

## Diffusion coefficient for interacting lattice gases

Magdalena A. Załuska-Kotur

*Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland*

Łukasz A. Turski

*Center for Theoretical Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland*

(Received 19 August 1994; revised manuscript received 3 October 1994)

Diffusion in an interacting adsorbate is analyzed with the use of a master equation for the lattice-gas model. The coefficient of chemical diffusion for the diluted, interacting adsorbate is calculated using concepts of diffusion theory in a disordered medium in which the random potential is related to the local field that affects each particle due to the particle interactions. We use the random-local-field method to evaluate the distribution of local fields in the equilibrium state. Results obtained for the simplest, interacting lattice gas are successfully compared with Monte Carlo simulations.

The aim of this paper is to provide a simple description of the diffusion processes in interacting lattice gases, which would be valid for dense adsorbates undergoing phase transformation. In the abundant literature<sup>1-3</sup> diffusion is almost always envisaged as the continuum time limit of a random-walk process. We do have extensive knowledge of how lattice properties, no matter how exotic, i.e. fractal, random, etc., can affect diffusion.<sup>2,4</sup> Considerably less is known about how the interparticle interactions affect the diffusion. Indeed, when one mimics repulsive short-range interactions (which precludes double occupancy of the lattice sites) by so-called blocking factors, the theoretical description becomes very complex.<sup>5-7</sup> The situation gets considerably worse when long-range interactions are also taken into account. The latter situation is relevant for adsorbates undergoing phase transformations.

In the conventional, random-walk theory of diffusion, the diffusion coefficient  $D$  is proportional to the product of the jump rate  $W_0$ , and a purely geometrical factor with dimension of *length*; it is determined by the lattice spacing, the coordination number, and the dimensionality of the lattice. It has been shown<sup>8</sup> that when the random walk is such that the jump rate becomes a random quantity, then the diffusion coefficient is proportional to the inverse averaged jump rate  $D \sim \langle W^{-1} \rangle^{-1}$ . In this paper we adopt the idea that the interactions between lattice-gas particles, causing local changes of the particle density, result in fluctuating effective jump rates to be used in a proper master equation. We shall prove that the diffusion coefficient is then given in terms of suitably averaged inverse jump rates. To develop our theory we will employ the local-mean-field method, adopted from studies of magnetic models, particularly dipolar glasses. Our results are in a remarkably good agreement with the Monte Carlo simulation for diffusion in an interacting lattice gas.<sup>9,10</sup> Indeed, for attractive interactions our theoretical predictions differ from the Monte Carlo data by a few percent over the range of the coupling constants.

We assume that a dense adsorbate, for example, He on a metal surface, can be sufficiently well described by a simple lattice-gas model. The lattice gas is a natural way of mapping

the system of adsorbing sites<sup>9-12</sup> and its Hamiltonian, assuming two-particle interactions only, has the form

$$\mathcal{H} = -\frac{1}{2} \sum_{i,j} J_{i,j} n_i n_j - V \sum_i n_i. \quad (1)$$

Here  $n_i = 0, 1$  is the occupation number of lattice site  $i$  and the interaction coupling  $J_{i,j}$  depends, in general, on the distance between corresponding lattice sites. The one site "potential"  $V$  describes adatom interactions with the solid below the surface and on the parameters of ambient gas.<sup>12</sup> It is known that this model accounts for all salient features of the equilibrium states of the adsorbate. The kinetics of such a system are then described by a master equation with properly chosen transition rates.<sup>9,10,12</sup> It is generally assumed that these transition rates depend on the energy of the site from which each particle moves, and usually allow for jumps between neighboring lattice sites only. We write

$$W_{ij}(\{n_l\}) = \nu_0 \exp\left(-\beta V - \beta \sum_k J_{i,k} n_k\right) n_i (1 - n_j), \quad (2)$$

where  $i$  and  $j$  are neighboring sites, the particle jumps from site  $i$  to site  $j$ , and  $\nu_0$  is an attempt frequency.

The master equation with transition rates in the form (2) represents a formidable mathematical problem. To obtain from it interesting physical information we have to use some approximate methods. In a previous publication we used the perturbation theory in which the coupling coefficient  $J_{i,j}$  was used as a "small" parameter.<sup>13</sup> Here, we would like to propose a new method, the random-local-field method, borrowed from magnetism theory, which reduces the problem to the diffusion in a many-body system to that in a system of effective, independent particles.<sup>14</sup> The basic idea in this method is that the interaction between particles results in an additional random local field  $h_i$  felt by an effective particle on site  $i$ . Next, we assume that in a not too dense system these local fields are essentially independent, and we calculate their distribution calculating the thermal and space average of temporary local field  $h_i^{\text{loc}} = \sum_j J_{i,j} n_j$ . As the result we map our interacting lattice gas on that of independent effec-

tive particles moving in a random field  $h_i + V$ . The distribution of these local fields changes when the system evolves in time. Unless, however, the system is driven far away from the equilibrium state, the local field distribution tends to be essentially stationary.

Having this in mind we can simplify the general form of the master equation, with transition rates Eq. (2), to the form describing evolution of the probability of finding an effective particle at site  $i$  at time  $t$ ,  $P(i, t)$ .

$$\frac{\partial}{\partial t} P(i, t) = \sum_{\langle l \rangle_i} \Gamma_{i+l} P(i+l, t) - \sum_{\langle l \rangle_i} \Gamma_i P(i, t). \quad (3)$$

In the above equation all the correlation terms from the microscopic, original equation have been omitted. Transition rates  $\Gamma$  for a system of independent, effective particles depend only on the local field at a given site. Now, from the definition of transition rates (2) we obtain an effective transition rate  $\Gamma$  dependent on the local field

$$\Gamma_i \equiv \Gamma(h_i) = \nu_0 \exp(-\beta V) \exp(-\beta h_i). \quad (4)$$

Let us assume that the field distribution is known. Equation (3) is analogous to that describing a random walk on a lattice with random potential. Standard analysis<sup>8</sup> leads to the equation for the time evolution of the rms particle displacement  $\langle r^2 \rangle(t) = (1/N_i) \sum_j \sum_i |i-j|^2 P(i, t)$  in the form

$$\frac{\partial}{\partial t} \langle r^2 \rangle = \frac{z}{n} \sum_i \Gamma_i P(i, t), \quad (5)$$

where  $z$  is the lattice coordination number,  $N_i$  is the total number of particles in the system, and  $n$  is the mean lattice-gas density. Now, using the  $H$  theorem one can prove that all solutions of Eq. (3) tend to the equilibrium one, which can be compactly written using the local field distribution function  $f(h)$  as

$$P^{\text{eq}}(h) = \Gamma^{-1}(h) \frac{n}{\int dh f(h) \Gamma^{-1}(h)}. \quad (6)$$

To calculate the equilibrium diffusion coefficient  $D_0$  we replace the time-dependent distribution function in Eq. (5) by its equilibrium value given by Eq. (6). This coefficient is given by

$$D_0 = \frac{z}{2dn} \int dh f(h) \Gamma(h) P^{\text{eq}}(h), \quad (7)$$

and can be calculated explicitly once the field distribution  $f(h)$  is known.

Now, using Eq. (6) we obtain a simple expression for the diffusion coefficient:

$$D_0 = \frac{z}{2d} \nu_0 \langle \Gamma^{-1} \rangle^{-1}, \quad (8)$$

where  $\langle a \rangle$  denotes the average over the equilibrium distribution of the local field and  $d$  is the space dimensionality.

The crucial point in our analysis is then evaluation of the field distribution  $f(h)$ . We adopt for our purpose a method proposed by Vugmeister and Stefanovich.<sup>14</sup> The field distribution is defined as

$$f(h) = \overline{\langle \delta(h - h_i) \rangle} = \frac{1}{2\pi} \int d\rho \overline{\langle \exp[i\rho(h - h_i)] \rangle}, \quad (9)$$

where the overbar denotes spatial, and angular bracket thermal average, respectively. Following Ref. 14 we write

$$\overline{\langle \exp(-i\rho h_i) \rangle} = \prod_j \overline{\langle \exp(-i\rho J_{ij} n_j) \rangle}. \quad (10)$$

Now, the product on the right-hand side of Eq. (10) can be written as

$$\left( \sum_i p_i \langle \exp(-i\rho J_{0i}) \rangle \right)^{N_i} = \left( 1 - \frac{1}{N} \sum_i p_i \langle 1 - \exp(-i\rho J_{0i}) \rangle \right)^{N_i}, \quad (11)$$

where  $p_i$  is the occupation probability of the  $i$ th site. Here  $N$  is the number of lattice sites. For systems not too far from equilibrium it is proper to use uniform site distribution, i.e.,  $p_i = 1/N$ . For low adsorbate densities  $n$  we obtain for the Fourier transform of the field distribution function  $\tilde{f}(\rho)$

$$\begin{aligned} \tilde{f}(\rho) &\approx \exp \left\{ -in \sum_i [1 - \exp(-i\rho J_{0i})] \right\} \\ &= \exp[-n \mathcal{F}_1(\rho) - in \mathcal{F}_2(\rho)], \end{aligned} \quad (12)$$

where

$$\mathcal{F}_1(\rho) = \sum_i [1 - \cos(\rho J_{0i})],$$

$$\mathcal{F}_2(\rho) = \sum_i \sin(\rho J_{0i}). \quad (13)$$

Using above expression for the field distribution function, we can evaluate the diffusion coefficient given by Eq. (7). Straightforward algebra leads to the final expression of our paper, written below, which can then be compared with Monte Carlo simulation results. We have

$$D_0 = \nu_0 \frac{z}{2d} \exp(-\{\beta V + nz[\exp(\beta J) - 1]\}). \quad (14)$$

For small values of  $\beta J$  Eq. (14) simplifies to a conventional expression for the diffusion coefficient with the diffusion activation energy  $\Delta$  equal to  $V + nzJ$ .

Tringides and Gomer,<sup>9</sup> have run an extensive Monte Carlo simulation of the diffusion coefficient in an interacting lattice gas. They obtained values of the diffusion coefficient for a range of coupling constants and above and below the lattice-gas critical point. For negative values of the couplings  $J$  the normalization used in Ref. 9 makes the comparison with our theory cumbersome. Delaying the full discussion of this point for future publication, in Figs. 1 and 2 we have shown a comparison of our formula, Eq. (14), with the Tringides and Gomer results for a range of coupling constants and for two densities  $n=0.3$  and  $n=0.5$ , respectively. To facilitate comparison we use the same values of parameters as in the

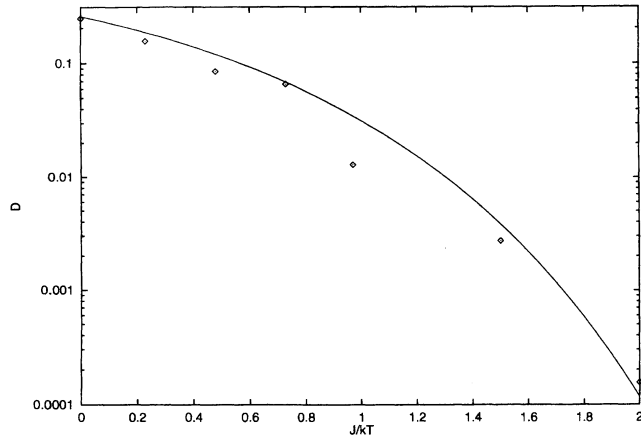


FIG. 1. Dependence of interacting lattice-gas diffusion coefficient  $D_0$  on  $\beta J$ , Eq. (14) (solid line) compared with Monte Carlo simulations (rhombuses) [from Ref. 9;  $z=4$ ;  $\nu_0 z/(2d)=0.25$ ;  $V=0$ ]. Density  $n=0.3$ .

Monte Carlo simulations, i.e.,  $V=0$  (no on-site binding potential) and  $z\nu_0/2d=0.25$ . The agreement is remarkably good in spite of the fact that Eq. (14) follows from a truly simplified version of the local-mean-field method.

To summarize, we have shown that simple use of the local-mean-field method borrowed from dipolar glass physics results in an analytic expression for the diffusion coefficient in an interacting lattice gas which agrees quite well with existing Monte Carlo data. The theory can be generalized for higher densities with slight improvement of the agreement with numerical experiments. The local-mean-field

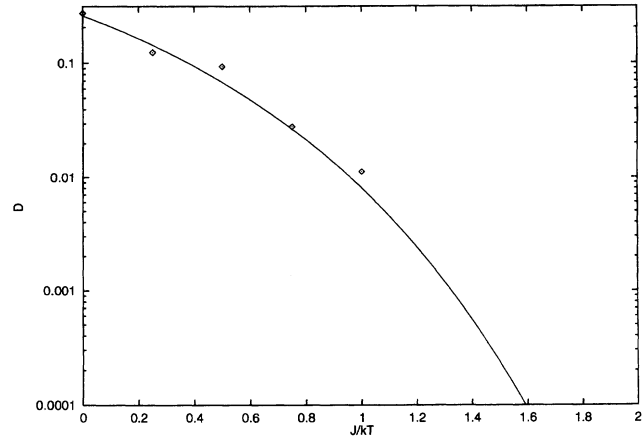


FIG. 2. Dependence of interacting lattice-gas diffusion coefficient  $D_0$  on  $\beta J$ , Eq. (14) (solid line) compared with Monte Carlo simulations (rhombuses) [from Ref. 9;  $z=4$ ;  $\nu_0 z/(2d)=0.25$ ;  $V=0$ ]. Density  $n=0.5$ .

method can readily be applied for systems with weak and long-range interactions, for example, dipolar forces. Further extension of our procedure is possible for the kinetic Potts model.<sup>15</sup> The inclusion of various other interactions, more detailed analysis of the role of the blocking factors, correlation effects, etc., is possible and work along this line is now in progress.

The suggestions, comments, and criticism of Zbigniew W. Gortel are kindly acknowledged. This work was partially supported by KBN (Poland) Grant No. 2P 302038 04.

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