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Diffusion on Diffusing Particles

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Abstract

We investigate random walk of a particle constrained on cells, where cells behave as a lattice gas on a two dimensional square lattice. By Monte Carlo simulation, we obtain the mean first passage time of the particle as a function of the density and temperature of the lattice gas. We find that the transportation of the particle becomes anomalously slow in a certain range of parameters because of the cross over in dynamics between the low and high density regimes; for low densities the dynamics of cells plays the essential role, and for high densities, the dynamics of the particle plays the dominant role.

Key words: Self-diffusion, first passage time, slow dynamics, lattice gas

1. Introduction

Diffusion or random walk of particles in random environments has been studied for a long time because of its versatility applicable to many phenomena [1,2]. It is known in some systems that the random environment fluctuates in time and a particle diffuses in the fluctuating environment. For example, surfactant molecules in a solution of micelles diffuse under the effect of fluctuation of the network structure of the micelles. Surprisingly, the self-diffusion constant shows a minimum as a function of surfactant concentration [3-5]. Another example is the fluid mercury in the super critical region, where electrons move on clusters of mercury which are formed and dissolved incessantly. It is known that the electron mobility becomes anomalously small in a certain range of the temperature and density domain, which is off the liquid-gas critical point [6]. This anomalous behavior of the transport property has not been well understood, although it has been suggested to be related to the competition between two transport regimes; the diffusion of micelles or clusters themselves and the diffusion of particles on the micelles or clusters [5,7].

In this paper, we introduce a generic model that is relevant to the diffusion of a particle on diffusing particles and investigate the transport property of the particle. We consider an assembly of cells distributed on the square lattice at a given density. The cells are assumed to be a lattice gas and the distribution of the cells fluctuates in time. We attach a particle to this system, which moves only on the cells. We assume that the particle makes a random walk within a cell and can jump from one cell to an adjacent cell on its nearest

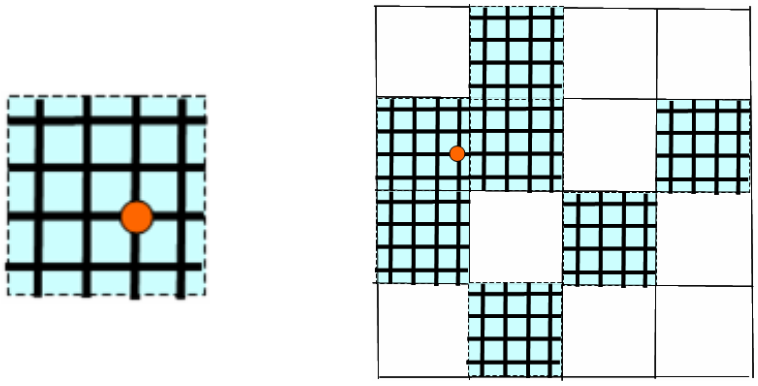
neighbor sites. As a transport property, we focus on the first passage time of the particle whose Lap lace-Fourier transform is related to the susceptibility for a boundary perturbation experiment [8,9]. The reason that we study the first passage time is that the diffusion constant cannot be obtained accurately by the Monte Carlo simulation in a finite system. In particular, when the system shows anomalous diffusion, the diffusion constant cannot be well defined. We obtain the first passage time as a function of the density and temperature of the cells, which determine the structure of the fluctuating environment. The first passage time shows a maximum, i.e. the transport becomes slow in a certain area in the parameter space.

In the next section, we explain the model system and the method of Monte Carlo simulation. In Sect. 3, we present the results of the simulation where the ratio of the jump rates of the particle and that of the cells is treated as another controlling parameter. Note that a preliminary result, when the dynamics of the particle is much faster than that of the cells, has been reported in a previous paper [10]. We discuss the results in Sect.4 where the analysis of the mean square displacement of the particle is also mentioned briefly. Conclusion is given in Sect. 5.

2. Model and method of simulation

2-1 Model

We prepare a lattice gas on an $L \times L$ square lattice and assume each atom is a cell which can accommodate a particle. We assume that a cell itself is an $\ell \times \ell$ square lattice [Fig. 1(a)] and the particle, which we call a carrier from now on, makes random walk on these lattice sites. The carrier is assumed to jump from a cell to an adjacent site in the adjacent cell [See Fig 1 (b)]. The temperature dependence of the jump rate can be absorbed into the time scale and is assumed not to depend on the temperature.



(a) (b)

Fig.1 (a) a cell consists of an $\ell \times \ell$ square lattice. The carrier makes random walk within the cell if it is isolated. (b) The cells form a lattice gas on an $L \times L$ square lattice at a given density. The carrier can hop between two adjacent cells through one of the bonds connecting the cells.

The energy of the lattice gas is given by

$$E = -J \sum_{<i,j>} n_i n_j \quad . \tag{1}$$

Here, the summation $< ij >$ is taken over the nearest neighbor pair of sites, $J(>0)$ is the coupling constant, and $n_i = 1$ when site i is occupied by a cell and $n_i = 0$ when site i is empty. Note that the lattice gas has a fluid-gas critical point T_C given by

$$\sinh\left(\frac{J}{2k_B T_C}\right) = 1 \quad , \tag{2}$$

where k_B is the Boltzmann constant.

We consider the equilibrium configuration of the lattice gas, that is the cell's move on the lattice, randomly under the effect of the interaction energy (1) and the heat bath at a given temperature T. When the density is sufficiently low, the carrier is trapped in one of the cells and the transport of the carrier is determined by the random walk of the cell. On the other hand, when the density is sufficiently high, the cells form a fixed network and the transport property of the carrier is determined by the random walk of the carrier itself on the network. Consequently, we expect a cross over in transport property when the density is increased from zero to unity.

2-2 Monte Carlo simulation and first passage time

The equilibrium distribution of cells is produced by the standard Metropolis algorithm. Namely, a randomly chosen cell is tried to move to a site in its neighboring sites. When it is occupied the attempt is stopped. When the site is vacant, the cell occupies the new site with probability $\exp[-\Delta E / k_B T]$ when $\Delta E > 0$ where ΔE is the difference in energy before and after the move: When $\Delta E \le 0$, the cell is always moved to the new site. When this step is taken N times where N is the number of cells in the system, then the Monte Carlo time is advanced by one. We impose the periodic boundary condition in the horizontal direction and assume the reflecting boundary at the top and bottom edges.

During one Monte Carlo step, the carrier performs random walk on the cells. We introduce a parameter m which represents the speed of the carrier. In one Monte Carlo step, the carrier makes m steps of random walk which are randomly distributed within N trials of the dynamics of cells.

We investigate the first passage time as the transport property of the carrier. In order to define the first passage time, we attach the carrier to one of the cells on the top boundary at $t = 0$. The first passage time is defined by the time that it takes to reach the opposite boundary and escape from the system for the first time. As the boundary conditions for the dynamics of the carrier to meet the measurement, we set the periodic boundary condition in the horizontal direction, the reflecting boundary at the upper edge and the absorbing boundary just out side of the bottom edge.

The first passage time shows some distribution and the first passage time distribution plays the role of response function in the boundary perturbation experiment [8,9]. Here we focus on the mean first passage time $F(\rho, T; m)$ as a function of the density $\rho = N / L^2$

and the temperature T for different values of m. When the mean first passage time is long, the diffusion is supposed to be slow.

3. Results

We set $L = 32$ and $\ell = 5$ for our simulation and obtained the mean first passage time by averaging over 10,000~20,000 samples. Although the first passage time has a wide distribution, the mean can be determined with sufficient accuracy.

3-1 Infinite temperature limit

Figure 2 shows the density dependence of $F(\rho,T;m)$ in the high temperature limit, where the cells make simple random walk. It is seen that $F(\rho,\infty;1)$ and $F(\rho,\infty;1000)$ are monotonically increasing and decreasing functions of the density, respectively, and $F(\rho,\infty;25)$ is approximately constant.

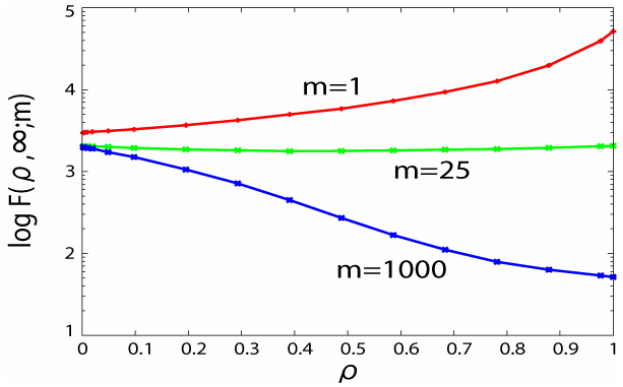


Fig. 2 The density dependence of the mean first passage time at $T = \infty$ for $m = 1000, 25$ and 1.

3-2 Finite temperatures

In order to produce equilibrium distribution of the cells, we first prepared the system by annealing it at $T/T_C = 3$ for 50000 Monte Carlo steps, and then reduced the temperature by $\Delta(T/T_C) = 0.1$. At each temperature, the system was again annealed for 50000 Monte Carlo steps before measuring the first passage time. Figure 3 shows the density dependence of $F(\rho,T;m)$ for various temperatures for $m = 1000$, 25 and 1.

For $m = 1000$ (Fig. 3(a)), $F(\rho,T;1000)$ is a monotonically decreasing function of ρ for high temperatures and shows a maximum (slow dynamics) for lower temperatures. We can define the cross over temperature T_X by the condition

$$\lim_{\rho\to 0}\frac{\partial F(\rho,T_X;1000)}{\partial\rho} = 0 \ . \tag{3}$$

We found $T_X/T_C \approx 2.5$, which coincides with the value obtained for $m = \infty$ [10]. It is interesting to note that the maximum observed at $T/T_C \geq 1$ occurs below the critical density $\rho = 0.5$. As the temperature is reduced below T_C, a new broad peak emerges

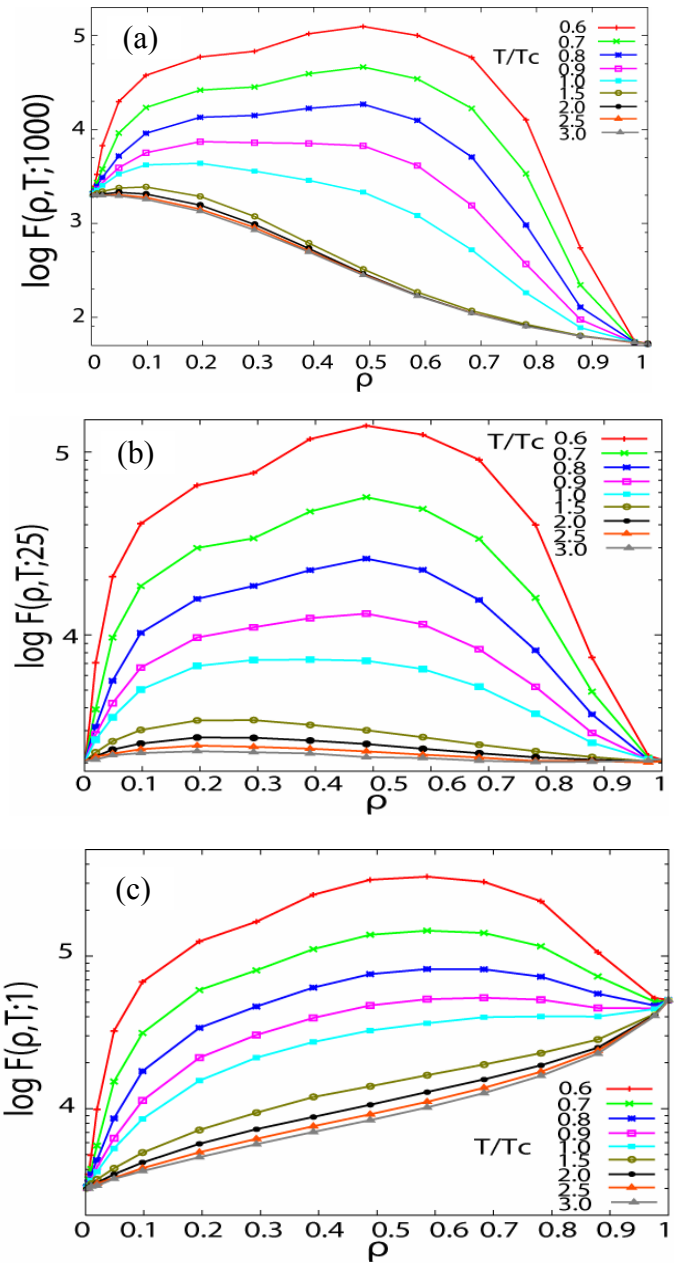


Fig. 3 Density and temperature dependence of the mean first passage time $F(\rho,T;m)$. (a) fast carrier $m=1000$, (b) intermediate carrier $m=25$ and (c) slow carrier $m=1$.

around $\rho = 0.5$. This broad peak is due to the phase separation of the lattice gas where a giant cluster (fluid phase) coexists with the gas phase and the giant cluster tends to be formed as a horizontal band because of the boundary conditions imposed. Once the carrier is trapped in the giant cluster, it takes a long time to escape from it and the mean first passage time becomes longer. However, in case of higher densities, the cluster can form a percolating channel connecting the top and bottom edges, though it fluctuates in time, and the carrier can travel along the channel with its own dynamics and the mean first passage time becomes shorter and shorter as the density approaches $\rho = 1$.

For $m = 25$ (Fig. 3(b)), $F(\rho, T; 25)$ has a broad peak for all temperatures we investigated. The peak position is shifted toward $\rho = 0.5$ as the temperature is reduced due to the same reason for $m = 1000$ explained above.

For $m = 1$ (Fig. 3(c)), the trend of the density dependence of $F(\rho, T; 1)$ is opposite to that of $F(\rho, T; 1000)$, since the dynamics of the carrier is slower than that of the cells. Therefore the mean first passage time in the limit of $\rho = 0$ is shorter than that at $\rho = 1$.

4. Discussion

We first note that at $\rho = 1$, the carrier makes a simple random walk on $L\ell \times L\ell$ square lattice with jump rate $m/4$. For an $M \times M$ regular square lattice, the mean first passage time F_M of a simple random walker with jump rate ω is rigorously given by [11]

$$F_M = \frac{1}{2\omega(2M+1)} \sum_{\mu=0}^{M-1} (-1)^{\mu} \frac{\cos^2\left(\frac{2\mu+1}{2M+1}\frac{\pi}{2}\right)}{\sin^3\left(\frac{2\mu+1}{2M+1}\frac{\pi}{2}\right)} \quad . \tag{4}$$

For our system, thus the mean first passage time is given by $51520/m$ which explains the value observed at $\rho = 1$.

In the limit of $\rho = 0$, the first passage time for $m = 1000$ and 25 is basically determined by the time during that a cell arrives at the bottom for the first time on $L \times L$ square lattice, which is 1984, since the dynamics in the cell is so fast that the first passage of the carrier is essentially identical to the first arrival of the cell at the lower boundary. For $m = 1$, however, the situation is rather complicated and the exact expression has not been obtained. Our result shows the mean first passage time is about 50% longer than that of the cell.

The enhancement of $F(\rho, T; m)$ below the critical temperature is due to the strong spatial fluctuation of the structure: At higher densities, the carrier moves on the percolating network of cells, and as the density is reduced, the connectivity of the network becomes less effective and the mean first passage time becomes longer. In the low-density side, the carrier is transported by a cell on which it resides, and as the density is increased, the dynamics of the cell becomes slow due to cluster formation and the first passage time becomes longer

When the dynamics of the carrier is fast ($m = 1000$), we observed the cross over temperature above which cluster formation does not affect the first passage time

significantly. The cross over occurs when the cluster formation reduces the mobility of the cell. When the two-cell cluster breaks easily with probability larger than 50%, then $F(\rho,T;1000)$ is a decreasing function of the density, otherwise it will increase as the density is increased. Therefore, the cross over temperature can be determined by the condition $\exp(-J/k_BT) \approx 0.5$, and thus T_X is given by $T_X/T_C \approx 2\sinh^{-1}(2)/\ln 2 \approx 2.5$.

In passing, we would like to refer to the diffusion constant. Using a larger system $L = 64$ and $\ell = 10$, we investigated the mean square displacement for various values of parameters. We found that the carrier shows anomalous diffusion in the area where the mean first passage time is long, and thus the diffusion constant cannot be well defined and may not be the relevant quantity to represent the dynamics of the carrier in the entire parameter space.

5. Conclusion

We have shown that the cells providing the space for the random walk of the carrier have two competing effects on the dynamics, and the transport of the carrier shows an extremum as a function of density in a certain range of the temperature. This density dependence is in line with experiments for micelles and fluid Hg [3-7]. These competing effects for $m = 1000$ diminish when the temperature is higher than T_X.

It should be emphasized that the first passage time can be related to a boundary perturbation experiment [9] and the first passage time distribution can be measured by experiments such as the intensity modulated photocurrent spectroscopy [12].

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