MONTE CARLO SIMULATIONS OF ONE DIMENSIONAL HARD PARTICLE SYSTEMS

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Abstract

Engineering and science students should be exposed to Monte Carlo computer models of materials. They also must be made aware of how these models can be validated. One dimensional systems provide ideal testing grounds for computer simulations since many properties can be analytically determined. The exact pair correlation function of a periodic one-dimensional fluid of hard particles is employed to probe how finite particle systems approach the thermodynamical limit (infinite number of particles). This affords the opportunity for a direct comparison of a Monte Carlo simulation and an exact result. It is found that over a wide range of particle numbers and densities, the simulated pair correlation functions reproduce the exact predictions. Additional student projects are suggested for investigation.

Introduction

In order to more fully understand the structural and thermodynamic properties of materials, engineering and science students need to learn how to develop computer models. These computer models must be validated by comparing results to known test cases. Few analytical solutions exist for three dimensional systems but many problems can be solved exactly[1] in one dimension even in cases with a finite number of particles, N. The confinement of hard particle systems to one dimension means that particles cannot change the identities of their initial nearest neighbors; they are restricted to an initial permutation of particle indices. This key fact simplifies the computation of many properties because factorization can be employed to decompose complicated integrals into products of much simpler ones[2]. Thus, one dimensional systems provide a convenient set of test cases for comparison with computer simulations which are, of course, always limited to a finite number of particles.

An important property of multi-particle systems in any dimension is the pair correlation function[3], G(X), which measures the relative number of particles at a distance X from the center of a reference particle. The change in the shape of the pair correlation function mirrors the underlying particle arrangements. It is well-known[4] that in the gaseous state there is little order and that particles are distributed at random whereas in the solid state the particles pack into long-ranged ordered crystals. Localization behavior characteristic of a fluid, the appearance of multiple, well-defined peaks in the pair correlation function at higher densities, has been previously observed in analytic calculations of the pair correlation function in one dimension by Salsburg, Zwanzig and Kirkwood[5].

Theory

The pair potential of one dimensional hard particles of length, σ separated by the distance X is given by

$$U(X) = \begin{cases} \infty & X < \sigma \\ 0 & X \geq \sigma \end{cases} \qquad (1)$$

Using Eq.1, Salsburg, Zwanzig and Kirkwood [5] derived the exact expression for G(X), in the thermodynamic limit, $N \to \infty$. They showed that

$$G(X) = \sum_{k=1}^{N} (X - k\sigma)^{k-1} \exp[-(X - k\sigma) / (1/\rho - \sigma)]\, \theta(X - k\sigma) / [\rho (k - 1)!(1/\rho - \sigma)^{k}] \qquad (2)$$

where $\theta(X - k\sigma)$ is the Heavyside step function and ρ is the density. The value of the pair correlation function at contact, $G(\sigma)$, obtained from Eq.2 is

$$G(\sigma) = 1 / (1 - \sigma\rho) \qquad (3)$$

Knowledge of $G(\sigma)$ is important because it is directly related to the equation of state[4]; i.e. the variation of the compressibility factor, Z, with density. The compressibility factor is defined as

$$Z = P\beta / \rho \qquad (4)$$

where β is $1/k_BT$ (k_B is Boltzmann's constant and T is the absolute temperature), and P is the pressure. In the case of hard particles Z is independent of the temperature. Then the equation of state[6] is related to $G(\sigma)$ by

$$Z = 1 + \rho B_2 G(\sigma) \qquad (5)$$

Here, B_2 is the second virial coefficient which has the value σ for an infinite number of particles in one dimension[7].

Substituting Eq.3 into Eq.5 yields the well-known one-dimensional Tonks[8] equation of state:

$$Z = 1 / (1 - \sigma\rho) \qquad (6)$$

To be able to compare computer simulations of hard particles with theoretical results, an expression of G(X) for finite N is required. Early work by Leff and Coopersmith[9] and Flicker[10] obtained an equation for G(X) for finite N in the special case of particles confined to a line with hard walls at 0 and L. Leff and Coopersmith were able to show that wall effects disrupted the translational invariance and hence the uniformity of both the density and the pair correlation function. Flicker demonstrated that the Salsburg, Zwanzig and Kirkwood result, Eq.2, was recovered from the finite hard wall case in the thermodynamic limit. Later, Bishop and Berne[11] examined the case of finite N in a periodic system, a ring in one dimension. The problems of non-uniformity caused by the hard walls do not exist in this periodic case. Their analysis was performed by considering a single permutation of the confined particles. Their equation for G(X) is

$$G(X) = \sum_{N1=0}^{N-2} (X - (N1+1)\sigma)^{N1} [1 - (X - (N1+1)\sigma) / \{N (1/\rho - \sigma)\}]^{N-N1-2} (N-1)!\, \theta1\, \theta2 / [\rho\, N1!\, (N - N1 - 2)!\, (1/\rho - \sigma)^{N1+1} N^{N1+1}] \qquad (7)$$

Here $\theta_1 = \theta(X - (N1+1)\sigma)$ and
$\theta_2 = \theta(L - X + (N1 + 1 - N)\sigma)$.

The thermodynamic limit is independent of the boundary conditions employed for the ends of the line. This can be seen from Eq.7 which reduces to Eq.2 in the thermodynamic limit. The finite $G(\sigma)$ which Eq.7 predicts has an N-dependence given by

$$G(\sigma) = (1 - 1/N) / (1 - \sigma\rho) \qquad (8)$$

Computer Simulation

The periodic one dimensional hard particle system has also been studied with a Monte Carlo (MC) computer simulation[12-15] method. In this kind of simulation a random walk, which asymptotically converges to the exact result after a large number of steps, is performed. A variety of interesting questions are associated with the MC procedure such as: how many steps are needed for convergence, what is the statistical error in the result, and how large must N be for G(X) to be indistinguishable from the thermodynamic limit?

To model a periodic system the particles are started at fixed positions on a ring and this permutation of particles is maintained throughout the simulation in order to be able to compare with theoretical predictions. Particles are moved by the standard Metropolis MC method[12] until an equilibrated state is achieved. The details of this computation for any dimension are given in Bishop, Whitlock and Klein[16] but the key ideas for one dimensional systems can be summarized as follows. The number of particles and the number density of the state of the system of interest are pre-selected input parameters. These determine the circumference, L, of the system simulation ring: $L = N/\rho$.

The simulation proceeds by attempting to move, in turn, each of the particles in the simulation ring. A pass is defined as a sequence of steps in which an attempted move is made for each of the N particles. To move a particle from its original location, $X_{original}$, a uniform random number, RN, between 0 and 1 is generated and used to select a new trial position,

$$X_{trial} = X_{original} + (2 * RN - 1) * MAXD \quad (9)$$

Here, MAXD is the maximum magnitude of an allowed displacement measured from the particle's center of mass. It is the largest possible move. A move is rejected whenever a particle overlaps another particle. If the attempted displacement is too large, the chance of an overlap with another particle will be great and too many moves will be rejected. However, if the displacement is too small, the simulation will not adequately converge. At low densities, when the particles are far apart, the maximum displacement should be large whereas at high densities it must be small enough so that a particle can never pass through or over one of its nearest neighbors since in this case a single permutation of particles is being simulated. If the new position is not accepted, the test particle remains at its current location. The acceptance ratio, AR, the number of accepted moves divided by the number of total moves, is monitored. This ratio, as well as MAXD for each density, is listed in Table I. The values of the MAXD have been determined with short runs. Standard periodic boundary conditions [17] are employed. This means that if a particle is moved such that X becomes either less than 0 or larger than L, an identical particle is placed in the ring at position modulo L. This procedure insures a ring geometry and maintains the selected permutation for the one dimensional system.

Since the successive positions of the particles are not independent, it takes many passes to converge from the initial state to an equilibrated or converged state. Only converged passes are employed in the final calculations. Hence, some number of passes must be discarded; we refer to these discarded passes as the pre-equilibrium stage (PreEq in Table I). Typically, on the order of 10^4 - 10^5 passes are needed in order to achieve convergence. Then an additional fifty thousand to a million passes are generated (PostEq in Table I) for analysis; the actual cpu timings ranged from 4 to 100 minutes.

Even after the converged regime is attained there is still serial correlation between each pass in the MC process. Here, we have handled this problem by two methods. First, we compute G(X) only at fixed intervals of 10 to 500 passes depending upon the density. This procedure allows some of the serial correlation to dissipate from the previously calculated value of G(X). Secondly, and considerably more effectively, statistically independent sets of simulations are carried out in parallel. These individual results are then averaged together.

The attainment of the converged state is an important prerequisite for the reliability of computer simulations. In our calculations the following order parameter[18], O, was utilized to decide when the system had converged.

$$O = \sum_{i=1}^{N} \cos(4\pi X_i \rho) \ / N \qquad (10)$$

Here, X_i is the position of the i-th particle. The order parameter has a value of 1 for a completely ordered lattice and randomly oscillates about 0 when the system has equilibrated in the fluid state. At this point all PreEq passes are discarded and the simulation is continued for PostEq additional passes.

The numerical representation of the pair correlation function is calculated by computing a histogram of the average number of particle separations as a function of separation distance (see Allen and Tildesley[17]). This histogram is normalized by dividing by the differential "volume" occupied by the particles, $2\Delta X$, and the actual number density of particles, ρ.

Sample Monte Carlo codes are available from many sources; see for example, Gould and Tobochnik[4] and Allen and Tildesley[17].

Results

The one dimensional hard particle system has been simulated for a variety of reduced densities $\rho = 0.1$ to 0.7 and a range of particle numbers ($N = 10$, 100 and 1000). Figure 1 presents a comparison of G(X) determined by our MC simulations with the exact finite N expression of Eq.7 when $N = 10$ and the exact expression of Eq.2 when $N = \infty$. A range of densities studied are illustrated: $\rho = 0.1$, 0.3, 0.5, and 0.7. We find that our MC calculations fluctuate about the exact finite N pair correlation function result but that there are significant differences from the thermodynamic limit G(X). The statistical errors in G(X), which are of order 10^{-3}, are smaller than the plotted symbols.

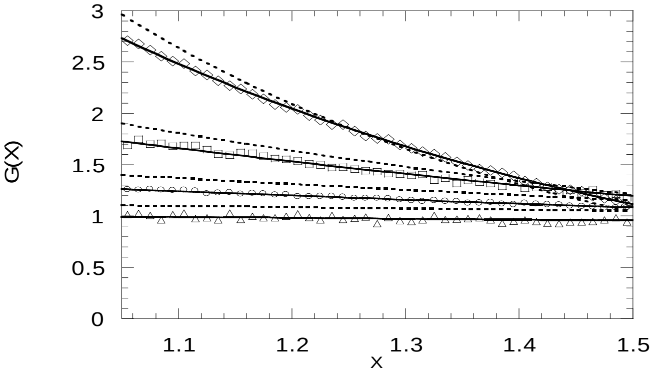

Figure 1: The variation of the pair correlation function, G(X), for different densities when $N = 10$. Dashed line: thermodynamic limit exact result Eq.2, solid line: finite N result of Eq.7, diamonds: $\rho = 0.7$, squares: $\rho = 0.5$, circles: $\rho = 0.3$ and triangles: $\rho = 0.1$.

In Figure 2 the convergence of the MC result to the exact expression of Eq.2 is shown at a single density, $\rho = 0.5$. Whereas this figure seems to show that $N = 100$ is a large enough system to essentially mirror the infinite case, the $G(\sigma)$ values in Table I indicate that systems with $N = 1000$ are needed to approximate the infinite result.

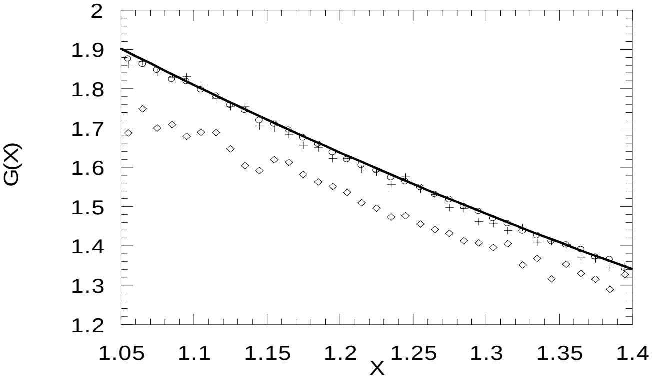

Figure 2: The variation of the pair correlation function, G(X), for different numbers of particles and $\rho = 0.5$; line: thermodynamic limit exact result Eq.2, diamonds: $N = 10$, plus: $N = 100$, and circles: $N = 1000$.

Table I contains the details of all of the MC runs and comparisons among our MC simulations, the finite $G(\sigma)$ predicted by Eq.8 and the thermodynamic limit given by Eq.3.

To estimate an empirical error on the extrapolated $G(\sigma)$ value, the first five G(X) points for which X is greater than σ are fit[19] by a linear least-squares line varying each point by 1.96 standard deviations; i.e. the 95% confidence interval. This fitting procedure is shown in Figure 3 where a variety of densities and number of particles are presented.

The error estimates range between 1×10^{-3} and 5×10^{-3}. These errors on $G(\sigma)$ do not include any contributions from extrapolation which would make the errors larger. The extrapolated MC $G(\sigma)$ values follow the trend of the finite N predictions. As expected, these values approach the thermodynamic limit as N increases. The largest discrepancy is observed

TABLE I Results for G(σ)

ρ	N	PreEq	PostEq	MAXD	AR	MC	Finite N	Infinite N
0.10	10	8000	1000000	2.00	0.90	0.992	1.000	
0.10	100	100000	200000	2.00	0.90	1.090	1.100	
0.10	1000	300000	600000	2.00	0.90	1.110	1.110	1.111
0.30	10	8000	1000000	1.20	0.80	1.293	1.286	
0.30	100	8000	50000	1.20	0.78	1.426	1.414	
0.30	1000	8000	50000	1.20	0.79	1.428	1.427	1.429
0.50	10	8000	1000000	0.80	0.71	1.750	1.800	
0.50	100	8000	50000	0.80	0.69	1.981	1.980	
0.50	1000	8000	50000	0.80	0.69	1.993	1.998	2.000
0.70	10	8000	1000000	0.40	0.67	2.996	3.000	
0.70	100	8000	50000	0.40	0.65	3.272	3.300	
0.70	1000	8000	50000	0.40	0.65	3.314	3.330	3.333

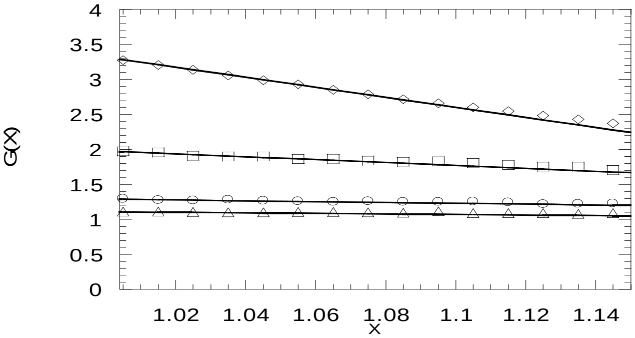

Figure 3: The extrapolation to contact of the pair correlation function, G(X), for different particle numbers and densities. Solid lines: linear fit using the first five points, triangles: ρ = 0.1 and N = 1000, circles: ρ = 0.3 and N = 10, squares: ρ = 0.5 and N = 100, and diamonds: ρ = 0.7 and N = 1000.

for the N = 10 value. The overall N-dependence behavior of the MC G(σ) mimics that predicted by the finite results.

Conclusion

We have investigated one dimensional periodic hard particle systems by Monte Carlo simulations for a variety of particle numbers and densities. The MC G(X) values agree with the theoretical finite N predictions. Moreover, the higher N value results approach the thermodynamic limit and validate the accuracy of the computer model.

Possible Projects

Change one of the published MC codes to study one dimensional systems. Start the N particles on a one dimensional lattice with N = 10 and study a variety of densities.

1) Investigate the number of pre-equilibrium steps needed for convergence at different densities by noting how G(X) changes as you vary the number of discarded passes.

2) For the same number of pre-and post-equilibrium steps calculate G(X) for different initial random number seeds. How sensitive is G(X) to the different random number sequences?

3) Fit a straight line to each G(X) obtained from project 1 and/or project 2. How does the resultant G(σ) value depend upon these parameters?

4) Use the G(σ) values listed in the table to compute Z and then plot Z vs. ρ compared to the Tonk's equation of state.

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