PHYSICAL REVIEW B VOLUME 52, NUMBER 23 15 DECEMBER 1995-I

Diffusion coefficient for interacting lattice gases: Repulsive interactions

Zbigniew W. Gortel
Department of Physics and Theoretical Physics Institute, University of Alberta, Edmonton, T6G 2J1 Edmonton, Alberta, Canada

Magdalena A. Załuska-Kotur
Institute of Physics, Polish Academy of Sciences and College of Science, Aleja Lotników 32/46, 02-668 Warszawa, Poland

Łukasz A. Turski
Center for Theoretical Physics, Polish Academy of Sciences and College of Science, Aleja Lotników 32/46, 02-668 Warszawa, Poland

(Received 7 June 1995)

Following a previous model for a diffusion process in a dense lattice gas with attractive interactions, we propose a model which deals with repulsive interactions and permits the analysis of diffusion in adsorbates undergoing order-disorder phase transformations. Using a generalization of the local random mean field method we derive an explicit expression for the diffusion coefficient and analyze its behavior when the thermodynamic parameters, the adsorbate concentration and temperature, are varied within a physically relevant part of the parameters space.

In our previous rapid communication,[1] a description of diffusion processes in interacting lattice gases was presented and shown to be in good agreement with Monte Carlo simulation results for dense adsorbates with attractive interactions. Our approach was based on a properly tailored application of the random local mean-field theory to the Master equation description of a lattice gas kinetics. In an absence of interactions between the lattice gas particles, the transition rates in the Master equation are site independent. When the interparticle interactions are present, they result in local fluctuations of the transition rates. In our recent model,[1] we have assumed that in the interacting system, the effective transition rates can be considered to be functions of a random local potential. In general, the diffusion coefficient for the one particle random walk in a random potential field is inversely proportional to the inverse jump rate averaged over the potential field distribution,[2,3] $D \sim \subset W^{-1} \supset^{-1}$, rather than being proportional to the average of W. The same dependence is exhibited in our model.[1] We have shown then that when a local mean-field theory for an interacting system with short range *attractive* interactions is used to calculate the distribution of the random local potential field,[4] a simple formula for the diffusion coefficient emerges. Numerical implications of this formula agree very well with the results of Monte Carlo simulations.[1,5]

Our approach can be generalized and used for dense adsorbates undergoing order-disorder phase transformations. This is done here and we extend its applicability to cover systems with *repulsive* interactions between particles. We investigate here a behavior of the diffusion coefficient when the system undergoes an ordering transformation to a 2×2 phase as the concentration and temperature are changed. Our model is a simple but not trivial example demonstrating how the diffusion activation energy may change when the surface layer orders.

To model a dense adsorbate, we map the system of adsorption sites onto a simple lattice gas[5-8] with the Hamiltonian

$$\mathcal{H} = J \sum_{\langle i,j \rangle} n_i n_j - V \sum_i n_i \, . \tag{1}$$

Here $n_i = 0, 1$ is the occupation number of the lattice site i. The on-site "potential" V describes an adatom interaction with the host solid and contains information about the ambient gas state through its dependence on the chemical potential.[8] The summation in the first term in Eq. (1) is over all neighboring pairs of lattice sites and the interaction between the gas particles is assumed to be repulsive, so the coupling constant J is positive. Therefore, for some range of parameters (adsorbate concentration and temperature), the system forms ordered structures. Depending on the interactions and on the lattice type, these structures may be of different types. The simplest one, for a square lattice with the nearest neighbor repulsive interactions, is the 2×2 phase. In so, ordered phase the particles occupy every second lattice site. To model this structure in the mean-field approach, we divide all lattice sites into two sublattices, A and B, and treat them separately. This enables us to write the mean-field equations[9] for the adsorbate occupation numbers for each sublattice as follows:

$$\begin{aligned} n_i^A &= \frac{1}{2} + \frac{1}{2} \tanh(\beta h_i^A/2), \\ n_i^B &= \frac{1}{2} + \frac{1}{2} \tanh(\beta h_i^B/2), \end{aligned} \tag{2}$$

where $\beta = 1/k_B T$. In this formulation, the local field h_i^A at a site belonging to the sublattice A depends only

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on the occupation number at neighboring sites in the sublattice B: $h_i^A = V - J\sum_{\langle j\rangle_i} n_j^B$, where the summation is over the sites adjacent to the site i. Similarly, $h_i^B = V - J\sum_{\langle j\rangle_i} n_j^A$. The separation of the lattice gas into two sublattices does not result in loss of generality, and in further calculations, we assume that h^A and h^B are given by two different distributions.

To describe the static properties of the system we assume in the lowest order approximation that at equilibrium, the system is globally uniform and the field distributions are sharply peaked around $h_i^{A,B} = V - zJn^{B,A}$, where $n^{A,B}$ are global mean adsorbate concentrations for each sublattice, $n^{A,B} = \sum_i n_i^{A,B}/N$, with N being the number of sites in each sublattice. For such a field distribution, the phase diagram can be entirely characterized in terms of two parameters: the total mean adsorbate concentration $n = (n^A + n^B)/2$, and the parameter that measures the difference between global occupations of both sublattices, $m = (n^A - n^B)/2$. Straightforward algebra leads from Eqs. (2) to the the following expression for the line that separates the phases

$$\frac{k_B T}{J} = 1 - 4(n - \tfrac{1}{2})^2. \tag{3}$$

We plot this line in Fig. 1 as a function of the global adsorbate concentration n. Above the line, the system is not ordered and $m = 0$. Below it, we have the 2×2 phase and $m \neq 0$. This line represents the locus of continuous phase transition points, plotted as a function of n. Note that in this "antiferromagnetic" model, the concentration n is not a critical variable and the proper order parameter for the transition is the "staggered magnetization" m.

To study the diffusion process, we adopt the model that we have used for the lattice gas with attractive interactions.[1] We effectively replace the *interacting* gas with a system of *independent* effective particles in a randomly fluctuating field. We have to regard two sublattices separately. Thus, in contrast to the analysis in Ref. 1, we have now two Master equations,

$$\frac{\partial}{\partial t}P^A(i,t) = \sum_{\langle l\rangle_i}\Gamma_{i+l}^B P^B(i+l,t) - \sum_{\langle l\rangle_i}\Gamma_i^A P^A(i,t)\ ,$$
$$\frac{\partial}{\partial t}P^B(i,t) = \sum_{\langle l\rangle_i}\Gamma_{i+l}^A P^A(i+l,t) - \sum_{\langle l\rangle_i}\Gamma_i^B P^B(i,t)\ , \tag{4}$$

where $\langle l\rangle_i$ indicates that the summation is over all vectors l connecting the site i with its nearest neighbors. The transition rates are given by[1]

$$\Gamma_i^{A,B} \equiv \Gamma(h_i^{A,B}) = \nu_0 \exp(-\beta V)\exp(-\beta h_i^{A,B})\ . \tag{5}$$

The local field distributions are evaluated by means of formulas being direct generalizations of those used earlier:[1,4]

$$f(h^{A,B}) = \overline{\langle \delta(h^{A,B} - h_i^{A,B})\rangle}$$
$$= \frac{1}{2\pi}\int d\rho \overline{\langle \exp[i\rho(h^{A,B} - h_i^{A,B})]\rangle}\ , \tag{6}$$

where the angular bracket and the overbar denote thermal and spatial averages, respectively. Using the same as in our earlier approach[1] (the random local field approach), we finally get the Fourier transforms of the field distribution functions $\tilde{f}(\rho^{A,B})$,

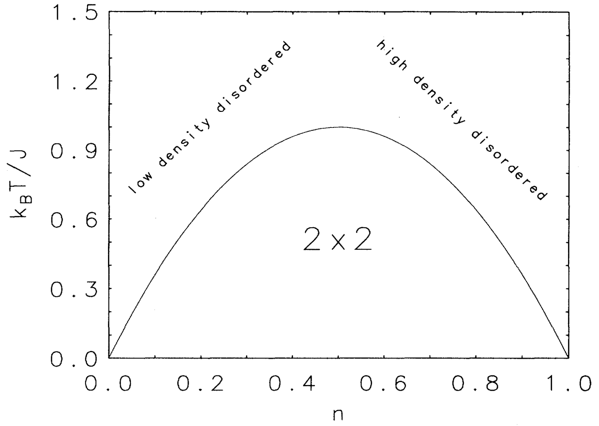

FIG. 1. The mean-field phase diagram for lattice gas with repulsive interactions.

$$\tilde{f}(\rho^{A,B}) \approx \exp\left\{-in^{B,A}\sum_i[1 - \exp(-i\rho^{A,B}J_{0i})]\right\}$$
$$= \exp[-n^{B,A}\mathcal{F}_1(\rho^{A,B}) - in\mathcal{F}_2(\rho^{A,B})]\ , \tag{7}$$

where $\rho^{A,B}$ are Fourier variables conjugated to $h^{A,B}$ and

$$\mathcal{F}_1(\rho^{A,B}) = \sum_i[1 - \cos(\rho^{A,B}J_{0i})],$$
$$\mathcal{F}_2(\rho^{A,B}) = \sum_i \sin(\rho^{A,B}J_{0i})\ . \tag{8}$$

We note that the local field h^A depends only on the concentration n^B, and h^B depends only on the density n^A.

To calculate the time evolution of the root mean square particle displacement

$$\langle r^2\rangle(t) = \frac{1}{N_i}\sum_j\sum_i |\, i - j\,|^2\, P(i,t),$$

we note that

$$\frac{\partial}{\partial t}\langle r^2\rangle = \frac{z}{n}\sum_i[\Gamma_i^A P^A(i,t) + \Gamma_i^B P^B(i,t)]\ , \tag{9}$$

and use the equilibrium values for probabilities at both sublattices

$$P_{\mathrm{eq}_i}^A = n\frac{(\Gamma_i^A)^{-1}}{\sum_j(\Gamma_j^A)^{-1} + \sum_j(\Gamma_j^B)^{-1}},$$
$$P_{\mathrm{eq}_i}^B = n\frac{(\Gamma_i^B)^{-1}}{\sum_j(\Gamma_j^A)^{-1} + \sum_j(\Gamma_j^B)^{-1}}. \tag{10}$$

With that, the final formula for the diffusion coefficient becomes

$$D = \nu_0\frac{z}{2d}\frac{\exp(-\{\beta V + nz[\exp(\beta J) - 1]\})}{\cosh\{mz[\exp(\beta J) - 1]\}}\ . \tag{11}$$

For $m = 0$, i.e., for the disordered phase, it reduces to the expression derived earlier.[1]

We plot in Fig. 2 the diffusion coefficient given in Eq. (11) as a function of the inverse temperature βJ for several concentration values (upper panel) and as a function of the adsorbate concentration n for several temperatures (lower panel). The on-site potential strength is $V = 1.5J$, and for its other values, the results are qualitatively similar. The region corresponding to the 2×2 ordered phase is bounded by the dashed lines. We see that the behavior of the diffusion coefficient changes dramatically across the transition line in both plots. Using the Arrhenius parametrization for the diffusion coefficient $D = D_0 \exp(-\beta\Delta)$, we can analyze the activation energy Δ dependence on temperature and concentration.

From the β dependence of curves in Fig. 2(a), the effective activation energy Δ can be obtained as a function of temperature for several values of the adsorbate concentration. Initially, at high temperatures, the slope of the curves is positive, thus, the activation energy is negative and has no physical meaning. Then, at lower temperatures, we note a slow increase of Δ, as the temperature falls down. At still lower temperatures, when the system starts to order, i.e., when we enter the region corresponding to the 2×2 phase, the activation energy increases discontinuously to relax downwards with further temperature decrease towards its stable value for the ordered phase.

The diffusion coefficient increases rapidly in Fig. 2(b), with increasing adsorbate concentration, when the system is disordered (note the logarithmic scale used). Upon crossing the transition line into the ordered region, the concentration dependence weakens at first to become stronger again and then slows down returning to the original increase law as one leaves the ordered phase. The lower the temperature below the critical temperature, the more dramatic is the change in the diffusion behavior due to ordering. The rapid decrease of the diffusion coefficient upon ordering in the adsorbate is consistent with the results of experiments,[10] of simulations,[5,6] and agrees with the conclusions based on the entropy calculations.[10–12] In Ref. 10, the experimentally determined diffusion coefficient for Pb on (100) surface of Cu was given as a function of adsorbate concentration for several temperatures. At high temperatures, the concentration dependence of D follows closely our theoretical curves for concentrations above $n = 0.2$. Upon entering the ordered phase, the experimental data of Ref. 10 exhibit negative slopes on the $D(n)$ curves, clearly indicating an admixture of nonequilibrium processes. These negative slopes are obviously missing from our purely *equilibrium* considerations.

The model analyzed in this work is quite simple. Nevertheless, it describes remarkably well the diffusion process in the system undergoing the order-disorder phase transition. Recall that the expression (11) has been derived assuming a two sublattice model of the adsorbate and using the simplest possible mean-field approach for the equilibrium properties of the system. We have also used quite a simple assumption concerning the local field distribution (6). Several improvements of our model and of the ensuing analysis are possible. The static part of the analysis can be made more accurate by going beyond a simple mean-field theory. The local field distribution calculation can also be made more precise. An important advantage of the local mean-field approach is that it can be extended to models of adsorbates other than a simple lattice gas model. More sophisticated Hamiltonians than (1) can be used, and more complex Master equations can be postulated and analyzed. The Potts model Hamiltonian and Potts model kinetics are of primary interest here.[13] Work along this line is in progress.

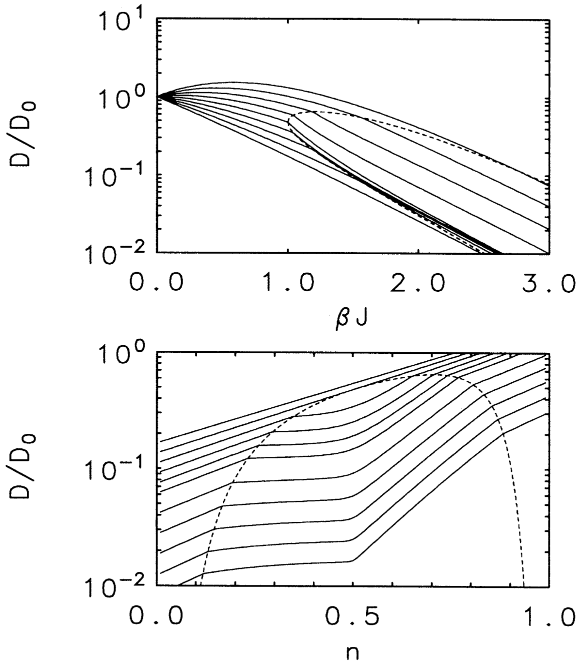

FIG. 2. (a) Diffusion coefficient of the interacting lattice gas D/D_0 versus βJ. Adsorbate concentrations n decrease by 0.1, from $n = 0.9$ for the topmost line down to $n = 0.1$ for the lowest one. (b) Adsorbate concentration dependence of D/D_0. Parameter βJ increases by 0.1 from $\beta J = 0.9$ for the topmost line up to $\beta J = 1.4$ and then by 0.2 up to 3.0 for the lowest one. $V = 1.5J$ and $D_0 = \nu_0 z/2d$ in both panels.

This work was partially supported by KBN (Poland) Grant No. 2P 302038 04 and ZWG's Natural Sciences and Engineering Research Council (NSERC, Canada) research grant. M.Z.K. and Ł.A.T. would like to thank the Physics Department of the University of Alberta for the hospitality extended during the period when part of this work was carried out.

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