MONTE CARLO SIMULATIONS OF TWO DIMENSIONAL HARD PARTICLE BINARY MIXTURES WITH VARIOUS COMPOSITIONS

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Abstract

Computer modeling is an important skill for engineering and science students to acquire. Monte Carlo simulations of two dimensional mixtures 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 Lasky and Bishop [1] presented their Monte Carlo (MC) simulations of homogeneous two dimensional hard particles. The results of their work was extended by Merriman and Bishop [2] to investigate 50:50 binary mixtures in which the larger component had twice the diameter of the smaller one. Here, the same methods are employed to study binary mixtures with 25:75, 50:50 and 75:25 compositions and diameter ratios of 1/2 and 2/3.

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

$$\eta = \rho\,(\pi/4)\,(X_1\sigma_1^{\,2} + X_2\sigma_2^{\,2}) \qquad (1)$$

The equation of state [3] 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 Z = 1. In the case of the hard binary mixture, Z is related [4] to the pair correlation functions at contact by

$$Z = 1 + \rho(\pi/2)\,[X_1^{\,2}\sigma^{2}_{11}G_{11}(\sigma_{11}) + 2X_1X_2\sigma^{2}_{12}G_{12}(\sigma_{12}) + X_2^{\,2}\sigma^{2}_{22}G_{22}(\sigma_{22})] \qquad (2)$$

Here

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2 \qquad (3)$$

is the contact diameter or the separation between the centers of the particles. The pair correlation functions at contact are $G_{11}(\sigma_{11})$, $G_{12}(\sigma_{12})$ and $G_{22}(\sigma_{22})$. A pair correlation function [5], G(R**),** measures the relative distribution of particles at a distance |**R**| from the center of a reference particle. The three different kinds of pair correlation functions indicate 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.

In this project the equations of state for a variety of packing fractions are obtained and compared to other simulations and theory.

Method

The details of our MC computer simulation are contained in the papers of Lasky and Bishop [1] and Merriman and Bishop [2]. The different particles are started at positions in a square lattice and then moved by the standard Metropolis Monte Carlo method [6-10] 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_{11} for the small-small pairs, less than σ_{12} for the small-large pairs and less than σ_{22} for the large-large pairs. 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.

However, since the successive positions of the particles are not independent, it will take many MC 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 MC process. We have addressed this problem by computing the pair correlations at fixed intervals which encompass many MC steps. Thus, the different pair correlation functions 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].

Results

We have developed the simulation using the gnu C compiler on a PC loaded 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 2,500 steps so that there were 4,000 equilibrated samples to average over. The equation of state has been obtained by finding the value of the pair correlation functions at contact. These are determined by fitting a line to the first peaks of the pair correlation functions and then extrapolating to the appropriate contact value. In Figure 1 the fit procedure is shown for the case of $G_{11}(R)$ when r=1/2, N=256, η= 0.5 and $X_1 = X_2$ = 0.5. The first five data points are input into a linear least-squares fit routine [11] which returns the slope, -7.67143, and intercept, 6.51622, of the $G_{11}(R)$ line: $G_{11}(R)$ = -7.67143 + 6.51622 R. The $G_{11}(R)$ contact value, 2.68051, is found by substituting the contact value, 0.5, of the small disks into the $G_{11}(R)$ equation.

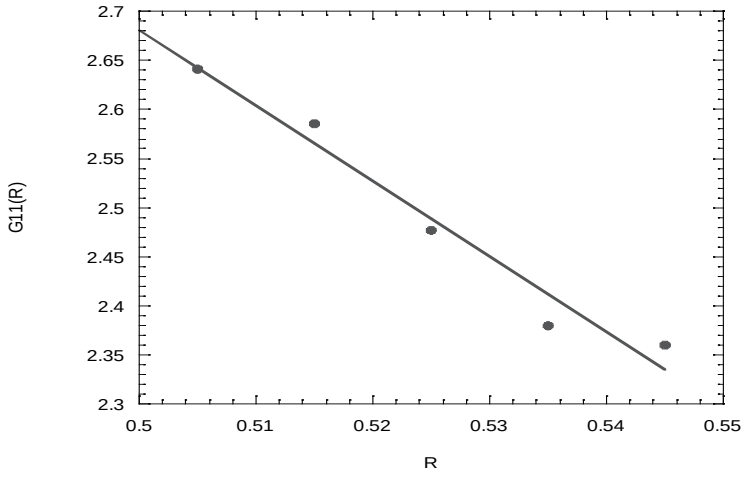

Figure 1: The solid line is the linear fit. The filled circles are the $G_{11}(R)$ MC data. Here, r=1/2, N=256, η= 0.5 and $X_1 = X_2$ = 0.5.

Once the contact values have been determined, the equation of state is found from Eq. 2. The Z values for all the systems studied are contained in Table I. Zt are the theoretical values predicted by Santos, Yuste and de Haro [12] :

$$Zt = (1 - \xi)/(1- \eta) + \xi\,(1 + \eta^2/ 8)\,/(1- \eta)^2 \qquad (4a)$$

where

$$\xi = (X_1\sigma_1 + X_2\sigma_2)^2 / (X_1\sigma_1^2 + X_2\sigma_2^2) \qquad (4b)$$

Table I: Equation of State Data for diameter ratios, r, of 1/2 and 2/3.

R	Zt	Zbs	Zmc100	Zmc256	Zmc400	Zt	Zbs	Zmc100
r= 1/2						r=2/3		
25:75								
0.100	1.223			1.222		1.232		1.232
0.200	1.536	1.537	1.534	1.532	1.531	1.559	1.560	1.561
0.250	1.743			1.751		1.775		1.789
0.300	1.996	1.999		1.995		2.041	2.046	
0.350	2.310			2.302		2.372		2.367
0.400	2.708	2.712	2.700	2.703	2.687	2.792	2.795	2.803
0.450	3.221	3.222		3.204		3.333	3.335	
0.500	3.897	3.890				4.049	4.043	
0.550	4.814	4.789				5.021	5.002	
0.600	6.099	6.039	6.033			6.387	6.329	6.333
50:50								
0.100	1.224			1.223		1.231		1.231
0.200	1.538	1.540	1.534	1.540	1.528	1.558	1.560	1.540
0.250	1.746			1.749		1.774		1.783
0.300	2.000	2.004		2.006		2.039	2.043	
0.350	2.317			2.305		2.370		2.392
0.400	2.717	2.719	2.711	2.706	2.711	2.788	2.792	2.789
0.450	3.232	3.234		3.218		3.329	3.332	
0.500	3.913	3.907		3.877		4.043	4.042	
0.550	4.835	4.814		4.785		5.013	4.995	
0.600	6.128	6.070				6.376	6.319	
75:25								
0.100	1.229			1.229		1.233		1.234
0.200	1.552	1.554	1.555	1.542	1.546	1.563	1.565	1.569
0.250	1.765			1.768		1.781		1.799
0.300	2.027			2.034		2.048	2.053	
0.350	2.353	2.031		2.351		2.382		2.336
0.400	2.766	2.770	2.766	2.759	2.756	2.805	2.810	2.822
0.450	3.299			3.298		3.351	3.353	
0.500	4.002	3.996		3.983		4.074	4.071	
0.550	4.958	4.937		4.905		5.055	5.033	
0.600	6.299	6.238	6.255	6.197	6.196	6.434	6.371	6.391

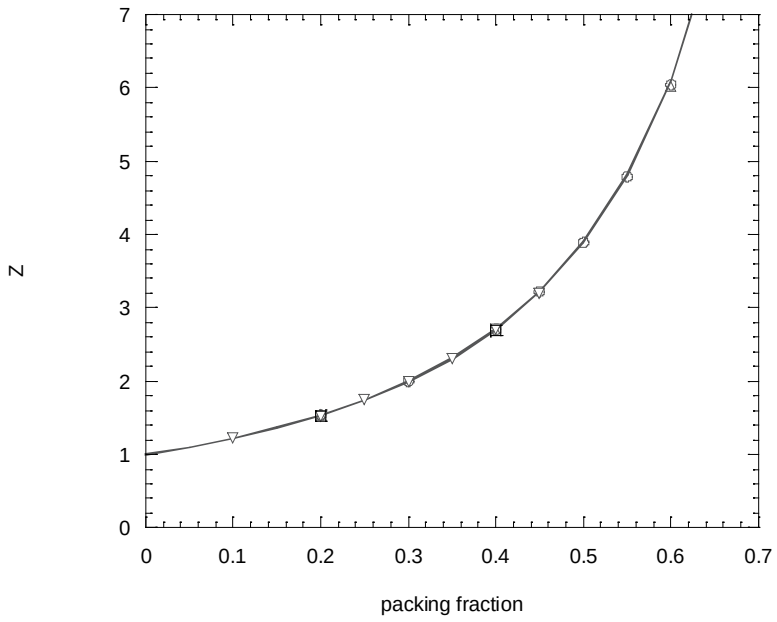

Figure 2: The equation of state, Z, as a function of the packing fraction when r=1/2 for a composition of 25:75. The solid line is the theoretical prediction, Eqs. 4a and b, circles are the Barrio and Solana MC N=256 data, up triangles, down triangles and squares are the current MC results for N=100, 256 and 400, respectively.

Also Zbs are the MC values found by Barrio and Solana [4] with N=256 for the diameter ratios, compositions, and packing fractions listed in the Table; Zmc100, Zmc256 and Zmc400 are our new MC results when N=100, 256 and 400, respectively. In all cases the MC data are consistent with each other within 1%. Since typically a 400 particle simulation required more than ten times the computer time needed for the corresponding 100 particle one, unless one wants extremely high accuracy, the smaller particle system should be adequate for simulation studies. Also our new data confirm the accuracy of the theoretical predictions for the mixture equation of state.

Figure 2 presents the equation of state, Z, as a function of the packing fraction when r=1/2 for a composition of 25:75. All the MC data are in excellent agreement with the theoretical curve.

Conclusion

We have investigated two dimensional binary mixtures of hard disk systems with different diameter ratios, packing fractions and compositions by Monte Carlo simulations. Numerical tools, such as linear least squares line fits, have been used to compute the equations of state from the contact pair correlation functions. The results are in excellent agreement with other simulations and theories. 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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Biographical Information

Jonathan Havlicek is currently a student in the computer engineering program at Manhattan College.

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