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Tracer diffusion of particles with soft-core interactions studied by Monte Carlo simulations

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Abstract. We consider, using Monte Carlo simulations, diffusion of particles on a square lattice. The particles do not interact among themselves, except that at the same lattice site there cannot be more than $\mathcal{N}$ particles. Since the interactions in our model are a milder version of the well known hard-core (HC) lattice gas, for which $\mathcal{N} = 1$, we decided to call our model the soft-core (SC) lattice gas.

We find the dependence of the correlation factor on the concentration of completely filled sites and show that the correlations decrease with increasing $\mathcal{N}$. We calculate analytically and via the Monte Carlo simulations the distribution function of the average number of sites occupied by a given number of particles. The curves show that for our model the 'particle–hole' symmetry, typical for the HC lattice gas, disappears. In addition, we have found in 1D two regimes of diffusion for $\mathcal{N} = 2$. For shorter times the diffusion is anomalous, while for longer times it becomes normal.

1. Introduction

Theoretical investigations of adatoms diffusion on metal surfaces have been carried out for many years (see e.g. [1, 2]). Recently computer simulations have come to play an increasingly important role. Generally the Monte Carlo method is used and the system of diffusing particles is reduced to the lattice gas model [3–5]. One of the essential ingredients of the model is the exclusion principle, also referred to as the hard core (HC), consisting in forbidding two particles to occupy the same site. There are numerous variations played around the HC lattice gas theme (for a review see e.g. [4, 6]), but the HC restriction remains. In a recent work Kutner *et al* [7] lifted the limitation. In their model an arbitrary number of particles is allowed to stay at the same time in the same site. There is also a well defined rule governing the order of leaving such a multiply occupied site. The authors call the model a 'bosonic lattice gas'.

In the following we decided to consider a model in which at each lattice site we allow for a maximum of $\mathcal{N}$ particles. One may think of the lattice sites as being substrate atoms and particles being adatoms. It is known from experiment [8] that if the diffusing adatoms are small (like e.g. Li atoms), then it is possible that a few of them may be found at the same time around one, bigger, e.g. Mo, substrate atom. The model may also prove useful in describing the formation and diffusion of Te dimers on the Mo(110) plane [9] as well as the transport in a material with fine pores where more than one particle of the fluid may

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be blocked [6]. Still another application of the model is the description of diffusion for systems where the deposit of adatoms exceeds, at some sites, the monolayer [2].

Since the HC repulsion is much weakened in our model we call this kind of interaction soft core (SC).

In this paper we consider the simplest version of our model, i.e. apart from the SC interactions the adatoms do not feel each other. In more realistic systems one would like to add other forms of interaction, but here we want to study the effect on diffusion of the weak form of the exclusion principle. Our model is a purely classical lattice gas. It is not directly connected, even for $\mathcal{N} \to \infty$, to the bosonic lattice gas considered by Kutner *et al* [7]. The difference lies in additional rules governing ordering of particles at a given site, imposed in [7]. No such rule is present in our model but if two neighbouring sites are occupied by less than $\mathcal{N}$ particles each, the particles from the two sites can move. If in one site there are $\mathcal{N}$ particles and in the second less than $\mathcal{N}$, then a particle from the first site can jump to the second, but not vice versa. For simplicity, we assume jumps of the particles only to the nearest neighbours. For such a model we want to find the dependence of the correlation factor, f, on the concentration, c, of particles (adatoms) and $\mathcal{N}$. There are theoretical [10, 11] and Monte Carlo [5, 12] results for the HC model. The correlation factor can be defined there via the diffusion coefficient for tracer diffusion, D^*, and for random walk, D_{RW}:

$$D^*(c) = f(c)(1-c)D_{\mathrm{RW}} = f(c)v(c)D_{\mathrm{RW}} \tag{1}$$

where the concentration, c, is defined here as the number of particles, M, present in the system divided by the number of sites, N, and $v(c) = 1 - c$, is called the site availability factor (lattice constant and total jump rate were set as unity here). For a lattice of dimension d we have the asymptotic formulae

$$D_{\mathrm{RW}} = \frac{1}{2d} \qquad \text{and} \qquad D^* = \frac{\langle R^2(t)\rangle}{2dt} \tag{2}$$

where $\langle R^2(t)\rangle$ is the average square distance covered by a diffusing particle in time t, hence $f(c)$ may be rewritten as

$$f(c) = \frac{\langle R^2(t)\rangle}{(1-c)t}\,. \tag{3}$$

Sankey and Fedders [10] and later Nakazato and Kitahara [11] and Beijeren and Kutner [3] derived approximate formulae for the correlation factor of the HC lattice gas in 2D. The formulae yield correct limiting values (i.e. for $c \to 0$ and $c \to 1$) and are approximate in between. Monte Carlo simulations on the square lattice done by Kutner [12] confirm the behaviour of f predicted by the approximate analytical formulae as a nearly straight line dropping from $f(c = 0) = 1$ to $f(c = 1) = 0.474\,748$. Equation (3) is no longer valid for our SC model, since the concentration, c, of particles differs from the concentration of completely filled sites. We define the concentration, c, of particles in the SC system as

$$c = \frac{M}{\mathcal{N}N}\,.$$

It is seen that $c \leqslant 1$.

For increasing $\mathcal{N}$ we expect the particles to be more and more independent for all values of c, since then the back-jump correlations become less and less important. For $\mathcal{N} \to \infty$ one should have $f(c) \to 1$, and the diffusion should reduce to the random walk, D^* should tend towards D_{RW}. This is fulfilled by the renewal definition below.

Let us introduce $c_f = c_f(c, \mathcal{N})$ the concentration of completely filled sites and $c_v = 1 - c_f$ the concentration of vacancies, i.e. sites occupied by less than $\mathcal{N}$ particles. An empty site counts as a single vacancy, irrespective of the value of $\mathcal{N}$. With these definitions we rewrite (3) as

$$f(c_f) = \frac{\langle R^2(t)\rangle}{c_v(c,\mathcal{N})t}\,. \tag{4}$$

This is the *ad hoc* asymptotic formula we use in our simulations.

2. Occupation distribution functions

We now want to find the dependence of c_f and c_v on physical parameters like c and $\mathcal{N}$ or, equivalently, the distribution of M identical particles among N sites, each accommodating up to $\mathcal{N}$ particles. This is a combinatorial problem of counting the number of distinct ways in which M objects can be placed in a total of N distinct boxes. To put it in a different way—what is the most probable number of boxes occupied by I objects for given N, M and $\mathcal{N}$?

Let us denote by $h(\mathcal{N}, N, M)$ the number of all possible distributions of M identical objects in N boxes with maximum capacity of a box equal to $\mathcal{N}$ and by $g(\mathcal{N}, N, M; I)$ the number of boxes occupied by exactly I objects in all possible distributions, i.e.

$$h(\mathcal{N}, N, M) = \sum_{\sigma_1+\cdots+\sigma_N=M} \frac{M!}{\sigma_1!\sigma_2!\ldots\sigma_N!} \tag{5}$$

$$g(\mathcal{N}, N, M; I) = \sum_{\sigma_1+\cdots+\sigma_N=M} \frac{(\delta_{\sigma_1,I}+\cdots+\delta_{\sigma_N,I})M!}{\sigma_1!\sigma_2!\ldots\sigma_N!} \tag{6}$$

where $\sigma_i (= 0, 1, \ldots, \mathcal{N})$ is the occupancy of the ith site and $\delta_{\sigma_j,I}$ is the Kronecker delta. The occupation distribution function we are looking for is given by

$$W(\mathcal{N}, N, M; I) = \frac{g(\mathcal{N}, N, M; I)}{Nh(\mathcal{N}, N, M)} \tag{7}$$

where $W(\mathcal{N}, N, M; I)$ is the average number of boxes occupied by I particles. Hence, after simple algebra we get from (7)

$$g(\mathcal{N}, N, M; I) = N \binom{M}{I} h(\mathcal{N}, N-1, M-I)\,. \tag{8}$$

Hence

$$W(\mathcal{N}, N, M; I) = \binom{M}{I} \frac{h(\mathcal{N}, N-1, M-I)}{h(\mathcal{N}, N, M)}\,. \tag{9}$$

Using the saddle-point method (see e.g. [13]) we get

$$W(\mathcal{N}, N, M; I) = \frac{z^I}{I!}\left(1 + z + \cdots + \frac{z^{\mathcal{N}}}{\mathcal{N}!}\right)^{-1} \tag{10}$$

with the condition

$$c\mathcal{N} = \left(1 + z + \cdots + \frac{z^{\mathcal{N}-1}}{\mathcal{N}!}\right) \tag{11}$$

where $W(\mathcal{N}, N, M; I)$ is the concentration c_I of the lattice sites occupied exactly by I particles.

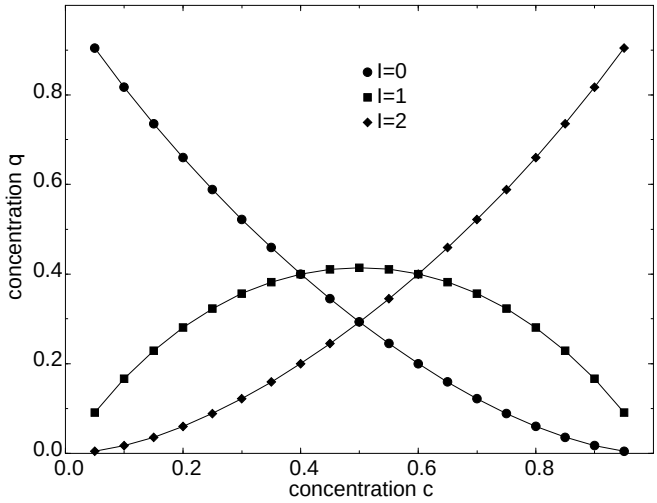

Figure 1. Percentage of sites, c_I, occupied by two particles, $I = 2$; one particle, $I = 1$ and empty, $I = 0$, versus the concentration of particles, c, for $\mathcal{N} = 2$. The full curve shows data from (13), symbols—data from the simulations.

In the particular case of $\mathcal{N} = 2$ we get from (11) the following expression for z:

$$z = \frac{-2(2c-1) - \sqrt{\Delta}}{4(c-1)} \tag{12}$$

where

$$\Delta = 4(2c-1)^2 - 32(c-1)\,.$$

This gives, with (10), the concentrations, c_I, of sites occupied by I particles

$$\begin{aligned} c_0 &= W(2, N, M, 0) = \frac{3 - 2c - \sqrt{1 + 4c - 4c^2}}{2} \\ c_1 &= W(2, N, M, 1) = \sqrt{1 + 4c - 4c^2} - 1 \\ c_2 &= W(2, N, M, 2) = \frac{1 + 2c - \sqrt{1 + 4c - 4c^2}}{2}\,. \end{aligned} \tag{13}$$

These formulae have been used in obtaining figure 1. For higher values of $\mathcal{N}$ the formulae become much more complicated and one gets them numerically from equations (10) and (11).

3. Results and conclusions

Formulae (13) have been checked by simulations. The comparison of theoretical and simulation results, for $\mathcal{N} = 2$, is shown in figure 1, where the dependence of c_I ($I = 0, 1, 2$) on the total concentration of particles in the system, c, has been presented. The agreement is excellent. Figure 2 shows the data for the occupation distribution for $\mathcal{N} = 5$. In this case only the simulation results are presented. One can notice that the symmetry of the curves with respect to $c = 0.5$, present for $\mathcal{N} = 2$ and HC, is lost here. This is so because the 'particle–hole' symmetry typical for the HC lattice gas is not present in our model for $\mathcal{N} > 2$. We do not impose any additional rules telling which one of the particles present at

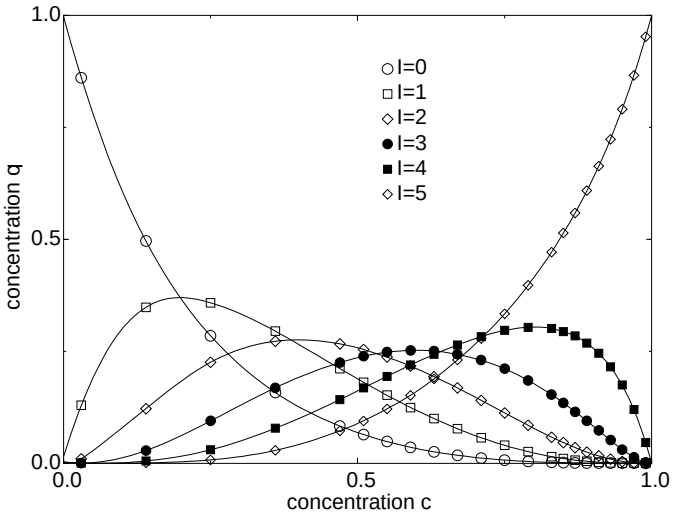

Figure 2. Same as in figure 1 but for $\mathcal{N} = 5$ and c_I with $I = 0, 1, 2, 3, 4, 5$. Only the results of the simulations are shown. Full curves are to guide the eye only.

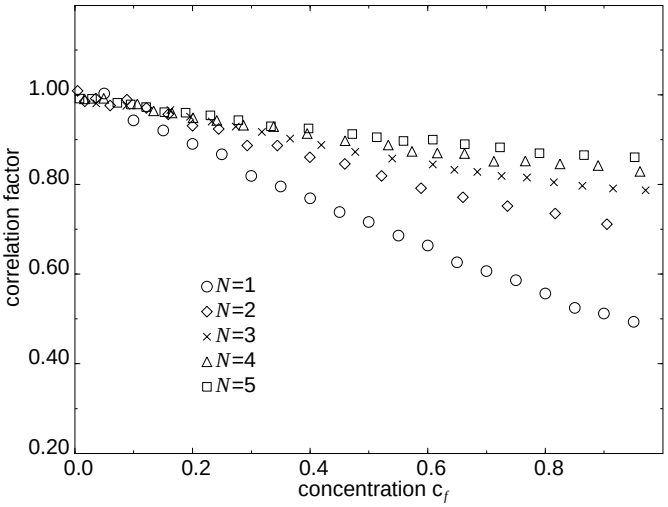

Figure 3. Correlation factor, f, versus concentration, c_f, of completely filled sites for different $\mathcal{N}$.

a given site should be displaced. For $\mathcal{N} > 2$ we can have a move of a particle between two neighbouring sites, neither of which is completely filled up. This would not correspond to any movement of a vacancy, in contrast to the HC case where a move of a vacancy always accompanies a particle's move.

Figure 3 shows the change of the correlation factor versus concentration of completely filled sites, caused by different $\mathcal{N}$. As expected, with increasing $\mathcal{N}$ the particles are becoming more and more free, with decreasing correlations, i.e. $f(c_f) \to 1$. The change in the correlation is inversely proportional to $\mathcal{N}$. The reason for the diminishing of the

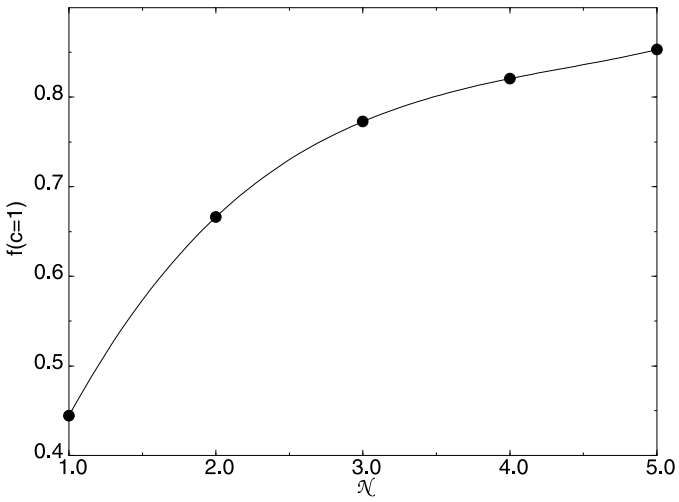

Figure 4. Correlation factor, $f(c = 1)$, versus the maximum number of particles, $\mathcal{N}$, allowed at a site.

correlations with increasing $\mathcal{N}$ lies in the reduction of the restrictive character of the occupied sites.

Figure 4 shows how the correlation factor, $f(c = 1)$, increases, i.e. the particles become more and more free, with increasing $\mathcal{N}$. The points have been obtained from linear fits to the respective curves in figure 3.

3.1. Diffusion in 1D

We have also investigated the diffusion in the 1D SC model. It is known [14] that the HC lattice gas shows anomalous diffusion in 1D, i.e. the exponent α in the relation

$$\langle R^2(t)\rangle \sim t^{\alpha} \tag{14}$$

takes the value $\alpha = 0.5$ in 1D HC. We have been looking for a similar effect in the closest 1D SC version, i.e. $\mathcal{N} = 2$. For simulation we have used a lattice of 10^2 and 10^3 sites with periodic boundary conditions. The concentration of diffusing particles varied between $c = 0.1$ and $c = 0.9$. Averaging was done over 10^6 particles. The results obtained for $L = 10^3$ are summarized in figure 5. Data for other L do not differ in any significant way.

As can be seen, there are two regimes of diffusion. At shorter times, up to 10^3 MCS (in one MCS each particle, on average, is chosen for a displacement) the diffusion is anomalous and the value of α decreases with concentration. This is understandable since for large c the blocking effect, even for short times (see below) is more pronounced. With increasing time the diffusion becomes less and less dependent on c, and $\alpha \to 1$. This is so since only for a short time is a particle really blocked by fully occupied sites on its left and right. With passing time at least one of the sites will become occupied by one particle only and the particle becomes 'liberated'. The particle may therefore interchange its location along the diffusion axis with any other particle. This is quite different from the HC case, where the order of particles remains unchanged with time. If $\mathcal{N} > 2$ the diffusion in SC is always normal, i.e. $\alpha = 1$. Obviously to determine the exponent α to a good degree of accuracy much finer simulations would be needed. Here we did not aim for such standards but only wanted to get a reliable estimate.

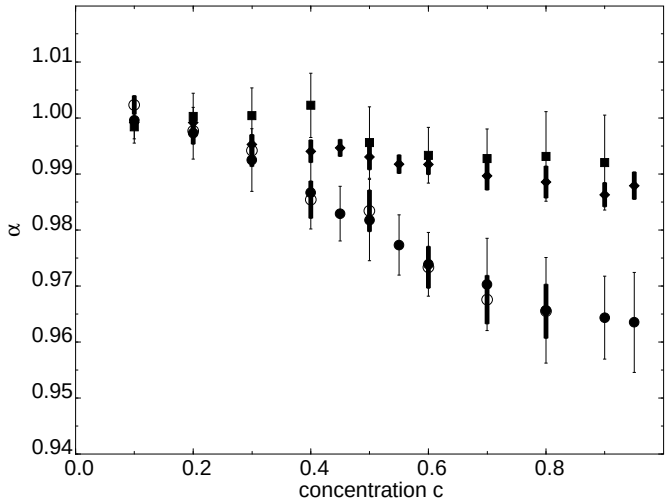

Figure 5. Diffusion exponent α versus concentration, c, of diffusing particles in the SC model with $\mathcal{N} = 2$, full circles were calculated from the simulations between 10^2 and 10^3 MCS. Full diamonds between 10^3 and 10^4 MCS and full squares between 10^4 and 2×10^4 MCS. The linear dimension of the system was $L = 10^3$ sites. Open circles are the data from a smaller system ($L = 10^2$ sites), time between 10^2 and 10^3 MCS. In all cases averaging was over 10^6 particles.

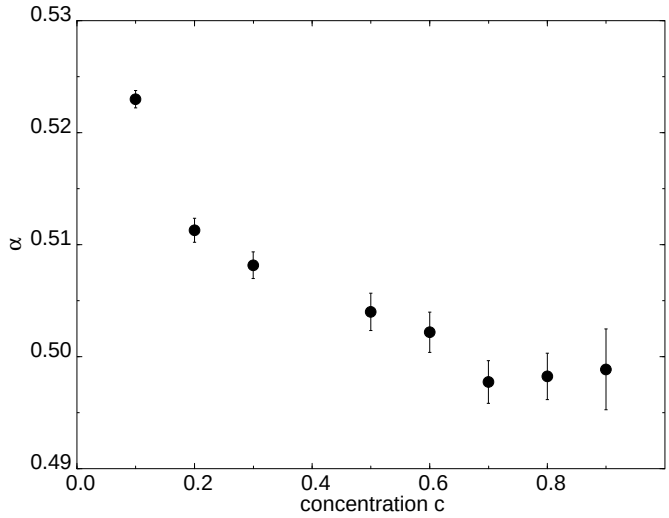

Figure 6. The exponent α versus c for HC lattice gas ($\mathcal{N} = 1$). Here $L = 10^3$, time between 10^3 and 10^4 MCS. Averaging is over 10^6 particles.

It should also be noted that a similar two-region diffusion has been found for tracer diffusion in ordered structures by Sadiq and Binder [15].

We have also estimated the α exponent in the 1D HC lattice gas. For analogous conditions, $L = 10^3$ and 10^3 to 10^4 MCS, we obtained the results shown in figure 6. As expected, for the small concentrations and time intervals considered, the particles do not feel the HC limitations so strongly and $\alpha > 0.5$.

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