Difference Between Canonical and Grand Canonical Ensembles in Discrete Lattice Gas Models

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We calculate the site occupation probabilities of one-dimensional lattice gas models within the canonical and grand canonical ensembles. The appearing differences do not vanish if we increase the system size keeping the site energies discrete. In this way one can explain the surprising numerical results of Barszczak and Kutner. This effect in the single-site occupation number disappears in higher dimensions.

In lattice gas models (where double occupancy of the sites is prohibited) the motion of a given particle is strongly influenced by the distribution of the others. The effect of exclusion can be seen in many different processes. Here we want to mention only one of them, the Bardeen Herring backjump correlations[1–4]: When a particle is exchanged with a vacancy, there is a tendency for the reversed process, resulting in a backward correlation in the particle hopping.

Recently Barszczak and Kutner[5] found surprising effects simulating simple lattice gas models. They found that the occupation probability does not follow the Fermi distribution, as one would expect. Looking for the best fit with a Fermi function, they always found a fitting temperature lower than the physical one and they did not see any serious size dependence of this effect. BK argued that these effects have their origin in the dynamics.

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On the other hand, finite Fermi systems (e.g., fine metal particles or mesoscopic rings) have, in general, a nondegenerate energy level spectrum and, therefore, the thermal activation process could also be modeled by a one-dimensional lattice gas (forgetting for the moment about the spin degeneracy) where the different sites correspond to the energy levels. Therefore, there is a possibility of seeing the effects found in lattice gas models directly in the experiments.

In the following we calculate the occupation numbers in the canonical ensemble. From the numerical method of ref. 5 it is physically appealing that they were simulating within the canonical ensemble, since the particle number was conserved. On the other hand, one can explicitly show, starting from the master equation for the distribution probability, that the equilibrium distribution belongs to this ensemble.[6]

The concrete model which we investigate is a one-dimensional non-interacting lattice gas. The Hamiltonian is simply

$$H = \sum_{i=1}^{N} E_i n_i \tag{1}$$

where E_i denotes the energy belonging to site i and n_i is the occupation number ($n_i = 0, 1$). The canonical partition function can be written as

$$Z_{\text{can}} = \sum_{\{n_i\}}^{(K)} e^{-\beta H} \tag{2}$$

where the summation runs over all possible configurations $\{n_i\}$ at a given particle number K. This latter constraint can be expressed with the help of a δ-function. Using an integral representation of the δ-function

$$\delta(x) = \beta \int_{-i\infty}^{i\infty} \frac{d\mu}{2\pi i} e^{\beta \mu x} \tag{3a}$$

one arrives at

$$Z_{\text{can}} = \beta \int d\mu \, e^{-Nf(\mu)} \tag{3b}$$

with

$$f(\mu) = -\beta\mu\rho + \frac{1}{N} \sum_{i=1}^{N} \log\{1 + \exp[-\beta(E_i - \mu)]\} \tag{3c}$$

where $\rho = K/N$ is the average density. Following BK, we treat only the $E_i = i$ case in detail and use an integral representation of the discrete sum

to get closed expressions for the different quantities. Using the trapezoidal rule,[7] one arrives at

$$
\frac{1}{N} \sum_{i=1}^{N} \log\{1 + \exp[-\beta(i-\mu)]\}
$$

$$
= \frac{1}{N} \int_0^N dx \log\{1 + \exp[-\beta(x-\mu)]\}
$$

$$
- \frac{1}{2N} \log[1 + \exp(\beta\mu)] + \frac{1}{2N} \log\{1 + \exp[-\beta(N-\mu)]\}
$$

$$
+ \frac{\beta}{N} \frac{\exp[-\beta(\varphi-\mu)]}{\{1 + \exp[-\beta(\varphi-\mu)]\}^2} \tag{4}
$$

where $\varphi \in (0, N)$. We cited this expression explicitly here to see that the last correction term is of the order $\sim \beta/N$ ($\leqslant \beta/4N$). This situation would not be changed by using a higher-order correction (i.e., it would always be proportional to $1/N$); only the numerical prefactor would be different. The reason for this fact is simply the discreteness of the levels even in the thermodynamic limit, i.e., that not $E_{i+1} - E_i \nrightarrow 0$ as $i \to \infty$.

Now supposing $\beta\mu \gg 1$ and $(N-\mu)\beta \gg 1$ (which is easily satisfied with finite ρ in the limit $N \to \infty$), one arrives at $\mu_0 = K + 1/2$, i.e., the chemical potential lies halfway between two energies. Generally it is satisfied in a finite system only at low temperatures. In the exceptional half-filled case ($\rho = 1/2$) this equation always holds because of the particle–hole symmetry. Actually, only this latter case was investigated in ref. 5.

In the grand canonical ensemble the occupation number would be given simply by $n_l = \partial f(\mu_0)/\partial E_l$. In the following we show that the canonical treatment gives a different result, namely that the saddlepoint value μ_0 will be changed. The occupation probability at an arbitrary, but given site l is the ratio of the partition sum, when the site l is always occupied, and of Z_{can}. (The number of particles is, of course, the same, K, in both cases.) Performing the former calculation, one gets instead of Eq. (3b)

$$
\tilde{f}(\mu) = -\beta\mu\rho + \frac{1}{N} \sum_{i=1}^{N} \log\{1 + \exp[-\beta(E_i-\mu)]\}
$$

$$
- \frac{1}{N} \log\{1 + \exp[\beta(E_l-\mu)]\} \tag{5}
$$

since the lth site is always occupied in this case. From the saddlepoint equation one has

$$
\mu_l = K + \tfrac{1}{2} - \{1 + \exp[-\beta(l-\mu_l)]\}^{-1} \tag{6}
$$

i.e., the new saddlepoint value μ_l becomes smaller and the difference is the grand canonical occupation probability. Using the notation $\Delta = \mu_0 - \mu_l$, we obtain the following coupled equations:

$$\langle n_l \rangle = \exp(\tfrac{1}{2}\beta\Delta^2) \cdot \{1 + \exp[\beta(l - \mu_0 + \Delta)]\}^{-1}$$
$$\Delta^{-1} = 1 + \exp[-\beta(l - \mu_0 + \Delta)] \tag{7}$$

Figure 1 compares this prediction with the exact result and with the Fermi distribution. (The numerical data of ref. 5 coincide with the exact ones.)

There are two points which have to be recognized. The first one is that Eq. (6) does not contain explicitly the size of the system. Consequently, the found deviations are not size effects, but result from the discreteness of the level spacing.

The other point is that Eq. (6) holds only for sites where $g_l \gg \beta/N$. In Eq. (4) we dropped the terms of order of magnitude β/N; therefore, to be consistent, we have to keep only larger contributions. It means that $\exp[\beta(l - \mu)] \gg 1$ has to be satisfied. This constraint belongs clearly to the integral approximation of the sum, but the original sum cannot be evaluated analytically. (The result of the numerical evaluation can be seen in the figure.) For $l > K$ one gets a lower occupation probability n than the
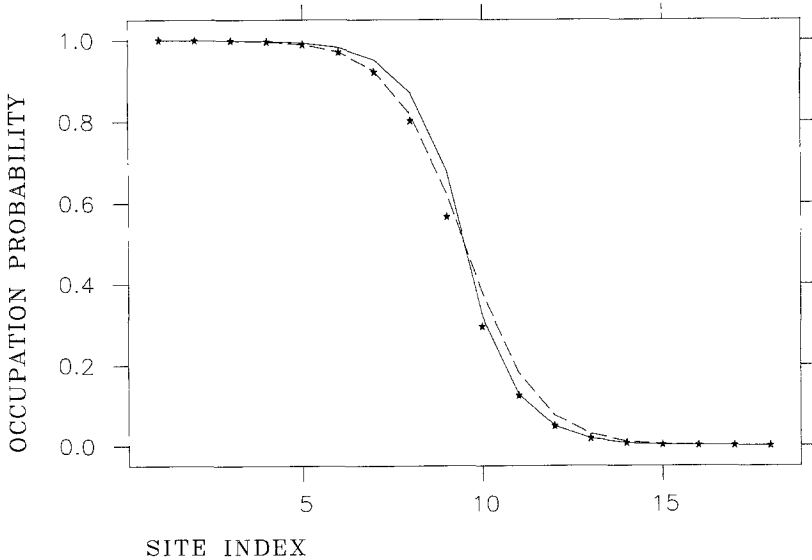

Fig. 1. The occupation probabilities as functions of the site index at $\beta = 1$ for $N = 18$. (1) Canonical distribution; (2) Fermi distribution (dashed line); (3) approximation of Eq. (6) (stars).

original Fermi one n_F and, therefore, $(n - n_F) > 0$ has to be satisfied for lower site indices because of the particle number conservation (in this latter regime the above approximation does not work).

As a conclusion, we can say that the canonical calculation recovers the numerical data of ref. 5, showing that the found deviation comparing the distribution function with the Fermi one has its origin not in the dynamics, but in the difference between the canonical and grand canonical ways of calculation. If we fitted the distribution with a Fermi function, then we got always a fitting temperature which was lower than the physical one. The reason for this is rather simple: calculating the occupation probability, one has to keep at least one particle sitting on the given site. This extra constraint means smaller fluctuations and it appears as a smaller fitting temperature.

All the calculation concerning this temperature difference were done in one dimension. Naturally the question arises of whether one can also find similar effects in higher space dimensions. In $d > 1$ one has a saddlepoint equation of the form $\rho N^d = \mu^d + a\mu^{d-1} + \cdots$, where N denotes the linear size. If we follow the presented calculation, then corrections appear as products of the lower-dimensional corrections. The contribution of the extra summand in Eq. (3) is at most $\sim N$ and is negligible for $d > 1$ compared with μ^d. (In one dimension it results in a finite shift in μ.) It means that there is a "natural" fluctuation of μ, which is larger than the one caused by the extra constraint if $d > 1$. Therefore, one cannot see similar effects in the particle distribution. However, the situation is different if one is interested in the probability of the simultaneous occupation of a $(d-1)$-dimensional subsystem.

In real physical systems the average energy level spacing and the system size are connected; therefore, one finds the above behavior as a finite-size effect. In computer simulations and model calculations they can be separated. The calculation presented above and the simulation in ref. 5 show that the difference found between the two ensembles is due to the discrete level spacing and not to the finite size.

Generally one expects the same value for thermodynamic averages upon calculating within the different ensembles. This statements holds only for quantities which are averages over the system (e.g., specific heat, energy, etc.) or for quantities which are local variables, but have a uniform distribution within the system, i.e., *can be* expressed as averages over the different subsystems. In the above case we have a strongly nonuniform distribution (Fermi-like) and, therefore, it is not really surprising that local variables which are strongly influenced by fluctuations show different behavior.

ACKNOWLEDGMENTS

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