MONTE CARLO SIMULATIONS OF TWO DIMENSIONAL HARD PARTICLE BINARY MIXTURES

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Abstract

Engineering and science students should be exposed to the techniques of computer modeling. Monte Carlo methods provide an opportunity for students to develop their computer skills while deepening their knowledge of the behavior of materials. The graphics capabilities of the Maple software package allow students to easily visualize the changes in particle configurations.

Introduction

In a previous publication in this journal Lasky and Bishop [1] presented a Monte Carlo simulation of a homogeneous two dimensional hard particle system. In this article their methods are extended to examine binary mixtures in two dimensions. A general discussion of mixtures can be found in the classic textbook of Rowlinson and Swinton [2]. A binary hard particle mixture contains two kinds of particles: N_1 particles with a diameter of σ_1 and N_2 particles with a diameter of σ_2. The key parameters of interest are the diameter ratio, $r = \sigma_1/\sigma_2$, the mole fraction of each particle, $X_i = Ni / (N_1+N_2)$ where i = 1 or 2, the total number of particles, $N = N_1 + N_2$, and the total system number density, $\rho = \rho_1 + \rho_2$, where ρ_1 and ρ_2 are the number densities of the two particles.

An important property of any material is its pair correlation function [3], G(R**),** which measures the relative distribution of particles at a distance |**R**| from the center of a reference particle. In binary mixtures there are three different kinds of pair correlation functions, $G_{11}(R)$, $G_{12}(R)$, and $G_{22}(R)$. These measure the relative distribution of small-small, small-large and large-large particles, respectively. Here small and large refer to the particles with the smaller and larger diameters respectively. The change in the shapes of these pair correlation functions indicates the underlying particle arrangements. It is well-known [4] that in the gaseous state there is little ordering and particles are distributed at random whereas in the solid state particles pack into long-ranged ordered crystals. Thus, the appearance of multiple, well defined peaks in the pair correlation function at higher densities mirrors the onset of localization behavior.

In this project the three pair correlation functions are computed for different densities. The project also illustrates how the graphics capabilities of the Maple software package can be combined with a simulation program coded in C to help students understand some of the behaviors of binary mixtures.

Method

A periodic, two dimensional hard particle binary mixture system has been studied with a Monte Carlo computer simulation [5-9] method. The different particles are started at alternative positions in a square lattice and then moved by the standard Metropolis Monte Carlo method [5] until a random equilibrated state is achieved. The square lattice determines the length, Lx, and the width, Ly, of a rectangular simulation box:

$$Lx = [\, N / \rho \,]^{1/2} \qquad (1a)$$

$$Ly = Lx \qquad (\ b)$$

Figure 1 illustrates the starting square lattice configurations when the number of each type of particle (σ_1 = 0.50 and $\sigma 2$ = 1.00) is set to 50 and both particle mole fractions are set to 0.50. We have employed Maples' Plottools package to draw the different kinds of disks centered on the coordinates of the system particles. This figure shows a large unoccupied space at the relatively low density of ρ = 0.25. The densities are measured in reduced units in which the diameter of the larger particle is taken to be one so that the reduced density of the larger particle is 0.20 and the reduced density of the smaller one is then 0.20 X (¼) = 0.05.

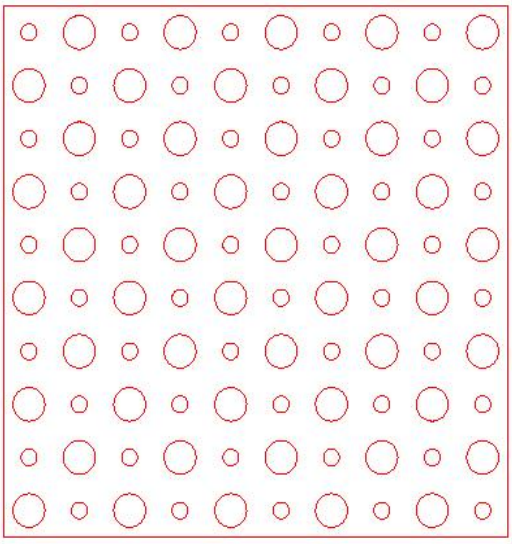

Figure 1: The starting square lattice for ρ = 0.25.

The calculation proceeds by attempting to move, in turn, each of the particles in the simulation box. To move a particle from its original location, ($X_{original}$, $Y_{original}$), two uniform random numbers, RN_1 and RN_2, between 0 and 1 are generated and used to select a new trial position,

$$X_{trial} = X_{original} + (2 * RN_1\text{-}1) * MAXDX \quad (2a)$$

$$Y_{trial} = Y_{original} + (2 * RN_2\text{-}1) * MAXDY \quad (b)$$

Here, MAXDX and MAXDY are the maximum magnitude of an allowed displacement in the X and Y directions, respectively, measured from the particle's center of mass. It is the largest possible move. In the current simulations MAXDX and MAXDY have been set to 0.50 in reduced units (relative to a particle with a diameter of 1.0). A move is rejected whenever a particle overlaps another particle; e.g. the separation between their centers becomes less than 0.50 for the small-small pairs, less than 0.75 for the small-large pairs and less than 1.0 for the large-large pairs. If the new position is not accepted, the test particle remains at its current location. The acceptance ratio, the number of accepted moves divided by the number of total moves, is monitored. The acceptance ratio was 0.74 when ρ = 0.25 and 0.41 when ρ = 0.50, reflecting the fact that at higher densities the particles are more likely to overlap when they are moved. Standard periodic boundary conditions [9] are employed. This means that if a particle is moved such that if X and/or Y becomes either less than 0 or larger than Lx or Ly, respectively, an identical particle is placed in the box at position modulo Lx and/or Ly. This procedure maintains the number of particles in the box and makes the simulation more representative of bulk matter.

Results

We have developed the simulation using the gnu C compiler on a PC loaded with the Linux operating system. First, we performed timing runs to see how the code behaves. At a density of ρ = 0.25 we ran 500 Monte Carlo steps for four different N values but always kept the mole fractions as 0.50 and the diameter ratio as 2.0. These timing results are contained in Table I.

N	Time (secs)
16	0.04
100	1.12
144	2.28
256	7.21

Table I: The timing results for different numbers of particles.

We assume that the CPU timing scales as a power law in the number of particles,

$$T(N) = A\ N^{P} \qquad (3)$$

where A, the coefficient, and P, the power, are constants. The power can be determined by taking logs in Eq. 3. to yield

$$P = \log [\ T(N2)\ /T(N1)\ ]\ /\ \log [\ N2\ /N1]\qquad (4)$$

We selected N1 = 16 and then found that the P values for 100, 144 and 256 particles are 1.82, 1.84 and 1.87, respectively. Since the main time intensive portion of the simulation is the computation in the pair correlation functions which involve averaging the number of interactions between different particle pairs, we expect that

$$T(N) \approx\ N\ (N-1)\ /\ 2 \qquad (5)$$

Hence, as N becomes large, P should be about 2.0. This prediction is supported by the data.

We then examined the effect on timing when the number of Monte Carlo steps for a fixed number of particles was altered. In these test runs, N = 100, and $\rho = 0.25$. Table II contains these timing results as the number of Monte Carlo steps is changed. It is clear from the data that the CPU time needed, T(MC steps), scales linearly with the number of MC steps:

$$T(\text{MC steps}) \approx K(\text{MC steps}) \qquad (6)$$

where K is a constant.

Steps	Time (sec)
100	0.11
1000	1.14
10000	11.3

Table II: The timing results for different numbers of Monte Carlo steps.

On the basis of these timing investigations it was decided to examine systems containing 100 particles. However, since the successive positions of the particles are not independent, it will take many Monte Carlo steps to converge from the arbitrary initial state to a representative equilibrated state. Only the equilibrated steps are employed in the final calculations. Hence, some number of steps must be discarded before the runs are continued to obtain equilibrated steps. Even after the equilibrated regime is reached there is still serial correlation between each step in the Monte Carlo process. We have addressed this problem by computing the pair correlations at fixed intervals which encompass many Monte Carlo steps. Thus, the different G(R)s are 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].

Production runs for $\rho = 0.25$ and 0.50 were generated for 6,000,000 Monte Carlo steps and 1,000,000 steps were discarded. The sampling interval was set at 250 steps so that there were 20,000 equilibrated samples to average over. Figures 2 and 3 display configuration snapshots at the end of the runs when $\rho = 0.25$ and $\rho = 0.50$, respectively. The simulation boxes have been scaled to be the same size on this page and thus the particles appear to be larger at the higher density. There is clearly more free space in which particles can move at the lower density.

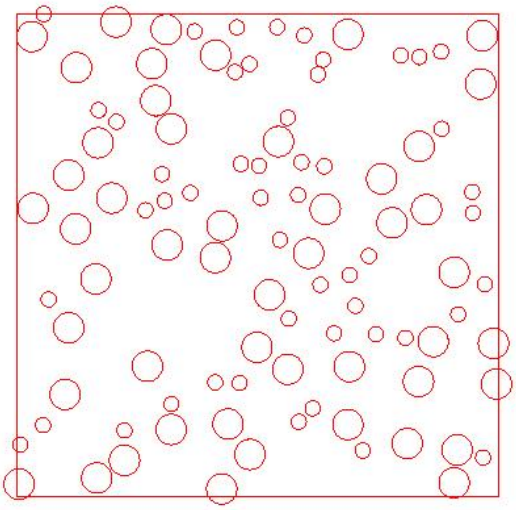

Figure 2 Final Configuration, when ρ = 0.25.

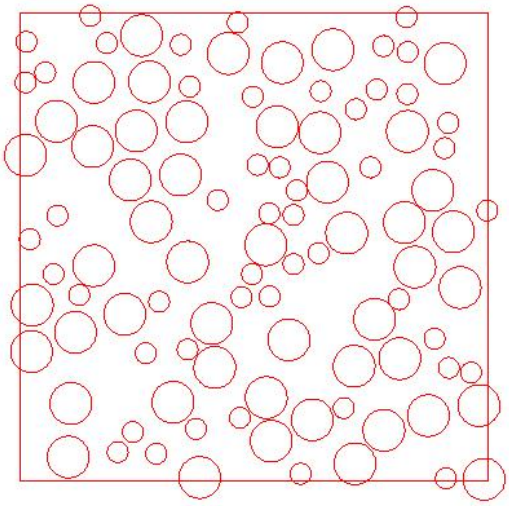

Figure 3 Final Configuration, when ρ = 0.50.

We have also used the plot facility of Maple to obtain the G(R) plots presented below. In Figure 4 at ρ = 0.25, all three G(R)s display behavior which is typical for dilute fluids in that no particles interpenetrate, G(R) = 0, there is a sharp first peak corresponding to the nearest neighbor shell and this is followed by a rapid decrease in the function to a value expected for a uniform fluid, G(R) =1.0.

We then examined a system with ρ = 0.50. The results for ρ = 0.50 are displayed in Figure 5. Now all three G(R)s display behavior which is more typical of dense fluids in that there is a higher and narrower first peak and developing secondary peaks. The secondary peaks indicate strong correlations between second-nearest neighbors. This expected as the fluid becomes more close packed.

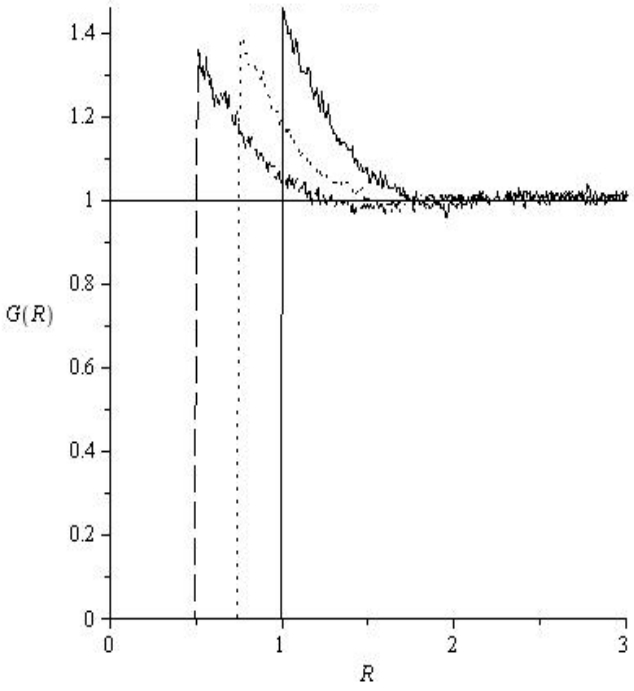

Figure 4: Pair correlation when ρ = 0.25.
--- small-small … small-large ___ large-large

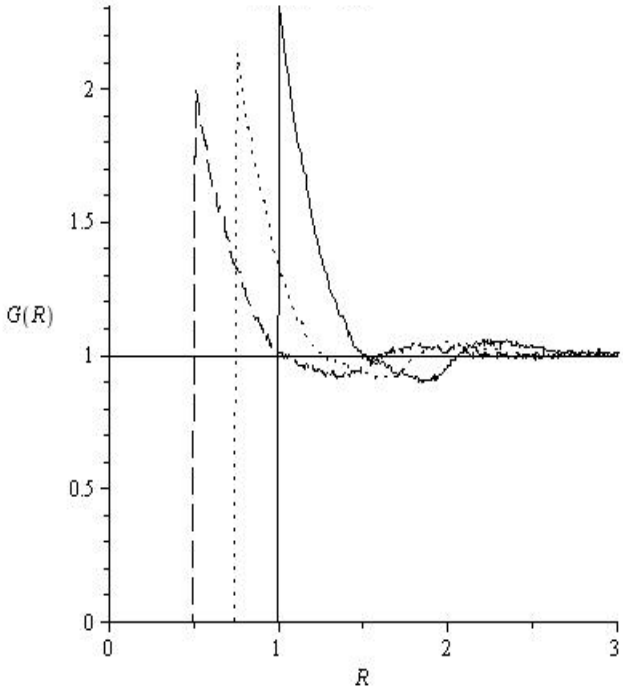

Figure 5: Pair correlation when ρ = 0.50.

Conclusion

We have investigated two dimensional periodic binary mixture hard disk systems by Monte Carlo simulations and have indicated how the pair correlation functions reveal the underlying molecular structure. Graphic tools such as those employed 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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