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Surface diffusion of particles over bivariate trap lattices

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Abstract

We investigate the diffusion of particles on heterogeneous lattices with two kinds of non-equivalent sites. General analytical expressions for the chemical and jump diffusion coefficients have been derived in the case of strong inhomogeneity. We have calculated coverage dependencies of the diffusion coefficients and other necessary thermodynamic quantities for some representative values of the lateral pairwise interaction between the particles. The analytical data have been compared with the numerical data obtained by the kinetic Monte Carlo simulations. Almost perfect agreement between the respective results has been found.

1. Introduction

The diffusive mass transfer controls the rates of a multitude of physical, chemical and biological processes. Theory primarily aims at understanding the details of migration process in these application areas. The theoretical description of various kinetic phenomena observed in experimental studies presents a considerable challenge. Appropriate models must reflect the elementary microscopic migration acts of particles, which depend on the structure and mutual particle-particle interaction. Therefore, it is not surprising that a great deal of effort has been devoted to developing the simplest possible models, which offer the advantage of exact treatment, despite of oversimplifying the real phenomena. To include all these aspects it is most convenient to employ the lattice gas models. In these models particles perform stochastic jumps among the sites of a discrete lattice. During migration acts, affected by thermal activation, the particles have to surmount barriers separating the sites. The effective barrier height depends on the specific atomic environment and, as a consequence of the particle-particle interaction, also on the number and configuration of the neighbor particles. In the majority of models the particles occupy the equivalent lattice sites formed by the minima of the potential relief. Such simplification differs substantially from the real crystals, where different binding sites have been experimentally identified.

In general, the determination of the diffusion coefficient requires the solution of a kinetic equation for a many-particle system. However, under simplifying assumptions such as slowly varying particle density fluctuations and neglecting memory effects, the problem can be reduced to the calculation of purely thermodynamic quantities: free energy and its derivatives over the chemical potential and interaction parameters [1,2,3]. This approach has been used widely for the theoretical treatment of particle diffusion. The task of computing thermodynamic quantities is substantially simpler and computationally less expensive by orders of magnitude than direct kMC simulations of kinetic phenomena which suffer from the statistical uncertainty of the results. It turns out that the approximations involved when connecting diffusion coefficients with the thermodynamic quantities are rather reliable for the lattice gas systems. Results obtained by different analytical methods (quasi-chemical approximation, cluster variation approach, RSRG method and others) show quite good agreement with the numerical data. The analytical expressions for the diffusion coefficients are quite simple and valid over wide regions of particle density and temperature down to the subcritical values. These expressions work perfectly in homogeneous lattices with different dimensions and symmetries. Yet there is no general upper bound to the errors established for these approximations just as there is no guarantee for the kMC results to converge to the required statistical accuracy for the general case with limited computer resources. Compared to purely numerical schemes, the theoretical methods of statistical mechanics reveal correlations between the kinetic coefficients and some thermodynamic quantities thereby providing the basis for the additional insight. Diffusion in homogeneous systems has been investigated intensively and now is largely understood.

But heterogeneous systems are more complex. A lot of possible models have been proposed and investigated. In the simplest models a quantity influencing the particle migration assumes only two values depending on the site position. There are dichotomic or bivariate models. For example, the lattice with deep and shallow adsorption sites is the so-called bivariate trap model, and the lattice with high and low potential barriers separating the sites is the bivariate barrier model. Due to diversity of these models it is not surprised that the understanding of the diffusion in such systems is far from complete despite the large efforts. In the case of inhomogeneous lattices the ordinary expressions for the diffusion coefficients, give qualitatively correct results for high temperatures only, when the lattice inhomogeneity is small and really can be neglected. With decreasing temperature the deviations between analytical results and MC data grow considerably. The coverage dependencies for tracer, jump and chemical diffusion coefficients differ qualitatively from those obtained for the homogeneous lattice.

In the present work we have investigated the effect of the lattice inhomogeneity on the particle diffusion. The purpose of the investigation is to present the analytical expressions for the jump and chemical diffusion coefficients which describe the particle diffusion over the inhomogeneous lattices with two kinds of adsorption sites. We have derived such simple expressions which occur quite universal and valid for many types of inhomogeneous lattices. Using the RSRG approach and kMC simulations we check these expressions for some simple inhomogeneous lattices. We have obtained the density dependencies of the tracer, jump and chemical diffusion coefficients for attractive and repulsive lateral interaction between particles. Also the mean square surface coverage

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fluctuations or isothermal susceptibility, the adsorption isotherms (the particle density as a function of the chemical potential) and pair correlation function for the nearest neighbor sites have been calculated in the whole density region for different temperatures. It has been shown that for the strong lattice inhomogeneity there is a rather specific behavior of the particle migration over the lattice. The ordinary analytical expressions fail to even qualitatively describe density dependencies of jump and chemical diffusion coefficients. The new analytical expressions coincide almost perfectly with the kMC data.

We have investigated the particle diffusion in honeycomb [4], square [5-9], simple cubic [10], triangular [11] and dice [12] inhomogeneous lattices. In these lattices (except triangular and dice) every deep site has the nearest neighbor (NN) shallow sites only, and vice versa, every shallow site has the deep NN sites. Such inhomogeneity produces a rather specific correlation in the particle jumps. The coverage dependencies of the diffusion coefficients are quite different from the homogeneous case. It occurs that the particle diffusion can be suitably described by the particle jump pairs, not by the particle single jumps as in the case of the homogeneous lattices. Using such pair jump sequences, we have derived analytical expressions for the jump and chemical diffusion coefficients and check them by the kMC simulations. The results of the theoretical approach fit the numerical data amazingly well. This perfect coincidence confirms strongly the correctness of the new approach. The calculations of the diffusion coefficients in such lattices are reduced to the computation of some thermodynamic quantities like the chemical potential, isothermal susceptibility and pair correlation functions of NN particles.

The organization of the paper is as follows. In Section 2 we consider the model and definitions of the diffusion coefficients. The particle diffusion over 1D chain with alternating deep and shallow sites is described in Section 3. This is followed by the discussion of the results in Section 4.

2. The model, Hamiltonian and diffusion coefficients

Let us consider the 1D chain shown in Fig.1 with the site spacing a=1. Like in all heretofore-studied cases - honeycomb, square, cubic - the 1D lattice can be decomposed into two interpenetrating sublattices with the same type of sites deep (d) or shallow (s) with different depths. If the adsorption energies ε_d , ε_s for the d and s sites, respectively, are large relative to the temperature $k_B T$, the particles will stay almost exclusively within the potential minima jumping occasionally to empty NN sites. A set of occupation numbers n_i describes all possible states of the particle system. In the thermodynamic equilibrium the system behavior is described by the grand partition function Q or by its corresponding potential $F = N^{-1} \ln Q$ termed free energy. The Hamiltonian is given by

$$H = \sum_{i=1} \varepsilon_i n_i + \varphi \sum_{ij} n_i n_j$$

Here φ is the pair interaction energy of the NN particles. We introduce the surface coverage $\theta = N_a / N$ where N_a and N stand for the numbers of particles and sites, respectively.

To describe the particle migration the whole process must be resolved into its elementary acts. Particle transport is described in the terms of jumps of single particles in a regular or random energy landscape. A particle in the initial site i-th can jump to final f-th site (any of the i-th NN empty sites). The jumping particle must surmount the potential barrier separating the sites. In the simplest case of the Langmuir lattice gas the barrier height is a constant ε_d or ε_s depending on the type of the i-th site. For interacting particles the activation energy depends on the number of adjacent particles. We assume that the interactions affect the minima of the potential landscape and neglect the influence on an activated particle at the saddle point of the potential barrier. The model should be appropriate for a short-range lateral interaction. It is certainly important to note that the transition algorithm describes how particles move over the lattice. Different algorithms are conceivable and have been used in the diffusion theory and kMC simulations [13].

Some diffusion coefficients have been defined to describe the particle migration. Conceptually, the simplest diffusion coefficient is a single particle (tracer) diffusion coefficient D_t. It addresses the random walk of individual tagged particles. Another useful quantity is the jump diffusion coefficient D_j. The coefficients are well-suited for the kMC simulations as they are expressed in terms of directly accessible quantities – mean squares of the particle random walk displacements. The chemical diffusion coefficient D_c is determined by Fick's first law which constitutes the relationship between the flux of particles and the gradient of the surface coverage.

The tracer, jump and chemical diffusion coefficients are equal in a zero-coverage limit. In completely occupied lattice the tracer and jump diffusion coefficients are equal zero, but their ratio $D_t / D_j \neq 1$. It depends on the dimensionality and symmetry of the lattice. The reason of the different behavior of the tracer diffusion coefficient is the following: while the total change of the lattice gas state is a Markov process, the migration of a tagged particle is not Markovian due to the noticeable backward correlation. Any particle left a vacancy - empty site behind itself after every jump. If the other NN sites are empty, there is no effect, but if some of them are occupied, the probability for the backward jump is greater than for the forward or sideward jumps. The backward correlation is taken into account by a correlation factor f as follows: $D_t = fD_j$.

Let us consider the particle migration on an inhomogeneous lattice in detail. All particles tend to occupy d-sites resulting in either an almost empty s-sublattice and partially filled d-sublattice ($\theta < 0.5$), or a completely filled d-sublattice and partially filled s-sublattice ($\theta > 0.5$). The inhomogeneity implies a higher jump probability for $s \to d$ jumps, than for $d \to s$ jumps. A rather specific correlation between the particle jumps arises in this case: Any $d \to s$ jump transfers a particle to the s-

sublattice and creates an unstable local non-equilibrium configuration consisting of a pair of neighboring sites with s-site occupied and d-site empty. There are two fast ways for decaying of this configuration: either the particle jumps to any of the NN empty d sites, or the deep site is filled by another particle from any filled NN s sites. As (slow) creation and (fast) decay of the non-equilibrium configuration take place on largely different time scales, their combination ought to be considered as the central entity of the diffusion process. The particle jumps collect into pairs: Any $d \to s$ jump is followed almost immediately by a $s \to d$ jump. Such jump pairs are the most frequent events and they govern the particle migration. The frequency of this event is determined by its slowest component, the $d \to s$ jump frequency. Despite of the fact that the individual jumps are statistically uncorrelated, the lattice inhomogeneity imposes a strong pair-wise correlation between $d \to s$ and $s \to d$ jumps. Correlation between jump pairs is absent. This specific correlation will be especially important at half monolayer coverage when all deep sites are occupied and all shallow sites are empty. This characteristic coverage separates regions with distinctly different types of jump pairs dominating the particle migration. For $\theta < 0.5$ the s-sublattice is empty and any migration act starts by a slow $d \to s$ jump from a deep (initial) site to any empty NN shallow (intermediate) site. Very soon the particle performs fast $s \to d$ jump from the intermediate site to some empty (final) d site. The $s \to d$ jump probability depends on the total number of empty NN d sites, n_{empty}, as follows $1/n_{empty}$. The migration of the particles proceeds over the d-sublattice using the empty s sites as the intermediate steps. The probability of the jump pair depends not only on the occupation numbers of the initial and final sites, but on the occupation numbers of the intermediate NN sites.

For $\theta > 0.5$ the d-sublattice is filled and the s-sublattice is partially occupied. Again any act of migration starts by a slow $d \to s$ jump from an (intermediate) d site to a final empty s site. The jump creates vacancy in the completely occupied d-sublattice and initiates fast $s \to d$ jump from some (initial) shallow NN site to the intermediate d site. The $s \to d$ jump probability depends upon the number of occupied NN sites, n_{occ} at the intermediate d site, i.e. $1/n_{occ}$. The pair of successive $d \to s$ and $s \to d$ jumps cause particles to migrate over the s-sublattice using d sites as intermediate steps. The $s \to d$ jump probability determines the total probability of backward jumps, where initial and final sites are identical. The total probability of the backward jump is increased relative to all other possibilities as either initial (for $\theta < 0.5$) or final site (for $\theta > 0.5$) are always unoccupied and occupied, respectively. There is some similarity to the backward correlation of the motion of tagged particles.

3. The particle diffusion over inhomogeneous lattices

Let us consider the particle diffusion on an inhomogeneous 1D lattice. We should consider the evolution of the occupation numbers. The balance equation can be written in the following form:

$$n_i(t+\Delta t) - n_i(t) = J_{i-2,i}(\Delta t) - J_{i,i-2}(\Delta t) + J_{i+2,i}(\Delta t) - J_{i,i+2}(\Delta t),$$

where $J_{i,i+2}(\Delta t)$ denotes the contribution of the pair jump successions, transferring particles from the i-th to the i+2-th site after short time interval Δt. The form depends on the type of the succession. For the first type (particle jumps from the i-th deep site to the shallow i+1-th site and next to the deep i+2 site) $J_{i,i+2}(\Delta t)$ can be written as follows

$$J_{i,i+2}(\Delta t) = \nu_{i,i+1} n_i h_{i+1} h_{i+2} \Delta t / 2,$$

where $\nu_{i,i+1}$ is the jump rate from the i-th d site to the i+1 s site, and $h_i = 1 - n_i$.

The second type of the jump successions (particle jumps from the deep i+1-th site to the shallow i+2-th site and another particle jumps from the shallow i-th site to the empty deep i+1-th site) give the contribution in the following form

$$J_{i,i+2}(\Delta t) = \nu_{i+1,i+2} n_{i+1} h_{i+2} n_i \Delta t / 2.$$

Invoking the local equilibrium approximation and neglecting memory effects, the balance equation is easily reduced to the ordinary diffusion equation (for details, see Refs. [1, 3, 8]). The chemical diffusion coefficient has the following form

$$D_c = D_0 [P_2^< + P_2^>] \exp(\mu / k_B T) / \chi_T,$$

where D_0 is a zero-coverage diffusion coefficient, χ_T denotes the isothermal susceptibility, μ is the chemical potential, and the correlation functions $P_2^>, P_2^<$ have the following form

$$P_2^> = \left\langle h_i^{(d)} h_{i+1}^{(s)} n_{i+2}^{(d)} \right\rangle \text{ and } P_2^< = \left\langle h_i^{(s)} h_{i+1}^{(d)} n_{i+2}^{(s)} \right\rangle.$$

It should be noted that the approach, described above, is rather universal and can be applied to many lattices of different symmetries and dimensionality such as one-dimensional chain, two-dimensional (square, honeycomb, triangular, dice), three-dimensional simple cubic inhomogeneous lattices. The analysis can be carried out in the general form for an inhomogeneous lattice with coordination number z. The expression for the chemical diffusion coefficient has the same form as written above with different correlation functions $P_z^>, P_z^<$.

We list these functions for different inhomogeneous lattices:

1. The honeycomb inhomogeneous lattice (z=3) [4]

$$P_3^> = \frac{1}{2}\left\langle h_0^{(d)} h_1^{(s)} n_2^{(s)} (2 + h_3^{(s)}) \right\rangle \text{ and } P_3^< = \frac{1}{2}\left\langle h_i^{(s)} h_1^{(d)} h_2^{(d)} (2 + n_3^{(d)}) \right\rangle.$$

2. The square inhomogeneous lattice (z=4) [5-9]

$$P_4^{>} = \frac{1}{3}\left\langle h_0^{(d)} h_1^{(s)} n_2^{(s)} (3 + 2h_3^{(s)} + h_3^{(s)} h_4^{(s)}) \right\rangle ,$$

$$P_4^{<} = \frac{1}{3}\left\langle h_0^{(s)} h_1^{(d)} h_2^{(d)} (3 + 2n_3^{(d)} + n_3^{(d)} n_4^{(d)}) \right\rangle .$$

3. The simple cubic inhomogeneous lattice (z=6) [10]

$$P_6^{>} = \frac{1}{5}\left\langle h_0^{(d)} h_1^{(s)} n_2^{(s)} (5 + 4h_3^{(s)} + 3h_3^{(s)} h_4^{(s)} + 2h_3^{(s)} h_4^{(s)} h_5^{(s)} + h_3^{(s)} h_4^{(s)} h_5^{(s)} h_6^{(s)}) \right\rangle$$

$$P_6^{<} = \frac{1}{5}\left\langle h_0^{(s)} h_1^{(d)} h_2^{(d)} (5 + 4n_3^{(d)} + 3n_3^{(d)} n_4^{(d)} + 2n_3^{(d)} n_4^{(d)} n_5^{(d)} + n_3^{(d)} n_4^{(d)} n_5^{(d)} n_6^{(d)}) \right\rangle$$

In the above written expressions subscripts 0,1,…, z refer to sites forming a cluster with central 0-th site and its z NN's. The superscripts (d), (s) mean d or s site, correspondingly, and the angular brackets $\langle \cdots \rangle$ denote ensemble average.

Due to the mixed symmetry of the dice lattice sites the diffusion coefficient for this lattice has combination of correlation functions calculated for z=3 and z=6 [12]. The dice lattice with triangular sublattice of the s sites and honeycomb sublattice of d sites has the following diffusion coefficient

$$D_c = D_0 [P_6^{<} + P_3^{>}] \exp(\mu / k_B T) / \chi_T .$$

And the dice lattice with triangular sublattice of d sites and honeycomb sublattice of s sites has the following diffusion coefficient

$$D_c = D_0 [P_3^{<} + P_6^{>}] \exp(\mu / k_B T) / \chi_T .$$

The situation is slightly more complex for the triangular inhomogeneous lattices. There are noticeable contributions to the particle diffusion produced by the ordinary, single particle jumps ($s \to s$ or $d \to d$ jumps). Nevertheless the contributions produced by the pair jump successions and single jumps can be calculated quite easily and analytical expressions for the diffusion coefficients coincide very well with the kMC data [11].

4. Conclusions

We have investigated the diffusion of particle on inhomogeneous lattices with two kinds of sites. Such systems display specific peculiarities which qualitatively affect the particle diffusion as compared to the homogeneous lattices. Notably, the lattice inhomogeneity causes specific correlation between the particle jumps. This correlation results in a qualitatively different non-monotonic behavior of the diffusion coefficients: the appearance of a minimum at the stoichiometric coverage $\theta = 0.5$ for the tracer and jump diffusion coefficients.

The numerical kMC technique, as well as the analytical RSRG method, have been used to compute the isothermal susceptibility, adsorption isotherms, and the coverage dependencies of the pair the lateral interaction between the adsorbed particles. The excellent agreement between the data indicates that the RSRG method can be applied

successfully for investigations of the thermodynamic properties of the lattice gas systems with strong lateral interactions. The standard model of single jumps works well in simple lattice gas systems provided the lattice inhomogeneity is not substantial. However, the model is doomed to failure even at a qualitative level of accuracy in the case of a strongly inhomogeneous potential surface. An extension to the model of jump pairs has been proposed which forms a sound basis for the quantitatively correct description of the particle diffusion in such cases. This approach is quite general. The analytical expressions for the chemical diffusion coefficient derived on the basis of this model extension are valid for inhomogeneous lattices of different symmetry and dimensionality. The proposed model of jump pairs gives a simple and natural explanation of the peculiar characteristics of surface diffusion on inhomogeneous lattices as mentioned above.

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