Journal of Statistical Physics, Vol. 30, No. 3, 1983

A Monte Carlo Study of the Entropy, the Pressure, and the Critical Behavior of the Hard-Square Lattice Gas

Hagai Meirovitch[1]

Received January 21, 1982; revised September 14, 1982

An approximate technique for estimating the entropy S with computer simulation methods, suggested recently by Meirovitch, is applied here to the Metropolis Monte Carlo (MC) simulation of the hard-square lattice gas in both the grand canonical and the canonical ensembles. The chemical potential μ, calculated by Widom's method, and S enable one to obtain also the pressure P. The MC results are compared with results obtained with Padé approximants (PA) and are found to be very accurate; for example, at the critical activity z_c the MC and the PA estimates for S deviate by 0.5%. Beyond z_c this deviation decreases to 0.01% and comparable accuracy is detected for P. We argue that close to z_c our results for S, μ, and P are more accurate than the PA estimates. Independent of the entropy study, we also calculate the critical exponents by applying Fisher's finite-size scaling theory to the results for the long-range order, the compressibility and the staggered compressibility, obtained for several lattices of different size at z_c. The data are consistent with the critical exponents of the plane Ising lattice $\beta = 1/8$, $\nu = 1$, $\gamma = 7/4$, and $\alpha = 0$. Our values for β and ν agree with series expansion and renormalization group results, respectively. $\alpha = 0$ has been obtained also by matrix method studies; it differs, however, from the estimate of Baxter *et al.* $\alpha = 0.09 \pm 0.05$. As far as we know γ has not been calculated yet.

KEY WORDS: Monte Carlo; hard-square lattice gas; critical exponents; entropy; pressure.

1. INTRODUCTION

Calculation of the entropy S with the commonly used Metropolis Monte Carlo (MC)[1] simulation is difficult since entropy is related to the sampling

[1] Chemical Physics Department, Weizmann Institute of Science, Rehovot 76100, Israel.

0022-4715/83/0300-0681$03.00/0

probability which is not provided by this procedure. An approximate technique for estimating entropy with *any* computer simulation method has been suggested recently by Meirovitch and applied very successfully to the MC simulation of the square Ising lattice[2] and the square lattice gas model.[3] For the lattice gas model (described in the framework of the canonical ensemble) very accurate estimates for the chemical potential μ have been obtained by employing the method of Widom[4] and Jackson and Klein,[5,6] and a method suggested by Alexandrowicz.[7,8] These results for μ and S lead (using basic thermodynamic relations) to very accurate estimates also for the pressure P.[3] As far as we know this is the first time the pressure of a lattice gas has been calculated by MC, probably because the usual method for estimating P, based on the virial theorem, is not applicable to lattice systems. The new technique is based on an approximate formula for the entropy in which the entropy is expressed as a function of the frequency of occurrence of certain local states.[2] These frequencies are calculated from a *single* MC run, which makes this technique substantially more efficient than the commonly used reversible thermodynamic integration.[9] Also, in contrast to the "multistage sampling"[10] and Salsburg's method[11] the accuracy of the new technique improves with increasing system size. It is also more accurate than other methods for estimating entropy (see Ref. 8 and methods reviewed by Binder in Ref. 12). The formula for the entropy and the definition of the local states are based on the concepts of the stochastic models (SM) method, which is a computer simulation technique independent of the commonly used MC procedure, suggested by Alexandrowicz.[13–15] Understanding these concepts is therefore essential for applying the technique for the entropy to various systems. It should be pointed out that the entropy, in addition to being a measure of the extent of order in a system and an essential ingredient for calculating the pressure, leads to the free energy, which enables one to define the most stable state of a system as that with minimum free energy. This criterion is useful when two simulation runs lead the system to different free energy minima. The free energy enables one also to determine precisely the transition point in the case of a first-order phase transition, where two phases with the same free energy coexist.[16,17]

In view of the wide interest in the calculation of entropy, of the lack of efficient calculation methods, and of the extremely accurate results obtained with the new technique for the Ising and lattice gas models,[2,3] it seems desirable to extend the technique to continuum models for fluids as well. For such systems, (e.g., the model of hard spheres), the volume will be divided into cells (much smaller than molecular size) and a discrete set of

local states will be defined by taking into account the various possible ways to occupy a certain group of cells with molecules. The continuum model is thus approximated by a lattice gas in which occupation of a cell necessitates the exclusion of molecules in several neighboring cells. Such exclusion has not been treated yet by the SM method nor does it exist in the lattice gas model studied previously,[3] which only forbids double occupancy of a cell. We have therefore decided (before treating a complex continuum model) to test the efficiency of the technique for the MC simulation of the hard-square lattice gas with first neighbor exclusion, which is a simple model taking into account the effect of repulsion in a nontrivial manner. This model has been studied extensively by various approximate techniques[18–35]; however, as far as we know, no detailed MC study of it has been published. Many of these studies[26–35] have shown that the model undergoes a second-order phase transition, and relatively accurate estimates for the critical values of the activity, the density, the pressure, and the entropy have been obtained. In this work the entropy and other thermodynamic quantities are calculated in both the canonical ensemble (CE) and the grand canonical ensemble (GCE). It should be pointed out that in the GCE, in contrast to the CE, the isothermal compressibility K_T can be expressed as a function of the fluctuations in the density[36] and therefore can be conveniently calculated with the MC procedure. The MC results are compared to results obtained with Padé approximants (PA), based on the series expansion data of Gaunt and Fisher (GF)[26] and to results obtained by the matrix method.[27–29] We also suggest a new procedure for estimating the accuracy of our results based on calculating successive approximations for the entropy.

In the second part of this work (which is independent of the entropy study), we calculate the critical exponents of the hard-square lattice gas. Ground-state symmetry considerations classify this model in the same universality class as the zero-field two-dimensional Ising lattice, which suggest that the two models have the same critical exponents.[37] However, these considerations are phenomenological and therefore an effort has been made in recent years to check their validity by calculating the critical exponents of the model, with various techniques. Indeed, GF[26] and Baxter, Enting, and Tsang (BET),[30] using series expansion techniques, estimated with high credibility the Ising model value $\beta = 1/8$, where β is the critical exponent of the long-range order R; recent renormalization group studies (based on Nightingale method[38]) by Rácz,[32] Wood and Goldfinch,[33] and Kinzel and Shick[34] all estimate, with a very good approximation, the Ising model value $\nu = 1$, where ν is the critical exponent of the correlation length.[39] Substituting this result in the hyperscaling

relation[39] $d\nu = \alpha - 2$ leads to the Ising model result $\alpha = 0$, which means that the compressibility K_T diverges logarithmically. However, GF did not find divergence of K_T at the transition point and BET, who analyzed longer series, estimate $\alpha = 0.09 \pm 0.05$, which led them to speculate about the possibility of a non-Ising model set of exponents. On the other hand, transfer matrix studies of Runnels,[27] Ree and Chesnut,[29] and Runnels and Comb[28] show that, to a high degree of accuracy, the maximum compressibility of finite-width strips is proportional to the logarithm of the width, i.e., the compressibility has a logarithmic singularity. Another support for a logarithmic singularity is the estimate $-0.0196 < \alpha < 0.0174$ made in Ref. 33. It should be pointed out that the critical exponent γ of the staggered compressibility χ^+ has not been estimated by any of these methods. In view of the controversy about the value of α and the lack of an estimate for γ we calculate in this work the critical exponents of the model using the MC procedure. This can be carried out either by employing Fisher's finite-size scaling theory[40,41] (see also Refs. 42–46) or by a method suggested recently by Swendsen.[47,48] In the present work we use Fisher's method, which, however, requires knowing the critical activity z_c with sufficient accuracy. We do not attempt to calculate z_c, which would need a lot of computer time, but rather use the relatively accurate estimate of BET (which is also very close to the estimates obtained by other methods[29,32]). At z_c we carry out very long MC runs in the GCE for six lattices of size $(L \times L)$ from $L = 12$ to $L = 64$. The results for K_T, χ^+ and R enable us to estimate the corresponding critical exponents α, γ, and β, respectively, and also to obtain ν.

2. THEORY

2.1. The Hard-Square Lattice Gas

Consider a square lattice of $V = L \times L$ sites, each of which can be either empty or occupied by a molecule. There are N molecules on the lattice distributed among the V sites. The density of the molecules is defined as $\rho = N/V$. The multiple occupancy of sites is forbidden and the interaction potential is $+\infty$ for particles occupying nearest-neighbor sites but zero otherwise. At maximum density $\rho_0 = 1/2$ the particles pack in a regular array on the sites of one sublattice, which we take to be the A sublattice; the second sublattice, B, is empty. Of special interest is the critical behavior of the compressibility K_T, the staggered compressibility χ^+, and the long-range order R which is determined by the critical

exponents α, γ, and β respectively. R is defined by

$$R = (\rho_a - \rho_b)/\rho_0 = 2(\rho_a - \rho_b) \tag{1}$$

where ρ_a and ρ_b are the sublattice densities and

$$\rho = \rho_a + \rho_b \tag{2}$$

In the GCE, K_T and χ^+ can be expressed as functions of the fluctuations in $\rho(z)$ and $R(z)$, respectively, where z is the activity,[36]

$$kT\rho K_T = \left\langle (\rho(z) - \langle \rho(z) \rangle)^2 \right\rangle V / \langle \rho(z) \rangle \tag{3}$$

$$\chi^+ = \left\langle (R(z) - \langle R(z) \rangle)^2 \right\rangle V/4 \tag{4}$$

In these equations k is the Boltzmann constant, T the absolute temperature, and $\langle\ \rangle$ denotes the GCE average. Estimations $\bar{R}$ for $\langle R \rangle$, $\overline{\chi^+}$ for χ^+, etc. can be obtained from MC samples of M configurations:

$$\bar{R} = M^{-1} \sum_{t=1}^{M} R[i(t)] \tag{5}$$

$$\overline{\chi^+} = (4M)^{-1} V \sum_{t=1}^{M} \{ R[i(t)] - \bar{R} \}^2 \tag{6}$$

here $i(t)$ denotes the configuration i obtained at time t of the MC process. We estimate also the absolute value of R, by $|R|$,

$$|R| = M^{-1} \sum_{t=1}^{M} |R[i(t)]| \tag{7}$$

2.2. Estimation of the Chemical Potential

The chemical potential of the system, μ_s, can be calculated either by a method suggested by Widom[4,6] and by Jackson and Klein[5] or, alternatively, by a method suggested recently by Alexandrowicz.[3,7,8] For the present model, however, the two methods are identical and give

$$\mu_s/kT = \log z_s = -\log(\langle \rho_v \rangle) \tag{8}$$

where $\langle \rho_v \rangle$ denotes the average density (in the CE or the GCE) of vacant sites which are surrounded by nearest-neighbor vacant sites. An estimation $\bar{\mu}_s$ for μ is obtained similarly to Eqs. (5) and (6) by

$$\bar{\mu}_s = -\log\left\{ M^{-1} \sum_{t=1}^{M} \rho_v[i(t)] \right\} \tag{9}$$

2.3. Calculation of the Entropy

The entropy is estimated by means of a formula described recently for the square Ising lattice[2] and the square lattice gas model.[3] In this formula the entropy is expressed, approximately, as a function of the frequency of occurrence of certain local states, related to the occupancy of a site and its neighbor sites. This formula, derived on the basis of the SM method considerations (see Refs. 2, 14, and 15), is general in the sense that it does not depend on the model. The definition of the local states, however, changes from model to model. Since the hard-square lattice gas and the lattice gas previously studied[3] are both based on nearest-neighbor interactions and have the same geometry, their local states are very much the same. They differ only in the high-density regime where the antiferromagnetic-like long-range order of the hard squares should be taken into account.

In the present work we employ four sets of local states which define four approximations for the entropy S_6, S_{10}, S_{6L}, and S_{10L}. These approximations enable one to estimate the accuracy of our best approximation S_{10L} as will be discussed later. We shall describe now the local states for S_6. Consider an aribitrary site k of the lattice and six of its neighbor sites, as illustrated by the solid circles in Fig. 1. Two of these neighbor sites are on the left side of site k within the same row l and the other four belong to the $(l-1)$th row. Each site can be either occupied by a particle, or vacant, making up two different states, and therefore $2^6 = 64$ distinct local states are possible; however, in order to decrease their number we apply additional approximation. For sites $k-2$ and $k-L+3$ we distinguish only between the three states (rather than four) vacant–vacant, occupied–occupied, and vacant–occupied (see discussion in Refs. 1, 40, and 41). Therefore $m = 3 \times 2^4 = 48$ local states of the above defined six sites are

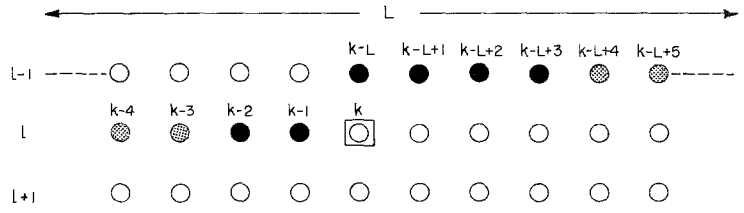

Fig. 1. A diagram explaining the definition of the local states $I,+$; $I,-$ and I, used for estimating the entropy [Eq. (10)]. The six solid circles around the central circle k denote the lattice sites which define the local states I for the lowest approximation of the entropy, S_6; two of them are in the same row l as the central circle k while the other four belong to the preceding row $l-1$. The solid and shaded circles (altogether 10) denote lattice sites around site k considered in the better approximation S_{10}.

defined (rather than 64) and are denoted by I, $1 \leqslant I \leqslant 48$. The two states of the central site k need also to be taken into account and are denoted by $-$ or $+$ according to whether the site is empty or occupied, respectively. Hence altogether $2 \times 48 = 96$ local states are defined and denoted by $I, +$ and $I, -$. The ensemble frequencies of occurrence of local states I, $I, +$, and $I, -$ are denoted by ν_I, $\nu_{I,+}$, and $\nu_{I,-}$, respectively. It is shown in Ref. 2 that an approximation S for the entropy can be defined by means of the local states frequencies:

$$\frac{S}{kN} \simeq -\sum_{I=1}^{m} \nu_{I,+} \log(\nu_{I,+}/\nu_I) + \nu_{I,-} \log(\nu_{I,-}/\nu_I) \tag{10}$$

$$\nu_I = \nu_{I,+} + \nu_{I,-} \tag{11}$$

We denote by S_6 the approximation based on six neighbor sites and $m = 48$, described above. It should be pointed out that because of the nearest-neighbor infinite repulsions many local states are excluded and the number of the allowed ones is much smaller than 48. The frequencies are calculated over a sample of M configuration,

$$\bar{\nu}_{I,+} = (MV)^{-1} \sum_{t=1}^{M} N_{I,+}[i(t)] \tag{12}$$

where $N_{I,+}[i(t)]$ is the number of times local states $I, +$ appear in configuration i, sampled at time t, just as in Eq. (5); $\bar{\nu}_{I,-}$ is defined in a similar way. Substituting the 96 $\nu_{I,+}$ and $\bar{\nu}_{I,-}$ into Eq. (10) gives an estimate for S_6. Equation (10) defines local states up to a cutoff of six neighboring sites instead of the entire row of L lattice sites $(k - L, k + L + 1 \ldots k - 1)$, which defines the *exact* set of local states (see discussion in Refs. 2, 14, and 15); therefore $S_6 \geqslant S_{\text{exact}}$. Obviously, the larger the number of sites considered the better the representation of the long-range density correlations and hence the approximation (which means lower entropy). We define also a larger set of local states, based on the former six lattice sites and the four sites $k - 3$, $k - 4$, $k - L + 4$, and $k - L + 5$, illustrated by shaded circles in Fig. 1. As in the previous approximation we distinguish only between three states for sites $k - L + 5$ and $k - 4$, and therefore the number of local states of type I is $m = 3 \times 2^8 = 768$. This approximation for the entropy based on 10 sites is denoted S_{10}.

The two sets of local states defined so far take into account short-range effects but ignore the long-range order which prevails at high densities. For example, if a site k (with local states I) belongs to sublattice A (which is assumed to be more occupied than B) the probability of finding it occupied is larger than for a site on sublattice B with the same local state I. We take into account the long-range order effect in the following way: in

addition to the "short-range" local states previously defined we define also two "long-range local states" for a site k, which are determined according to whether site k belongs to the more occupied sublattice or to the less occupied one. We therefore obtain two additional approximations for the entropy, based on S_6 and S_{10}: One with $m = 2 \times 48 = 96$ local states, which is denoted S_{6L}, and the second with $m = 2 \times 768 = 1536$, which we denote S_{10L}.

2.4. Calculation of the Pressure

The pressure P can be obtained from the free energy, the chemical potential, and the density by means of a basic thermodynamic relation (see Ref. 3). For the hard-square lattice gas, however, only the entropy contributes to the free energy and therefore

$$P/kT = \rho(\mu/kT + S/kN) \tag{13}$$

Since μ and S can be estimated by methods described in the previous sections, P can be estimated as well.

3. RESULTS AND DISCUSSION

3.1. Method of Calculation

We impose on the lattice gas periodic boundary conditions and simulate it with the MC procedure in both the CE (N, V, T) and the GCE (μ, V, T). In the CE the process is carried out as follows: one starts with a lattice filled with N randomly distributed molecules. In each step of the process a pair of occupied and vacant sites are selected at random with the help of a random number generator. If the move of the molecule from the occupied to the vacant site is forbidden another pair of such sites is selected. If the move is allowed a random number R, $0 \leqslant R \leqslant 1$ is provided, and the molecule exchanges sites if $R < 0.5$ and remains at its original site if $R \geqslant 0.5$. For $\rho \neq \rho_c$ the lattice size is $L = 80$. The results were obtained from runs of $nM = 1.44 \times 10^8$ MC steps where $M = 15000$ constitutes the number of configurations [Eq. (5)] sampled at intervals of $n = 1.5 \times L^2 = 9600$ MC steps. To exclude the relaxation to equilibrium from the starting configuration the averaging was started only after 0.6×10^6 MC steps.

The MC process in the GCE is started from a configuration with an arbitrary number of molecules distributed at random. The lattice sites are visited in a predefined order and a molecule is removed or added to each

site according to the following criteria:

(a) If site k is vacant but excluded the next site is treated.

(b) If k is a vacant not excluded site a molecule is added to it with probability p_{vo} (v—vacant, o—occupied):

$$p_{vo} = \begin{cases} 1 & \text{if } z > 1 \\ z & \text{if } z < 1 \end{cases} \tag{14}$$

Obviously, site k remains vacant with probability $p_{vv} = 1 - p_{vo}$.

(c) If site k is occupied the molecule is removed or remains with probabilities p_{ov} and $p_{oo} = 1 - p_{ov}$ respectively:

$$p_{ov} = \begin{cases} z^{-1} & \text{if } z > 1 \\ 1 & \text{if } z < 1 \end{cases} \tag{15}$$

Beyond the transition point we used $L = 80$ and performed $nM = 2.88 \times 10^8$ MC steps, where $n = 3 \times L^2 = 19200$ and $M = 15000$. At the critical activity z_c much longer MC runs were carried out (see Section 3.2.3). In order to exclude the relaxation to equilibrium the averaging was started after 1.92×10^7 MC steps.

3.2. Results

The MC results obtained in the GCE (at $z \neq z_c$) and in the CE are summarized in Tables I and II, respectively. In Table III we present the GCE results calculated at the critical density z_c for six lattices of size $L = 12$ to $L = 64$; this enables one to obtain the critical exponents. In order to compare the results of Tables I and II, the GCE simulations have been carried out at μ values which lie within the statistical error of the values μ_s appearing in Table II. For comparison we also provide estimates obtained from [6, 6] and [4, 4] PA (based on the series expansion data of GF) for the various thermodynamic quantities. One should bear in mind, however, that these estimates are approximate and their accuracy decreases as the transition point is approached.

3.2.1. Results for the Grand Canonical Ensemble. The MC results calculated in the GCE at $z \neq z_c$ are presented in Table I. It should be pointed out that μ_s, z_s, ρ, R, K_T and χ^+ are defined by Eqs. (1)–(9) without any approximation and therefore their accuracy depends mainly on the sample size M and the lattice size L. However, the accuracy of the results for the entropy S_{10L}, S_{10}, S_{L6}, and S_6 and hence for the pressure P, is determined also by the extent of approximation imposed on Eq. (10), i.e., the definition of the local states. The PA estimates become inaccurate as the transition point is approached; for example: for $\mu = 1.241$ the PA value

Table I. MC Results in the Grand Canonical Ensemble for $z \neq z_c$[a]

μ/kT	z	Method	μ_s/kT	ρ	P/kT	R	χ^+	$kT\rho K_T$	S_{10L}/kN	S_{10}/kN	S_{6L}/kN	S_6/kN
−1.73520	0.17636	MC	−1.7350(4)	0.09986(4)	0.12949(2)		0.148(2)	0.612(6)	3.0318(3)	3.0318(3)	3.0319(3)	3.0319(3)
		PA		0.09985	0.12944		0.148	0.609	3.0315			
−0.33120	0.71806	MC	−0.3309(2)	0.19986(1)	0.33690(1)		0.618(6)	0.396(2)	2.0168(3)	2.0168(3)	2.0169(3)	2.0169(3)
		PA		0.19983	0.33687		0.622	0.396	2.0156			
0.82272	2.27668	MC	0.8225(5)	0.29996(4)	0.62317(2)		5.3(2)	0.34(1)	1.2548(3)	1.2548(3)	1.2559(2)	1.2559(2)
		PA		0.29618	0.61867		8.9	0.28	1.266			
1.24100	3.45907	MC	1.2411(2)	0.3497(2)	0.7587(1)		71(5)	0.31(2)	0.929(2)	0.929(2)	0.931(1)	0.932(1)
		PA		0.3331	0.7423		—	0.26	0.987			
1.41982	4.13638	MC	1.4200(6)	0.3840(5)	0.82397(5)	0.682(3)	2.5(2)	0.376(4)	0.725(1)	0.728(1)	0.7258(8)	0.7347(8)
		PA		0.3845	0.82387	0.679	1.9	0.358	0.723			
1.54282	4.67776	MC	1.5432(2)	0.40007(3)	0.87221(4)	0.761(1)	0.53(2)	0.261(2)	0.6373(4)	0.6394(4)	0.6373(4)	0.6452(5)
		PA		0.40005	0.87220	0.760	0.62	0.274	0.6374			
2.22786	9.27999	MC	2.2272(4)	0.44978(3)	1.16568(1)	0.89666(5)	0.063(1)	0.108(1)	0.3638(2)	0.3639(2)	0.3637(2)	0.3652(2)
		PA		0.44983	1.16630	0.89677	0.063	0.107	0.3649			

[a] System chemical potential μ_s, density ρ, pressure P, long-range order R, staggered compressibility χ^+, compressibility K_T, and four approximations for the entropy S_{10L}, S_{10}, S_{6L}, and S_6 obtained with the MC procedure for given values of the chemical potential μ in the GCE. The lattice size is $L = 80$ and the sample size $M = 15000$ (see Section 3.1 for details about the sample). The broken line separates the low- and high-density regimes. The statistical error of the last decimal place appears in parentheses; for example 0.822(5) means 0.822 + 0.005. Estimates obtained with [6, 6] PA (in z) and [4, 4] PA (in $1/z$) (for the low- and high-density regimes respectively) appear below the MC results. The series expansion data are taken from GF.[26] The PA estimate for S has been obtained with Eq. (13).

for χ^+ is negative! And the PA estimate for ρ, which according to Table II should be very close to 0.35, is 0.33. Some indication for unreliable results is the existence of significant difference between estimates of different PA (e.g. [6, 7], [6, 6], [7, 6] etc.). In fact, in the low-density regime close to the transition the estimates of the [7, 6] PA agree much better with the MC results than the values of the [6, 6] PA appearing in the table.

The deviations of the average values of μ_s from μ are relatively small and range from 0.1% to 0.01%. The results for ρ should be very close to the corresponding values of ρ in Table II (see discussion in Section 3.1), and indeed the deviation is small, from 0.005% to 0.25%. The deviations of the average values of the MC results for ρ from the corresponding PA estimates are even smaller, except for $\mu = 0.82272$ and $\mu = 1.241$. The MC and the PA results for R agree within 0.01% to 0.5%, and those for K_T within 0.5% to 6% (again except for $\mu = 0.82272$ and $\mu = 1.241$). For χ^+, however, the two sets of results agree only far from z_c, probably due to the inaccuracy in the PA estimates discussed above.

Of special interest are the results obtained for the entropy. First, it should be noticed that in the low-density regime, where long-range order does not exist, $S_{6L} = S_6$ and $S_{10L} = S_{10}$, as expected. A slight deviation from this picture occurs only for $\mu = 1.241$, but this stems probably from finite size effects near the transition point. However, in the high-density regime (where $R > 0$) the "long-range order local states" affect the entropy and $S_{10L} \leqslant S_{10}$; $S_{6L} \leqslant S_6$. For the low-density regime the results for S_{10L}, S_{10}, S_{6L}, and S_6 are equal within the statistical error (except for $\mu = 0.82272$); for the high-density regime $S_{10L} = S_{6L}$ within the statistical error. We can therefore assume that for these calculations S_{10L} is accurate within the statistical error [since imposing better approximation on Eq. (10) probably would not lower the entropy to a detectable extent, see discussion in Section 2.3]. The PA estimates for the entropy have been obtained from μ and the PA values for P and ρ, using Eq. (13). Except for $\mu = 0.82272$ and $\mu = 1.241$ small deviations between the PA and the MC values are detected (from 0.05% to 0.2%), and this supports our previous estimation of the accuracy of the MC results for S. The MC results for the pressure have been obtained from S_{10L}, μ and ρ, employing Eq. (13). Again, except for $\mu = 0.82272$ and $\mu = 1.241$, these results agree well with the PA values, where the deviations range from 0.01% to 0.05%.

In Table III we present the GCE results for μ_s, z_s, ρ, P, and S obtained at the critical activity z_c (for details about the simulation see Section 3.2.3). For comparison we provide in the bottom rows of the table the critical values of these quantities obtained by Ree and Chesnut[29] and by BET and GF; in both rows the critical values for the entropy have been obtained by substituting μ_s, ρ, and P in Eq. (13). The agreement between the MC

Table II. MC Results in the Canonical Ensemble[a]

ρ/ρ_0	Method	μ_s/kT	z_s	P/kT	R	S_{10L}/kN	S_{10}/kN
0.2	MC	−1.7352(1)	0.17635(2)	0.12946(2)		3.0319(2)	3.0319(2)
	PA	−1.7329	0.17678	0.12968		3.0297	
0.4	MC	−0.3314(1)	0.7179(1)	0.33689(6)		2.0171(1)	2.0171(1)
	PA	−0.3295	0.7193	0.33726		2.0157	
0.6	MC	0.823(1)	2.278(2)	0.6232(2)		1.2542(1)	1.2542(1)
	PA	0.842	2.321	0.6230		1.2544	
0.7	MC	1.242(2)	3.464(5)	0.7590(1)		0.9275(5)	0.9278(5)
	PA	1.347	3.844	0.7574		0.9262	
0.736	MC	1.33	3.80	0.793		0.8223	0.8238
	PA	1.33400(3)	3.7962(1)	0.792(5)		0.818	
0.77	MC	1.424(4)	4.155(8)	0.826(1)	0.693(3)	0.7201(4)	0.7231(4)
	PA	1.421	4.142	0.825	0.695	0.7201	
0.80	MC	1.540(3)	4.66(2)	0.8707(8)	0.762(2)	0.6371(3)	0.6391(3)
	PA	1.542	4.67	0.8718	0.761	0.6377	
0.90	MC	2.2283(8)	9.284(5)	1.1654(2)	0.8968(1)	0.36247(5)	0.36257(5)
	PA	2.2315	9.314	1.1672	0.8972	0.36243	

[a] System chemical potential μ_s, system activity z_s, pressure P, long-range order R, and two approximations for the entropy S_{10L} and S_{10}, calculated by the MC procedure in the CE for various values of ρ. $\rho_0 = 1/2$ is the density of close packing. The lattice size is $L = 80$ and the sample size $M = 15000$ (for details about the sample see Section 3.1). The statistical error is defined in Table I. Estimates obtained with [6, 6] PA (in ρ) and [4, 4] PA (in $1 - 2\rho$) (for the low- and high-density regimes, respectively) appear below the MC results. The series expansion data are taken from GF.[26] $2\rho_c = 0.736$ is the value for the critical density obtained by BET.[30] For ρ_c, $L = 40$ the statistical error is not given since convergence has not been attained. For ρ_c are provided the critical values obtained by GF and BET (see details in Section 3.2.1). L is the lattice size and the sample size is $M = 10^5$ (more details about the sample appear in Section 3.2.3). The statistical error is defined in Table I. In the two last rows are presented the critical values estimated by GF and BET and by Ref. 29 (for details see Section 3.2.1).

Table III. MC Results in the Grand Canonical Ensemble at z_c[a]

L	μ_s/kT	z_s	ρ	P/kT	$\|R\|$	χ_1^+	χ_2^+	$kT\rho K_T$	S_{10L}/kN	S_{10}/k_N
12	1.3335(5)	3.794(3)	0.3742(3)	0.7920(2)	0.660(2)	16.7(1)	16.7(1)	0.376(3)	0.7824(8)	0.7855(8)
16	1.3338(5)	3.795(3)	0.3724(1)	0.7924(1)	0.634(2)	27.3(4)	27.5(4)	0.408(6)	0.7940(8)	0.7958(8)
24	1.3335(6)	3.795(3)	0.3711(1)	0.79260(8)	0.608(3)	54(2)	56.7(5)	0.449(3)	0.802(1)	0.803(1)
32	1.3340(3)	3.796(1)	0.3698(2)	0.7924(1)	0.575(5)	86(7)	92(1)	0.49(1)	0.808(1)	0.810(1)
40	1.3336(3)	3.795(1)	0.3698(2)	0.79227(8)	0.570(3)	138(2)	138(2)	0.50(1)	0.808(1)	0.810(1)
64	1.3341(3)	3.797(1)	0.369(1)	0.7922(1)	0.525(8)	275(50)	310(30)	0.56(3)	0.814(2)	0.815(2)
PA	1.33400(3)	3.7962(1)	0.368(1)	0.792(5)					0.818	
Ref. 29	1.33411(8)	3.7966(3)	0.36776(1)	0.7916(1)					0.8184	

[a] System chemical potential μ_s, system activity z_s, density ρ, pressure P, long-range order $|R|$, staggered compressibilities χ_1^+ and χ_2^+, compressibility K_T, and two approximations for the entropy S_{10L} and S_{10}, calculated with the MC procedure in the GCE at the critical activity $z_c = 3.7962$ (estimated by BET[30]). L is the lattice size and the sample size is $M = 10^5$ (more details about the sample appear in Section 3.2.3). The statistical error is defined in Table I. In the two last rows are presented the critical values estimated by GF and BET and by Ref. 29 (for details see Section 3.2.1).

values and the PA estimates is very good; for $L = 64$, the deviation is $\sim$0.08% for μ_s, 0.3% for ρ, and 0.5% for the entropy, and the values for the pressure are equal within the statistical error, which is 0.6%. A comparable agreement is found also between the MC results and the results of Ref. 29.

To summarize: very good agreement between the MC and the PA results for S, P, and ρ has been obtained at $z \neq z_c$ not too close to z_c. However, we have given some indications that close to z_c the PA estimates are not accurate. The accuracy of the MC results for ρ, S, and P, however, is less affected in the critical region, as can be deduced from the good results obtained in Table III at z_c itself. We therefore have reason to believe that close to z_c the MC results are more accurate than the PA ones.

3.2.2. Results for the Canonical Ensemble. Results obtained in the CE for given values of ρ are summarized in Table II. In this ensemble, in contrast to the GCE, we were not able to calculate K_T and χ^+ since they cannot be expressed as functions of fluctuations in ρ and R, respectively. Even though the same lattice size and approximately the same number of MC steps are used for both the CE and the GCE calculations the statistical error of the results for μ_s for $\rho/\rho_0 > 0.4$ is about an order of magnitude larger in Table II than in Table I. The statistical error of the entropy, however, is slightly lower than that detected in Table I, and the corresponding results for S are very close in the two tables. We have also calculated S_6 and S_{6L} in the CE and detected for them the same behavior as in Table I; therefore we present in Table II only S_{10L} and S_{10}. The PA estimates for the entropy have been obtained directly from series expansion for $S(\rho)$ derived by GF, and not with Eq. (13) as in Table I. The agreement between these estimates and the corresponding MC results is generally comparable to that of Table I. For $\rho/\rho_0 = 0.6$ and 0.7, however, the present results fit better, probably due to the more accurate PA values. The difference between the MC and PA results for R is also comparable to that which has been detected in Table I. The statistical error of the MC results for P, however, is affected by the relatively large statistical error in μ_s and therefore is about an order of magnitude higher than in Table I.

We have simulated the system also at the critical density, $\rho_c/\rho_0 = 0.736$, estimated by BET. For $L = 80$ the long-range order R did not change sign during the simulation (i.e., sublattice A was always more occupied than B); we therefore decreased the lattice size to $L = 40$ and R changed sign only once. The results at ρ_c for $L = 40$, $M = 15000$, and $n = 2400$, presented in the table, have been therefore obtained before a convergence has been detected. They are, however, very close to the corresponding results in Table III calculated at the critical activity z_c (where R changed sign much faster).

To summarize: we find the simulation in the CE to be less efficient than in the GCE with respect to the system chemical potential, the pressure, and the long-range order at ρ_c. The accuracy of the results for the entropy, however, is found to be about the same for the two ensembles.

3.2.3. The Critical Exponents. In Table III are presented the GCE results obtained at the critical activity $z_c = 3.7962$ (estimated by BET), for six lattices of different size, from $L = 12$ to $L = 64$. Very long MC runs have been performed with $M = 10^5$ and $n = 4L^2$ (see Section 3.1). For each lattice the results are the averages of results obtained from several such MC runs with different starting configurations and different random number sequences.

The critical exponents of χ^+, K_T, and R can be estimated by applying Fisher's finite-size scaling theory[40,41] (see also Ref. 42–46) to their results in Table III. According to this theory χ^+ should increase with L as

$$\chi^+ = BL^{\gamma/\nu} \qquad \text{at } z_c \text{ for large } L \tag{16}$$

where γ and ν are the critical exponents of χ^+ and the correlation length, respectively,[39] and B is a constant. A similar relation is expected for $|R|$ [Eq. (7)], $-\beta$ replaces γ.[46]

A plot of $\log|R|$ vs $\log L$ (for 5 points excluding for $L = 64$) gave a straight line with a slope $\beta/\nu = 0.125(5)$ and $B = 0.90(1)$ (the indicated error, here and below, refers to the last decimal place). This slope is equal, within the statistical error, to the value $\beta = 1/8$ estimated with high credibility by both GF and BET and therefore suggests that $\nu = 1$. This value is in agreement with the renormalization group estimates for ν of Refs. 32–34. At z_c one would expect $\langle R \rangle$ to vanish; in the simulation, however, we have obtained several times $\bar{R} \sim 0.2$ [Eq. (5)], due to imbalance in the population of sublattice A and b. We therefore present two sets of results for the staggered compressibility, χ_1^+ and χ_2^+, in which the fluctuations in R [see Eqs. (4) and (6)] are calculated around $\bar{R}$ and zero, respectively. For $L = 24$, $L = 32$, and $L = 64$ χ_1^+ differs significantly from χ_2^+. Log–log plots of the results for χ_2^+ give better fit to a straight line than those for χ_1^+, and therefore we use them for our analysis. A slope $\gamma/\nu = 1.74(2)$ with $B = 0.22(1)$ is obtained from five points excluding $L = 64$ (however, for $L = 64$ the best straight line passes very close to the MC value 310). This slope is very close to $\gamma = 1.75$ known for the two-dimensional Ising lattice[39] and we therefore assume $\gamma = 1.75$ also for the hard-square lattice gas, which is consistent also with our suggestion $\nu = 1$. For the compressibility K_T we apply a slightly different analysis. In order to check the possibility of both, a logarithmic ($\alpha = 0$) and an exponential

divergence ($\alpha > 0$), we fit the data (excluding for $L = 64$) to the function used by Domany *et al.*[49]

$$K_T = \frac{B}{\alpha}(L^{\alpha} - 1) + A \tag{17}$$

where B and A are constants. Obviously, when $\alpha \to 0$ this function becomes

$$K_T = B \log L + A \tag{18}$$

The best fit of the average results for K_T has been obtained for $B = 0.10646$, $A = 0.11563$, and $\alpha = 0.000016$, which means that the behavior is approximately logarithmic. Substituting $L = 64$ in Eq. (17) gives 0.558, which is very close to the MC value 0.56. For comparison, Ree and Chesnut[29] obtained $A = 0.10849$ and $B = 0.12372$ by fitting their data to Eq. (18). It should be pointed out, however, that our fit is based on the average values of K_T and does not take into account the statistical error. Hence in order to increase the accuracy of the above result larger lattices should be studied for larger samples.

It should be pointed out that finite-size scaling[40,41] applies to asymptotically large systems at the exact critical activity of the infinite system, whereas we use here relatively small lattices and an approximate value for z_c. However, the fact that the log–log plots of the results give straight lines indicates that the size $L = 12$, of the smallest lattice, as well as the accuracy of z_c are already sufficient. This conclusion is supported also by matrix method studies[28,29] which have used the present analysis with a slightly different value for z_c and obtained the same critical behavior for K_T.

To summarize: our data for the hard-square lattice gas model is consistent with the critical exponents of the zero-field plane Ising model, $\beta = 1/8$, $\nu = 1$, $\gamma = 7/4$, and $\alpha = 0$. These results are in accord with ground-state symmetry considerations of Domany *et al.*[37] which classify these two models in the same universality class. Our estimate for β agrees with the results of GF and BET. $\nu = 1$ has been estimated also by Rácz,[32] Wood and Goldfinch,[33] and Kinzel and Schick,[34] using renormalization group techniques. The result $\alpha = 0$ agrees with the matrix method results of Refs. 27–29 and with the estimation carried out in Ref. 33, but differs from $\alpha = 0.09(5)$ obtained by BET. As far as we know this is the first time γ has been calculated by any method.

3.3. Conclusions

In this work a MC study of the entropy, the chemical potential, and other thermodynamic quantities has been carried out for the hard-square lattice gas. The entropy has been calculated by an approximate method suggested recently by Meirovitch,[2] the chemical potential by Widom's method,[4,5] and the pressure from μ and S using basic thermodynamic

relations. The system has been simulated close to and at the transition point itself, in both the canonical and the grand canonical ensembles. The MC results are in a very good agreement with the Padé approximant estimates, and we argue that close to the transition point our results are more accurate. For example, at the critical activity z_c the estimates of the two methods for the entropy differ by 0.5%. Beyond z_c this deviation decreases to 0.01%. Similar accuracy is detected for the pressure calculated in the grand canonical ensemble. The accuracy of the entropy in the canonical and the grand canonical ensembles is about the same, whereas the chemical potential and the pressure are about an order of magnitude more accurate in the grand canonical ensemble than in the canonical ensemble. The high accuracy of the results obtained for the hard-square lattice gas gives reason to believe that the present technique for calculating the entropy will also be applicable to continuum models for fluids. It should be pointed out that these results for the entropy, obtained with relatively small sets of local states, demonstrate the local character of entropy even at the transition point, in contrast to the second derivatives of the entropy, K_T and χ^+, which are highly dependent on long-range correlations. A better accuracy can be achieved by using better approximations for the entropy [Eq. (10)] and enlarging both lattice and sample size. We have calculated also other thermodynamic quantities such as the compressibility, long-range order, etc. and found very good agreement with the Padé approximants results, not too close to the transition point. At z_c we employ Fisher's finite-size scaling theory[40,41] to the MC results of several lattices. The data are consistent with the critical exponents of the Ising model $\beta = 1/8$, $\nu = 1$, $\gamma = 7/4$, and $\alpha = 0$, supporting the ground-state symmetry considerations of Domany *et al.*[37] The values for β and ν agree with estimates of other studies. As far as we know γ has not been estimated yet and $\alpha = 0$ agrees with the matrix method and renormalization groups results, but differs from the series expansion estimates $\alpha = 0.09(5)$, obtained by BET. These results demonstrate that MC constitutes an important tool for calculating critical exponents which is complementary to other numerical techniques.

ACKNOWLEDGMENTS

This work has been supported by the Sir Charles Clore-Weizmann Fund Post Doctoral Fellowships. I would like to thank Drs. A. Baram, E. Domany, and D. C. Rapaport for helpful disucussions.

REFERENCES

1. N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.* **21**:1087 (1953).
2. H. Meirovitch, *Chem. Phys. Lett.* **45**:389 (1977).

3. H. Meirovitch and Z. Alexandrowicz, *Mol. Phys.*. **34**:1027 (1977).
4. B. Widom, *J. Chem. Phys.* **29**:2808 (1963).
5. J. L. Jackson and L. S. Klein, *Phys. Fluids* 7:228 (1964).
6. D. J. Adams, *Mol. Phys.* **28**:1241 (1974).
7. Z. Alexandrowicz, *J. Stat. Phys.* **13**:231 (1975).
8. Z. Alexandrowicz, *J. Stat. Phys.* **14**, 1 (1976).
9. J. P. Hansen and L. Verlet, Phys. Rev. **184**:151 (1969).
10. J. P. Valleau and D. V. Card, *J. Chem. Phys.* **57**:5457 (1972).
11. Z. W. Salsburg, J. D. Jacobson, W. Ficket, and W. W. Wood, *J. Chem. Phys.* **30**:65 (1959).
12. K. Binder, ed., in *Monte Carlo Methods in Statistical Physics* (Springer, Berlin, 1979).
13. Z. Alexandrowicz, *J. Chem. Phys.* **55**:2765 (1971).
14. H. Meirovitch and Z. Alexandrowicz, *J. Stat. Phys.* **16**:121 (1977).
15. H. Meirovitch, *J. Phys. A Math. Gen.* **15**:2063 (1982).
16. H. Meirovitch, *Chem. Phys.* **21**:251 (1977).
17. K. Binder, *Z. Phys. B* **45**:61 (1981).
18. C. Domb, *Nuovo Cimento* **9**, Suppl. **1**:9 (1958).
19. H. N. V. Temperley, *Proc. Phys. Soc. (London)* **74**:183, 483 (1959).
20. H. N. V. Temperley, *Proc. Phys. Soc. (London)* **77**:630, (1961).
21. H. N. V. Temperley, *Proc. Phys. Soc. (London)* **80**:813, 823 (1962).
22. D. M. Burley, *Proc. Phys. Soc. (London)* **75**:262 (1960).
23. D. M. Burley, *Proc. Phys. Soc. (London)* **77**:451 (1961).
24. D. Levesque and L. Verlet, *Phys. Lett.* **11**:36 (1964).
25. B. Jancovici, *Physica* **31**:1017 (1965).
26. D. S. Gaunt and M. E. Fisher, *J. Chem. Phys.* **43**:2840 (1965).
27. L. K. Runnels, *Phys. Rev. Lett.* **15**:581 (1965).
28. L. K. Runnels and L. L. Combs, *J. Chem. Phys.* **45**:2482 (1966).
29. F. H. Ree and D. A. Chesnut, *J. Chem. Phys.* **45**:3983 (1966).
30. R. J. Baxter, I. G. Enting, and S. K. Tsang, *J. Stat. Phys.* **22**:465 (1980).
31. K. Binder and D. P. Landau, *Phys. Rev. B* **21**:1941 (1980).
32. Z. Rácz, *Phys. Rev. B* **21**:4012 (1980).
33. D. W. Wood and M. Goldfinch, *J. Phys. A Math. Gen.* **13**:2781 (1980).
34. W. Kinzel and M. Schick, *Phys. Rev. B* **24**:324 (1981).
35. L. K. Runnels, in *Phase Transition and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic Press, London, 1972), Vol. 2, p. 302.
36. T. Hill, *Statistical Mechanics* (McGraw Hill, New York, 1956).
37. E. Domany, M. Schick, J. S. Waler, and R. B. Griffith, *Phys. Rev. B* **18**:2209 (1978).
38. M. P. Nightingale, *Physica A* **83**:561 (1976).
39. M. E. Fisher, *Rep. Prog. Phys.* **30**:615 (1967).
40. M. E. Fisher, in *Proc. Int. Summer School, Enrico Fermi, 1970*, Course 51 (Varrena, Italy) (Academic Press, New York, 1971).
41. M. E. Fisher and M. N. Barber, *Phys. Rev. Lett* **28**:1516 (1972).
42. C. Domb, *Proc. Phys. Soc.* **86**:933 (1965).
43. C. Domb, *J. Phys. C* **3**:256 (1970).
44. J. D. Gunton, *Phys. Lett.* **26**:406 (1968).
45. P. G. Watson, in *Phase Transition and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic Press, London, 1972), Vol. 2, pp. 150–159.
46. H. Müller-Krumbhaar and K. Binder, *Z. Phys.* **254**:269 (1972).
47. R. H. Swendsen, *Phys. Rev. Lett.* **42**:859 (1979).
48. R. H. Swendsen, *Phys. Rev. B* **20**:2080 (1979).
49. E. Domany, K. K. Mon, G. V. Chester, and M. E. Fisher, *Phys. Rev. B* **12**:5025 (1975).