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Petit and Grand Ensemble Monte Carlo Calculations of the Thermodynamics of the Lattice Gas*

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A direct Monte Carlo method for estimating the chemical potential in the petit canonical ensemble was applied to the simple cubic Ising-like lattice gas. The method is based on a simple relationship between the chemical potential and the potential energy distribution in a lattice gas at equilibrium as derived independently by Widom, and Jackson and Klein. Results are presented here for the chemical potential at various compositions and temperatures above and below the zero field ferromagnetic and antiferromagnetic critical points. The same lattice gas model was reconstructed in the form of a restricted grand canonical ensemble and results at several temperatures were compared with those from the petit canonical ensemble. The agreement was excellent in these cases.

1. INTRODUCTION

Recently, the Monte Carlo (MC) method has been applied to diffusion and ionic conductivity in highly disordered solids such as the superionic conductors, interstitial solid solutions, etc. [1–3]. These calculations have been couched in the form of the lattice gas model which seems to hold significant promise in accounting for the configurational components of the cooperative mechanisms of transport. Within this context it is convenient to study lattice gas models with a *constant* number of particles on a fixed number of sites at a constant thermodynamic temperature, i.e., the petit canonical ensemble. One drawback with this ensemble, however, has been the lack of a *direct* method for calculating equilibrium properties of interest, such as the chemical potential, μ. For the nearest neighbor interacting lattice gas it has been possible to estimate the partition function as a function of the number of particles. One can then differentiate numerically to obtain μ [4]. But such an estimate of the partition function is often poorly behaved and may even fail to converge for large volumes. Alternatively, of course, the μ/composition isotherms could be calculated from the grand canonical ensemble [5].

Recently, however, Baker [6] pointed out the applicability, for petit ensemble MC calculations, of the simple relationship between the chemical potential and the poten-

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tial energy distribution in the lattice gas at equilibrium, as derived some years ago by Widom [7] and Jackson and Klein [8]. The possible MC use of this relationship was also suggested by Chesnut [9].

Since the relationship is not well known, at least in MC form, we describe it in some detail in the present paper. This is followed by the presentation of results for μ/composition isotherms in the simple cubic Ising-like lattice gas at various temperatures above and below both the ferromagnetic and antiferromagnetic zero field critical points. Results for μ/composition isotherms from MC calculations in the *grand* ensemble are then presented at several of the same temperatures and compared with petit ensemble results.

2. THEORY AND METHOD OF COMPUTATION

Consider a lattice of B sites on which are distributed N interacting but indistinguishable particles. Occupancy of any site by more than one particle is excluded. We write for the configurational partition function in the petit canonical ensemble:

$$Q(N, B, T) = \frac{1}{N!} \sum_{\substack{j \\ \text{(all states} \\ \text{for } N \text{ particles)}}} \exp[-\beta E_j(N, B)], \tag{1}$$

where E_j is the total configurational energy for the lattice gas in state j and $\beta = (kT)^{-1}$.

If we note that the free energy is given by:

$$A(N, B, T) = -\beta^{-1} \ln Q(N, B, T), \tag{2}$$

and that the chemical potential is defined by:

$$\mu = (\delta A/\delta N)_{B,T}, \tag{3}$$

then μ can be written in the following finite-difference form:

$$\mu = \lim_{N\to\infty} -\beta^{-1} \ln[Q(N+1, B, T)/Q(N, B, T)]. \tag{4}$$

We substitute Eq. (1) into Eq. (4) and remove the limit notation for finite N:

$$\mu \approx -\beta^{-1} \ln \left\{ \frac{\sum_{m \text{ (all states for } N+1 \text{ particles)}} \exp[-\beta E_m(N+1, B)]}{(N+1) \sum_{j \text{ (all states for } N \text{ particles)}} \exp[-\beta E_j(N, B)]} \right\}. \tag{5}$$

If we define ΔE_j as the *change* in the configurational energy E_j on addition of the $N+1$ particle to the system of N particles in state j and if we note that B new states are thereby added to the old state sum, Eq. (5) becomes:

$$\mu \approx -\beta^{-1} \ln \left\{ \frac{B \sum_{j \text{ (all states for } N \text{ particles)}} \exp[-\beta E_j(N, B)] \exp(-\beta\, \Delta E_j)}{(N+1) \sum_{j \text{ (all states for } N \text{ particles)}} \exp[-\beta E_j(N, B)]} \right\}, \tag{6}$$

i.e.,

$$\mu \approx -\beta^{-1} \ln \left[\frac{B}{(N+1)} \langle \exp(-\beta\, \Delta E_j) \rangle\right], \tag{7}$$

where $\langle\ \rangle$ denotes the ensemble average.

The quantity $\exp(-\beta\, \Delta E_j)$ may be interpreted in the following way [7]. Consider a lattice gas at thermodynamic equilibrium but frozen in a given configuration j characteristic of equilibrium. Now let us attempt to add to the system another particle, identical to those already present, and imagine placing it *at each of the B lattice points* and thus measuring the hypothetical energy of interaction, ζ, with the existing particles. Assigning thus equal weight to each lattice site we write:

$$\exp(-\beta\, \Delta E_j) = B^{-1} \sum_{i=1}^{B} \exp(-\beta \zeta_i), \tag{8}$$

where ζ_i is the energy required to place a particle at site i. This energy may be positive or negative.

To evaluate the ensemble average the well-known "importance sampling" procedure of Metropolis *et al.* [10] may be used to generate a Markov chain of states, q_1, $q_2 \cdots q_M$, in which the relative frequencies of states in the limit are weighted in a Boltzmann fashion. Noting Eq. (8) we write for Eq. (7):

$$\mu \approx -\beta^{-1} \ln \left\{\frac{\sum_{l=1}^{M} [\sum_{i=1}^{B} \exp(-\beta \zeta_i)]_l}{(N+1) \cdot M}\right\}. \tag{9}$$

It is worth noting that in the case of athermal interactions (hard molecules) one can write for Eq. (9):

$$\mu \approx -\beta^{-1} \ln \left\{\frac{\sum_{l=1}^{M} [B - N(\bar{Z}_l + 1)]}{(N+1) \cdot M}\right\}, \tag{10}$$

where $\bar{Z}_l$ is the mean number of sites excluded by a particle (*not* including the site occupied) in a given configuration characteristic of equilibrium.

In the case of a lattice gas with "soft" nearest neighbor interactions of strength ϵ (we define $\epsilon < 0$ for attraction and $\epsilon > 0$ for repulsion) we can also write for Eq. (9) [7]:

$$\mu \approx -\beta^{-1} \ln \left\{\frac{\sum_{l=1}^{M} (B - N)[\sum_{r=0}^{C} \exp(-\beta r \epsilon)\, f_r]_l}{(N+1) \cdot M}\right\}, \tag{11}$$

where f_r ($r = 0, 1, 2, \ldots, C$) is the probability that, with the lattice gas at equilibrium, and, in a given configuration, an unoccupied site is surrounded by *exactly r* occupied sites and C is the lattice coordination.

In the present study we have used the above method leading to Eq. (9) in order to calculate the lattice gas chemical potential in a simple cubic lattice of 4096 sites with periodic boundaries and nearest neighbor interactions. To generate the Markov chain in the petit ensemble we applied the well-known method of Metropolis *et al.* [10]: the total configurational energy E_1 of the system is calculated. A particle is randomly selected and displaced to another site which has been randomly selected from all sites in the lattice. The configurational energy is recalculated; let this be E_2. If the energy has decreased (i.e., $E_2 \leqslant E_1$) then the new state is accepted. If the energy has increased, the probability of acceptance, $p = \exp[-\beta(E_2 - E_1)]$, is calculated; a random number, R, is generated, uniform on the interval (0, 1], and the new state is accepted only if R is less than p. The configurational energy of state q is calculated from the pairwise sum:

$$E_q = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \epsilon_{ij}, \qquad i \neq j. \tag{12}$$

Since we may expect a dependence of μ on the size of N we also recast the problem in the form of a grand canonical ensemble. The configurational partition function in the grand canonical ensemble can be written as:

$$\Xi(\mu, B, T) = \sum_{N=0}^{B} \exp(\beta N \mu) \frac{1}{N!} \sum_{\substack{j \\ \text{(all states} \\ \text{for } N \text{ particles)}}} \exp[-\beta E_j(N, B)]. \tag{13}$$

The probability that the system has *exactly* N particles, irrespective of energy, is given by:

$$P(N) = \frac{Q(N, B, T) \exp(\beta N \mu)}{\Xi(\mu, B, T)}, \tag{14}$$

and the ensemble average particle number $\langle N \rangle$ is given by:

$$\langle N \rangle = \sum_{i=1}^{N} P(N_i) N_i. \tag{15}$$

The method we used to construct the Markov chain is identical to that described in detail by Chesnut and Salsburg [5]. The weight assigned to each state q in the system is:

$$u_q = \exp(-\beta U_q), \tag{16}$$

where

$$U_q = (E_q - N_q \mu) \tag{17}$$

where E_q is given by Eq. (12).

An initial state is obtained by placing an arbitrary number of particles in the lattice. Each additional state is generated in the following way. A site is selected at random and an "occupant" i.e., particle or vacancy is also selected at random. If the selected site happens to have the same "occupant" as generated, the next state would be identical to the old state. Otherwise the quantity $\beta(U_2 - U_1)$ is computed where U_2

refers to the new state and U_1 refers to the old state. If $U_2 \leqslant U_1$ then the new state is accepted (this will involve either removal of a particle or addition of a particle to the system. If $U_2 > U_1$, the ratio, u_2/u_1, is calculated and compared with a random number R uniform on the interval (0, 1]. The new state is accepted only if R is less than u_2/u_1.

These calculations were performed on an IBM 370/195 computer at Argonne National Laboratory.

3. RESULTS

The equilibrium $\beta\mu$/particle density isotherms calculated from the petit ensemble for $\tilde{T}$ (= $\exp[-\beta\epsilon]$) from 0.32 to 2.70 are displayed in Fig. 1. The solid lines represent the best *visual* fit through the individual petit ensemble data points (not shown for clarity) which were mainly gathered at intervals of 0.01 in particle density, ρ ($\equiv N/B$). Each data point represented an average over 2×10^5 configurations once the configurational energy had converged, usually within 5×10^4 configurations. However, below the critical temperatures, convergence would usually require greater than 10^6 configurations.

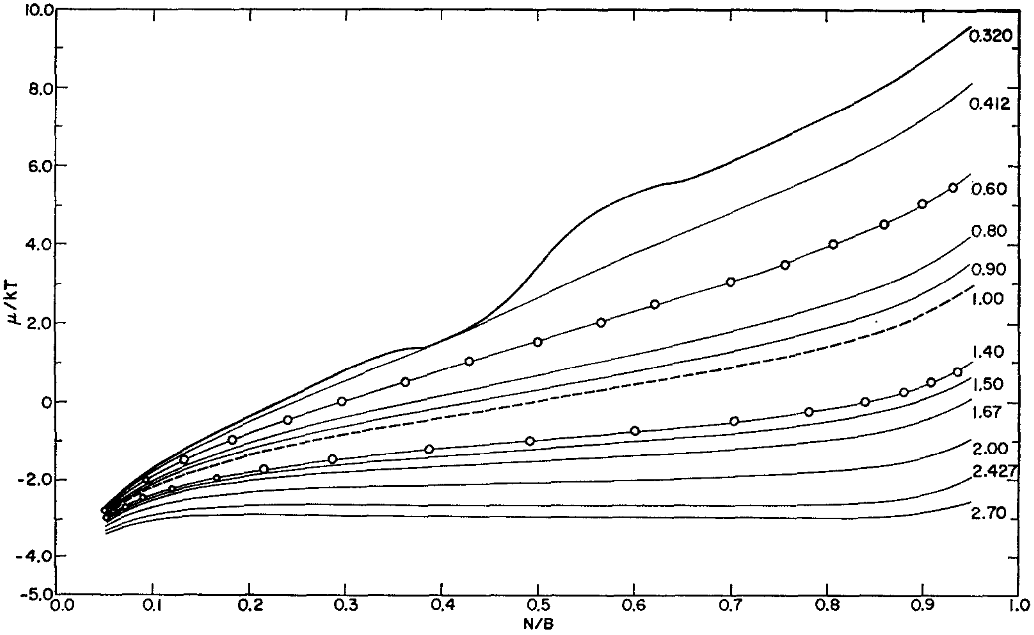

FIG. 1. The chemical potential as a function of density at various values of $\tilde{T}$: ——, best visual fit of data from the petit ensemble; o, data points from the grand ensemble; – – –, plot of Eq. (22).

The broken curve in Fig. 1, i.e., $\tilde{T} = 1.0$ is the result of a purely random distribution, i.e.,

$$\begin{aligned} \beta\mu &\approx -\ln[(B - N)/(N + 1)] \\ &\approx \ln[\rho/(1 - \rho)]. \end{aligned} \tag{18}$$

Historically Eq. (18) is the three-dimensional analog of the Langmuir adsorption isotherm.

The grand ensemble results are displayed in Fig. 1 as open circles for $\tilde{T} = 0.6$ and 1.4. The mean value of the particle number $\langle N \rangle$ was also averaged over 2×10^5 configurations once convergence had been achieved, usually within less than 15×10^3 configurations. The difference in the convergence rate between the two ensembles illustrates the fact that the grand ensemble approaches equilibrium exponentially fast whereas the petit ensemble does not.

There is excellent agreement between the results of the two ensembles, thus establishing that the finite-difference method for calculating $\beta\mu$ is a reliable and useful procedure for MC calculations in the lattice gas at a constant particle density. The internal consistency of the isotherms was tested using the following symmetry relation which is valid for the nearest neighbor interacting simple cubic lattice gas with periodic boundaries in the petit canonical ensemble [4]:

$$\beta\mu(B - N, B, T) = -\beta\mu(N - 1, B, T) + 6\beta\epsilon. \tag{19}$$

The petit ensemble results satisfied this relation to within a standard deviation as determined from the Markov chain. It was assumed that averages over successive groups of 10,000 configurations are uncorrelated.

Detailed $\beta\mu/\rho$ results from both ensembles are available on request from the authors.

4. DISCUSSION

The lattice gas in which the particles attract ($\tilde{T} > 1.0$) has frequently been studied as a model for the liquid/gas transition. Thus the temperature evolution of the isotherms here displays the usual condensation behavior into two phases—one a gas-like phase, the other, a liquid-like phase. The critical temperature has been accurately determined at $\rho = 0.5$ by high temperature series expansion [12]. $\tilde{T}_c$ was shown to be 2.43 which implies that the lowest isotherm but one in Fig. 1 is very nearly the critical isotherm. But it is not possible to verify this directly from the isotherm because of the uncertainty in slope. The lowest isotherm in Fig. 1 must inevitably cut the diphasic region. This isotherm exhibits no pseudo van der Waals loop, indicative of very small B [11]. This is not surprising since other studies, for example, see [5], have indicated that the present lattice of 4096 sites exhibits infinite system behavior. It is worth noting, however, that the present method for calculating $\beta\mu$ would seem to be useful for tracing the evolution of the shape of the loop at very small B.

The lattice gas in which particles repel ($\tilde{T} < 1.0$) has been used as a model for solidification [13] and adsorption [14]. Important recent applications have been in the area of superionic conductivity (see, for example, [15]). In lattices other than the "triangular" ones, interparticle repulsion produces specifically an ordered phase in which particles occupy alternate sites and which has a zero entropy at the absolute zero of temperature. The ordered phase is symmetrically centered around $\rho = 0.5$. The critical temperature occurs at about $\tilde{T}_c = 0.412$ [12]. The simulated isotherm at this temperature exhibits a very slight inflection at $\rho = 0.5$. The highest isotherm in Fig. 1, i.e., at $\tilde{T} = 0.32$ must cut through the ordered region. This isotherm exhibits apparently horizontal inflections at $\rho = 0.37$ and, of course, at $\rho = 0.63$. The first inflection may be interpreted as a continuous second order transition from the disordered "phase" to the ordered "phase". The second inflection may be interpreted similarly as a second order transition but from the ordered "phase" to the disordered "phase".

Comparison of these latter results with Ising theory can best be done in a magnetic language. In what is by now regarded as a classic paper, Lee and Yang [16] showed that the lattice gas is an analog of the Ising model. One associates a spin up ↑ with, say, an occupied site and a spin down ↓ with an unoccupied site. Since the Ising system is "open" with respect to magnetic spins, one can conveniently express the set of all possible spin values of B sites in terms of the isothermal/isobaric ensemble. This ensemble for the Ising problem is formally equivalent to the grand ensemble for the lattice gas in the restricted sense of Eq. (13). The role of the chemical potential for the lattice gas is taken by the magnetic field per spin H, and, for our definition of ϵ the equivalence is:

$$-2H \leftrightarrow \mu - 3\epsilon. \tag{20}$$

Using a high temperature series expansion, Bienenstock [17] determined the paramagnetic/antiferromagnetic boundary as a function of applied field in the simple cubic Ising magnet. This is, of course, equivalent to determining the order/disorder boundary in the lattice gas as a function of chemical potential. Bienenstock found that for $T/T_c = 0.779$ where T_c is the critical temperature in zero field (i.e., at a composition $\rho = 0.5$ in the lattice gas), $H/H_c = 0.697$ where H_c is the critical field ($\equiv -6J$) at $T = 0$. At this field *all* the antiparallel spins turn into the direction of the field. J is the isotropic coupling between neighboring spins ($4J \equiv -\epsilon$) and H is the magnetic field required to destroy the antiferromagnetic order at the given temperature T. For the same value of T/T_c (assuming that T_c as given by Bienenstock is "exact") the Monte Carlo results give $H/H_c = 0.785 \pm 0.012$ which is in only fair agreement with Bienenstock's value. Bienenstock has indicated, however, that the Padé approximants to the high temperature series expansion may not adequately represent the properties of the Ising system at large deviations from $\rho = 0.5$.

5. SUMMARY

A Monte Carlo method was used to calculate the chemical potential of the simple cubic lattice gas in the petit ensemble. Both nearest neighbor particle attraction and repulsion were examined. Petit ensemble results were in excellent agreement with those calculated from the grand ensemble at two temperatures. In addition, all petit ensemble results satisfied a basic symmetry relation. The value of the chemical potential required to destroy the long range order on the repulsion side at $\tilde{T} = 0.32$ was in fair agreement with the series expansion results of Bienenstock.

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