Measurement of Isothermal Pressure of Lattice Gas By Random Walk

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Abstract

We present a computational random walk method of measuring the isothermal pressure of the lattice gas with and without the excluded volume interaction. The method is based on the discretization of the exact thermodynamic relation for the pressure. The simulation results are in excellent agreement with the theoretical predictions.

I. Introduction

The pressure is defined as the force per unit area and is one of the measurable macroscopic thermodynamic quantities. It is a macroscopic manifestation of the microscopic phenomena of atomic collisions, by which atoms or molecules transfer the momentum and thus exert the force to the wall. At the macroscopic level, the pressure can be directly measured by monitoring or recording the force on the wall of a container. At the microscopic level, a conventional way is to design a method that keeps track of the momentum transfered by atoms to the wall via collisions, and this may be done by Molecular Dynamics(MD) simulations.\(^1\) However, developing and learning MD simulations is time consuming, and is often well beyond the scope of undergraduate or introductory graduate level statistical mechanics. To the best of the authors’ knowledge, no conventional introductory statistical

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mechanics textbooks have yet dealt with the computational methods of measuring the pressure. Considering the surge of computer-assisted course developments in recent years, it may be desirable to design a computational method of measuring the pressure. The purpose of this paper is to introduce such a Monte Carlo method, which is conceptually simple and extremely easy to implement with a minimal knowledge of computation, because it only deals with the random walk of point particles on a lattice. We first explain the mathematical basis of the method in section II and III, and then present simulation results for the lattice gas with and without excluded volume interaction in section IV.

II. Background

Our starting point is the mathematical expression of the pressure $P$ of a container of volume $V$ at a given temperature $T$, which can be found in any standard text book of statistical mechanics:

$$ P = -\frac{\partial F}{\partial V} = kT \frac{\partial \ln Z}{\partial V} $$

where $F = -kT\ln Z$ is the free energy of the system with $Z$ the partition function and $k$ the Boltzmann constant. The contribution to the partition function comes from two sources, one from the kinetic energy and the other from the potential energy. The latter is known as the configurational integral, which involves the integration of interaction energy among particles. The former is a function of temperature, and is independent of the volume. Therefore, at equilibrium, the contribution coming from the kinetics is decoupled, and is separated out from the configurational statistics, and the equilibrium pressure can be determined by considering only the configurational properties of the system. The nature of interactions among particles is determined by the form of the potential energy. In this paper, we consider the interaction potential $U$ to be either nonexistent, in which case the pressure is given by the ideal gas law, or the particles interact with each other via hard sphere potential. Even with hard sphere potential, the exact expression of the pressure for the continuum system is not yet known, even though a few approximate closed forms for the pressure have been reported in the literature. However, for the lattice gas, the situation becomes much simpler,
because in this case, the free energy can be computed exactly. In the lattice version, the hard sphere interaction may be equivalent to introducing the excluded volume interaction by prohibiting the multiple occupancy of particles on a given lattice site. Without such restriction, the system will follow the ideal gas statistics. Note that in both cases, the contribution to the free energy comes only from entropic part because the interaction energy is zero. Hence, \( F = -TS = -kT \ln Z \), with \( S \) the entropy of the system. We now compute the entropy of the lattice gas, the result of which will then be used to test the validity of the random walk method.

Consider now a lattice model, where \( N \) particles are confined to move only on \( d \) dimensional discrete lattice points of a container with the volume \( V = H \cdot L^{d-1} \) with \( H \) the height and \( L^{d-1} \) the area of the side wall, where the pressure is being monitored. Note that we set the lattice spacing to the unit value. In the absence of excluded volume interactions, the entropy of the system is given by:

\[
S = k \ln \Omega = k \ln (\omega^N)
\]  
(2)

where \( k \ln \omega \) is the entropy of a single particle, which is simply the volume \( V \). Hence, we obtain the ideal gas law.

\[
P = -T \left( \frac{\partial S}{\partial V} \right) = k \frac{N}{V} T = k \phi T
\]  
(3)

with \( \phi = N/V \) the density of the particle.

In the presence of the excluded volume interaction, the entropy of the system is no longer the product of one particle entropy. Rather, it is the total number of ways of putting \( N \) particles in a volume \( V \). In the discrete version, it becomes,

\[
S = k \ln \Omega(V,N) \approx -V[\phi \ln \phi + (1 - \phi) \ln(1 - \phi)]
\]  
(4)

where \( \Omega(V,N) = V!/N!(V - N)! \) and the Sterling’s formula has been invoked. The equilibrium pressure is then given by:
\[
P = -T \frac{\partial S}{\partial V} = -kT \ln(1 - \phi)
\]

One may use the grand partition function approach to obtain the similar result\(^2\). In this case, the grand partition function, \(Q\), becomes:
\[
Q = \sum_{N=0}^{\infty} z^N Z_N = (1 + z)^V,
\]
where the fugacity \(z = \exp(\beta \mu)\) and the canonical partition function \(Z_N = V!/N!(V - N)!\). Now, from the relations (see Chapter 7 of Huang in ref.\(^2\)) \(PV/kT = \ln Q\), and \(\bar{N} = z \partial \log Q / \partial z = zV/(1+z)\), and \(\phi = \bar{N}/V\), we can easily obtain eq.(2). Note that the pressure of the lattice gas exhibits the logarithmic singularity at the closed packed density. For the continuum system, it has been proved that the pressure exhibits the algebraic singularity.\(^6\)

**III. The Mathematical Basis for a Random Walk Monte Carlo Technique**

We now describe a mathematical basis for a Monte Carlo technique that computes the pressure of the lattice gas numerically. If the method is correct, then it should reproduce Eqs. (3) and (5). This is based on a method derived first for the continuum system by Percus\(^7\), and then extended to a lattice system to measure the pressure in polymeric fluids simulations.\(^8\)

For the sake of completeness, we will briefly describe the essence of the formalism here, but the reader is referred to ref.\(^7\) and especially ref. \(^8\) where the essential idea has been advanced. For a d dimensional lattice gas in a container of a height \(H\) along the \(z\) direction and the wall area \(L^{d-1}\), the derivative becomes the difference equation, and thus the discrete expression of the pressure is given by:
\[
P = - \frac{\partial F}{\partial V} = k(T/L^{d-1}) \ln(Z(H)/Z(H - 1))
\]

where \(Z(H)\) is the partition function with the height \(H\) and \(Z(H - 1)\) is that with \(H-1\). Note that \(Z(H - 1)\) is equivalent to \(Z(H)\) with an infinite repulsive potential at the wall, in which case the particles cannot approach the wall at \(z=H\) and thus with \(U\) the interaction potential between the wall and particles, the original partition function, \(Z(H, U = \infty)\), will reduce to \(Z(H - 1, U = 0)\). In order to utilize this observation in designing the Monte Carlo method, we introduce a parameter \(\lambda = \exp(-U/kT)\) with \(k\) the Boltzmann constant. Note
that \( \lambda = 0 \) corresponds to \( U = \infty \), and \( \lambda = 1 \) to \( U = 0 \). Let the total number of particles in the system be \( N \), and \( N_w \) be the particles at the wall. The partition function, \( \bar{Z} \), for this modified system becomes:

\[
\bar{Z}(H, \lambda) = \sum_{E} \exp(-E/kT) = \sum_{N_w=0}^{L^{(d-1)}} \lambda^{N_w} \Omega(N_w, N - N_w)
\]

where the summation is taken over all possible energy configurations and \( \Omega \) is the total number of configurations with \( N_w \) particles at the wall and \( N - N_w \) particles in the bulk. The probability, \( P(N_w) \), of finding \( N_w \) particles at the wall in the presence of the potential \( U \) is, \( P(N_w) = \lambda^{N_w} \Omega(N_w, N - N_w)/\bar{Z} \). Further, it is obvious that \( Z(H) = \bar{Z}(H, \lambda = 1) \) and \( Z(H - 1) = \bar{Z}(H, \lambda = 0) \). Therefore, if the mean number of particles at the wall is denoted by \( < N_w > \), then it is given by:

\[
<N_w> = \lambda \frac{\partial \ln \bar{Z}}{\partial \lambda}
\]

(8)

Next, we use a simple mathematical identity to express the ratio \( \ln(Z(H)/Z(H - 1)) \) in terms of \( < N_w > \) as:

\[
\ln(Z(H)/Z(H - 1)) = \ln(\bar{Z}(H, \lambda = 1)/\bar{Z}(H, \lambda = 0)) = \int_{0}^{1} d\lambda \frac{\partial \ln \bar{Z}(H, \lambda)}{\partial \lambda}
\]

(9)

Hence, we obtain the desired expression for the pressure:

\[
P/kT = \int_{0}^{1} \frac{d\lambda}{\lambda} \rho_w
\]

(10)

where \( \rho_w \equiv < N_w > / L^{d-1} \) is the density at the wall.

We now demonstrate here that Eq.(10) is indeed identical to Eqs.(3) and (5). Consider first the case where the excluded volume interactions are present. Since the partition function \( \bar{Z} \) (Eq.(7)) contains only the configurational term, it is straightforward to write down the expression for \( \bar{Z} \) for particles in a volume \( V = HA \equiv H \cdot L^{(d-1)} \) with \( A \equiv L^{d-1} \) the area of the container. We first consider the case with excluded volume. The partition function becomes,

\[
\bar{Z}(H, \lambda) = \sum_{N_w=0}^{L^{(d-1)}} \lambda^{N_w} \Omega(A, N_w)\Omega(B, N - N_w)
\]

(11)
where $B \equiv (H - 1)L^{(d-1)}$. The first term, $\lambda^{N_w}$ in (A-1) is due to the wall potential, and the second and the third terms are the total number of ways of putting $N_w$ particles in the wall of area A and $N - N_w$ particles in the bulk of a volume $B$. Both $\Omega$'s in the summation are given by the binomial coefficient, i.e. namely $\Omega(Q, R) = Q! / R! (Q - R)!$. Let the density of the particle, $N/B = \phi < 1$. Then, in the thermodynamic limit, $N_w << N$. Using the Sterling’s formula, we find:

$$\ln \Omega(B, N - N_w) \approx -B[\phi \ln \phi + (1 - \phi) \ln(1 - \phi)] + N_w \ln[\phi / (1 - \phi)] + O(N_w^2 / B)$$

Hence,

$$\Omega(B, N - N_w) \approx \exp(B s_o) [\phi / (1 - \phi)]^{N_w}$$

where $s_o$ is the bulk entropy per site; i.e. $s_o = -[\phi \ln \phi + (1 - \phi) \ln(1 - \phi)]$. By putting (12) into (11), we now obtain the closed expression for the partition function $\bar{Z}$:

$$\bar{Z} = \exp(B s_o) [1 + \lambda \phi / (1 - \phi)]^A$$

from which we obtain the exact formula for the density at the wall, $\rho_w$:

$$\rho_w = (\lambda / A) \frac{\partial \ln \bar{Z}}{\partial \lambda} = \lambda \alpha(\phi) / (1 + \lambda \alpha(\phi))$$

with $\alpha(\phi) = \phi / (1 - \phi)$. Note that $\rho_w(\lambda = 1) = \phi$ as expected. Hence, we find

$$P/kT = \int_0^1 d\lambda \rho_w / \lambda = -\ln(1 - \phi)$$

In the case when the excluded volume interaction is not present, the partition function becomes much simpler:

$$\bar{Z} = \sum_{N_w=0}^{N} \lambda^{N_w} \Omega(N, N_w) A^{N_w} B^{N-N_w} = B^N (1 + \lambda A / B)^N$$

Hence, in the thermodynamic limit of $A/B << 1$, the density at the wall, $\rho_w$, becomes:
\( \rho_w = (\lambda/A) \frac{\partial \ln \bar{Z}}{\partial \lambda} = \frac{\lambda \phi}{1 + \lambda A/B} \rightarrow \lambda \phi \)

(16)

from which follows the ideal gas law:

\[
P/kT = \int_0^1 \frac{d\lambda}{\lambda} \rho_w = \phi
\]

(17)

IV. Random Walk Simulations

We now carry out Monte Carlo random walk simulations to measure the density at the wall and compare them with the formulas (13) and (16).

We take a two dimensional lattice of size \( H = 20 \) and \( L = 10 \) with the volume \( V = HL \). We now turn on the repulsive wall potential \( 0 \leq U \leq \infty \) at \( z=H \), and introduce a parameter \( 0 \leq \lambda = \exp(-U/T) \leq 1 \). The wall potential is short range and thus acts only when the particle is right next to the wall, i.e., at \( z = H - 1 \). At \( z = H - 1 \), the particle moves to the wall at \( z = H \) with the probability \( p = \lambda \). This is the standard metropolitan algorithm. Otherwise, the particles are free to move in the bulk (with the exception of the excluded volume interaction). We also impose periodic boundary conditions along the vertical axis. With these simple rules, the Monte Carlo simulations proceed as follows. Initially \( N \) particles with the bulk density \( \phi = N/V \) are randomly placed on a lattice and they undergo random walk. With the excluded volume interaction, multiple occupancy on a lattice point is prohibited. Without the excluded volume interaction, multiple occupancy is allowed. When a particle is right next to the right wall, then it moves there with the probability \( \lambda \). When an attempt has been made to move all the \( N \) particles once, then one Monte Carlo(MC) step is elapsed. At each MC step, the number of particles at \( z = H - 1 \) is registered. Then, after \( M \) MC time steps, the density of the particles near the wall, \( \rho_w \) at \( z = H - 1 \) is computed as the average over MC time \( t \) and configurations, namely:

\[
\rho_w = \frac{[\sum_t N_w(t)/M]/L}{L}
\]

with \( N_w(t) \) the number of particles at \( z = H - 1 \) at a given MC time \( t \). \( \rho_w \) is then measured as a function of \( \lambda \) for different bulk density \( \phi'/s \). We now present simulation data.
We measured the particle density at the wall, $\rho_w(\lambda, \phi)$, with and without excluded interactions, for the bulk density $\phi = 0.1, 0.3, 0.5, 0.7, 0.9$ and for $\lambda = 0.1, 0.3, 0.5, 0.7, 0.9, 1.0$. By symmetry, $\rho_{\text{wall}}(1, \phi) = \phi$. The simulation data are presented in Fig.1 for the excluded volume interaction and in Fig.2 without the excluded volume interactions. The dotted lines in both Figures are the predicted formulas, (13) and (16), and the squares are the simulation data. Even for a small size of lattice used in the simulations, the agreement between simulation data and the predicted formula appear to be quite remarkable. The typical error bars are less than a few percent and the error bars are expected to vanish in the thermodynamic limit as the size increases. The good agreement between the simulations and the prediction, even for a small size of lattice, is precisely because of the fact that the ratio $A/B$, in equation (16) is essentially the ratio of one dimensional lattice sites over those of two dimensions, which is in the presence case of order $1/20 = 0.05 << 1$. Even for a modest size of two dimensional lattice, this ratio is small and its contribution is almost insignificant in higher dimensions. Further, the logarithmic singularity in the pressure at the closed packed density is also well captured in the lattice simulations with the typical error bars are less than a few percent. We now conclude with two comments.

First, while this method appears to produce excellent results, the method becomes a little problematic when there is an external bias, say the gravity toward the wall. In this case, unless the bias is small, it will eventually pull all the particles to the wall, giving the wall density essentially close to one, and largely independent of $\lambda$. In this case, it becomes quite difficult to exploit the relation (10) for different $\lambda$’s. We have not come up with a method to overcome this difficulty. Such a method, if successful, will be quite useful because it will enable one to directly measure the force profile of granular materials in a container, which is the subject of current studies [9-12].

Second, the method, however, is expected to work quite well in the absence of bias for other interacting systems. An example would be the charged or uncharged lattice gas with either long or short range interactions such as Coulomb interactions, or other Ising type interactions near the critical point. Such studies will require elaborate finite size scaling
analysis and extensive large scale simulations, which will be reported in future communications.

VI. Acknowledgements

This work was supported by NSF as a part of Research Experiences for Undergraduate Students program at Lehigh University. DCH wishes to express his thanks to Ronald Dickman for helpful discussions as well as for his independently obtaining eq.(14).
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Figure captions:

Fig. 1. Comparison between the Monte Carlo data and the exact formula (13) for the lattice gas with the excluded volume interaction for given bulk density $\phi$’s for different $\lambda$’s. The vertical axis is the particle density at the wall, $\rho_w$, and the horizontal axis is $\lambda$. From the bottom to top, $\phi = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$. Dotted lines are the exact formula (13).

Fig. 2. Same as in Fig. 1 except that multiple occupancy is allowed at the lattice sites. Dotted lines are the exact formula (16).
