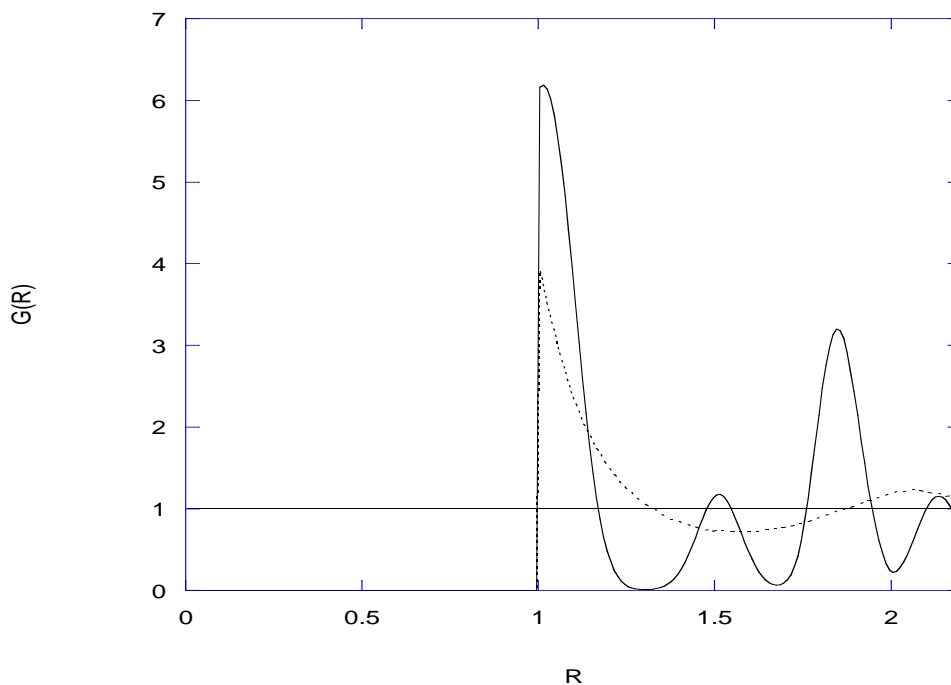


Figure 1: The pair correlation function for $\rho = 1.15$ (solid line) and $\rho = 0.80$ (dotted line).

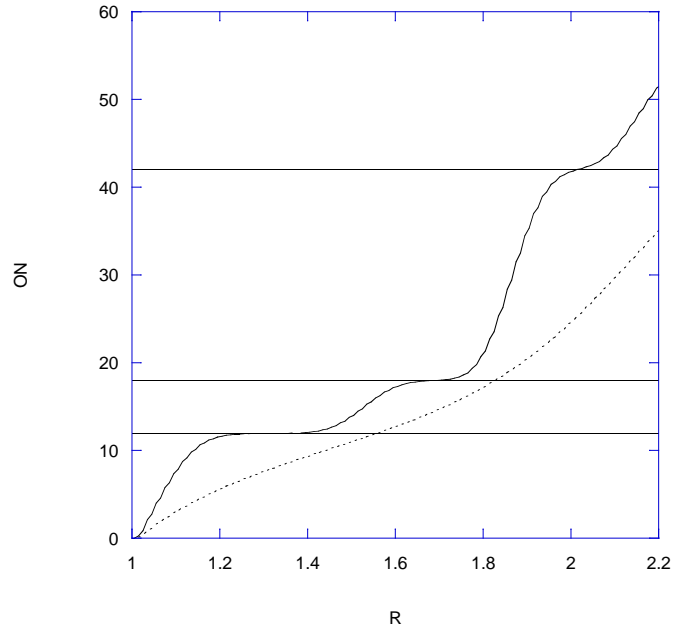


Figure 2: The occupancy number, ON, vs. the distance R from the center of the reference particle. The solid line is for $\rho = 1.15$ and the dotted line is for $\rho = 0.80$. The horizontal lines give the total numbers of particles in the fcc crystal structure layers: 12, 18 and 42.

The equation of state has been obtained by finding the value of the pair correlation functions at contact. This is determined by fitting a line to the first peak of the pair correlation function and then extrapolating to the appropriate contact value, as illustrated in Havlicek and Bishop [13]. Once the contact values have been determined, the equation of state is found from Eq. 3. The Z values for all the systems studied are contained in the Table. Zs are the theoretical values predicted by the Speedy equation of state [14] for hard spheres in the solid regime:

$$Z_s = \frac{3}{(1 - \rho/\rho_0) - 0.5921(\rho/\rho_0 - 0.7072)} \quad (5)$$

Here, ρ_0 , is the maximum density at the closest packed crystalline state.

$$\rho_0 = 2^{1/2} / \sigma^3 \quad (6)$$

Zcs are the predictions of the Carnahan and Starling equation of state [15] for hard sphere fluids;

$$Z_{cs} = (1 + \eta + \eta^2 - \eta^3) / (1 - \eta)^3 \quad (7)$$

Also listed in the Table are Zblw and Zahy which are the computer simulation values found via the Molecular Dynamics, MD, method employed by Bannerman, Lue and Woodcock [16] and Alder, Hoover and Young [17]. Zmc108 are the new MC results for $N = 108$ starting from an fcc lattice. In nearly all cases the simulation data are consistent with each other within 2%. However, it is clear that there are large differences from Zcs and better agreement with Zs as the density gets larger.

These facts are explained by Figure 3 which presents the equation of state, Z, as a function of the density. The vertical lines mark [16] the freezing density, $\rho = 0.943$, and the melting density, $\rho = 1.041$, respectively. The first few

Table: Equation of State.

| ρ | Zs | Zcs | Zblw | Zahy | Zmc108 |
|--------|--------|--------|--------|--------|--------|
| 0.800 | | 7.750 | | | 7.738 |
| 0.850 | | 9.099 | 9.119 | | 9.042 |
| 0.900 | | 10.746 | 10.763 | | 10.598 |
| 0.925 | | 11.707 | 11.722 | | |
| 0.950 | 9.436 | 12.775 | 12.791 | | 10.641 |
| 0.980 | 9.863 | 14.222 | 14.248 | | |
| 0.995 | 10.141 | 15.021 | 15.063 | | |
| 0.996 | 10.161 | 15.076 | | 10.170 | |
| 1.000 | 10.243 | 15.299 | 10.249 | | 10.233 |
| 1.050 | 11.501 | 18.473 | | | 11.552 |
| 1.052 | 11.561 | 18.617 | | 11.542 | |
| 1.100 | 13.266 | 22.514 | 13.267 | | 13.420 |
| 1.131 | 14.705 | | | 14.720 | |
| 1.150 | 15.762 | | | | 16.121 |
| 1.179 | 17.716 | | | 17.680 | |
| 1.200 | 19.468 | | 19.468 | | |

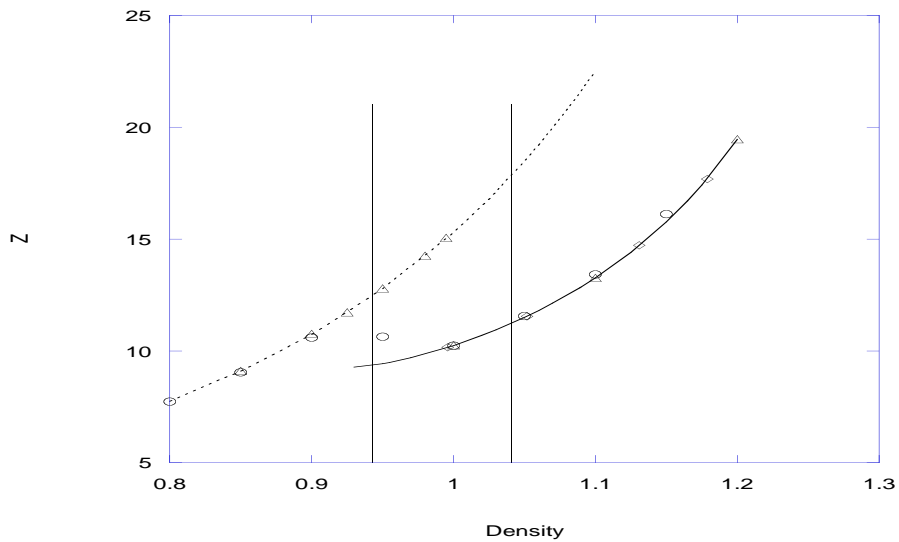


Figure 3: The equation of state, Z, as a function of the density. The solid line is the Speedy equation (Eq. 5) and the dotted line is the Carnahan and Starling equation (Eq. 7). The two vertical lines mark the freezing 0.943, and melting densities, 1.041. The up triangles are the MD data of Bannerman, Lue and Woodcock [16] and the diamonds are the MD data of Alder, Hoover and Young [17]. The circles are the current MC data for N = 108 systems.

data points at densities below the freezing density lie on the Carnahan and Starling equation of state [15] but the computer data points between the freezing and melting densities which also follow the Carnahan and Starling equation of state are in the metastable condition. The computer results at somewhat higher density values agree very well with the Speedy equation of state [14] for hard sphere solids.

Another characteristic for monitoring phase transitions is the order parameter [18]. It is defined as

$$\rho(\mathbf{k}) = (1/N) \sum_{j=1}^N \exp(-i\mathbf{k} \cdot \mathbf{r}_j) \quad (8)$$

Here, \mathbf{k} is a reciprocal lattice vector, i is $(-1)^{1/2}$ and \mathbf{r}_j is the coordinate vector of the j -th particle. The quantity, $|\rho(\mathbf{k})|$, measures the

presence of long ranged order. In the case of an fcc lattice, $\mathbf{k} = (2\pi/a)(1, -1, 1)$, where a is the unit cell edge. If the system is fully ordered, $|\rho(\mathbf{k})| = 1.0$ but in the fluid state, $|\rho(\mathbf{k})| \approx O(N^{-1/2})$.

Figures 4A and 4B present $|\rho(\mathbf{k})|$ at the densities of 0.80 and 1.15, respectively. In both cases each MC step represents 108 attempted MC moves. The horizontal line is drawn at the constant value of $(108)^{-1/2}$.

In the $\rho = 0.8$ case the order parameter first decays very quickly and then fluctuates randomly around $(108)^{-1/2}$, as expected for hard spheres in the fluid phase. However, when $\rho = 1.15$, the order parameter stabilizes at a much higher value which is the expected behavior in the solid regime.

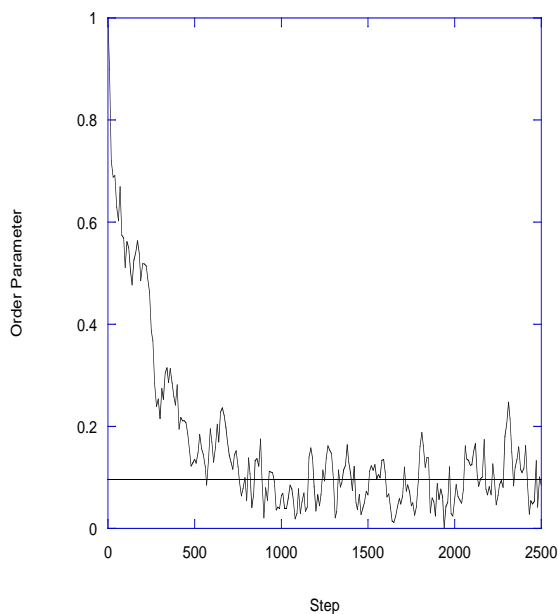


Figure 4A: The Order Parameter for $\rho = 0.8$.

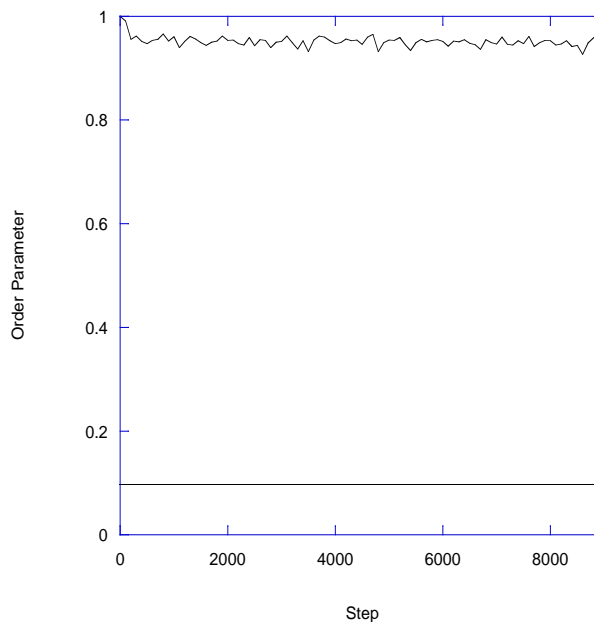


Figure 4B: The Order Parameter for $\rho = 1.15$.

Conclusion

Monte Carlo methods have been employed to investigate three dimensional hard sphere systems at higher densities. The equation of state has been computed from the pair correlation functions at contact. At lower densities the hard spheres are in the fluid phase but a transition to the solid state takes place as the density is increased. This transition is also revealed by the behavior of the occupancy number. Distinct layers, with the characteristic fcc particle values are found. In addition, the order parameter further indicates the transition from the fluid to the solid phase as the density is increased. 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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