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Diffusion on a one-dimensional sawtooth lattice with the nearest and the next nearest neighbor interactions

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HIGHLIGHTS

- I have derived the analytical expressions for the Fick and jump diffusivities.
- There are four different modes of migration depending on the interaction signs.
- Strong lateral interactions induce correlations between the successive particle jumps.
- The same coefficients describe diffusion in the homogeneous and heterogeneous lattices.

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ABSTRACT

The diffusion of particles adsorbed on a homogeneous one-dimensional sawtooth lattice with the nearest neighbor and the next nearest neighbor interactions between the particles is investigated using a theoretical approach and the kinetic Monte Carlo simulations. I have derived the analytical expressions for the diffusion coefficients. The calculated concentration dependencies of the coefficients have been compared with the numerical data generated by the simulations. The comparison reveals an interesting peculiarity of the particle diffusion. The lateral interactions induce correlations in the successive jumps of the particles. The thorough investigations of the dependencies clearly demonstrate how with the strengthening of the interactions the classical uncorrelated jumps are gradually replaced by the sequences of the correlated jumps. This behavior principally differs from the usual diffusion of particles in the homogeneous one-dimensional systems. It is an interesting and unexpected novelty of this system. Another uncommon feature of this model is a rich variety of the 'diffusion coefficients'. There are four combinations of the interaction parameter signs, and every combination has its own specific behavior of the particle diffusion, qualitatively opposite from the other combinations. Also, it should be noted a quite unusual result. In the homogeneous lattice gas system (all sites have an equal depth) with the strong, repulsive nearest neighbor and attractive next nearest neighbor interactions the diffusion is perfectly described by the diffusion coefficients derived for the heterogeneous lattices with deep and shallow sites. It is a direct evidence of the specific mode of the particle migration when the correlated pairs of jumps give the main contribution to the diffusion coefficients.

1. Introduction

Theoretical investigations of the transport processes in the multitude of physical, chemical, and biological systems attract the great attention. In the last decades a wave of interest arose to the investigations of the thermodynamics and kinetic

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processes in the one-dimensional (1D) systems like the diffusion of adsorbed atoms on the stepped and anisotropic surfaces, migration of fullerenes in the carbon nanotubes, diffusion of biomolecules in cell membranes, sliding of proteins along DNA. The 1D transport processes can be observed for the gas molecules within the molecular sieves, which have attained the practical relevance for the molecular sieving and catalysis.

The classical 1D models are known to be exactly solved. The exact data for all thermodynamic quantities for any values of the chemical potential and lateral interactions can be obtained quite easily. This unique property of the 1D systems was used for the validation of analytical expressions for the diffusion coefficients derived in the framework of the approach based on the theory of the non equilibrium statistical operator (NSO) [1–4]. The diffusion coefficients calculated for the 1D homogeneous and heterogeneous lattices exactly coincide with the corresponding very qualitative numerical data obtained by the kinetic Monte Carlo simulations (kMC) [5,6].

Here I present the further development of the above mentioned approach for the more complex case: the sawtooth lattice with the nearest neighbor (NN) and the next nearest neighbor (NNN) lateral interactions. This system is equivalent to the corresponding spin-$\frac{1}{2}$ model [7]. The first attempt to study the diffusion of adsorbates in the 1D lattice with the account of the NNN interaction along with the NN interaction was undertaken in [8]. The analytical expression for the diffusion coefficient was derived using the quasi-chemical approximation. Also, the diffusion in this system was investigated using the gradient expansion of the correlation functions in the master equation [9] and Monte Carlo simulations [10].

The paper is organized as follows. Section 2 introduces the model and definitions of the necessary quantities. The derivation of the diffusion equation and analytical expressions are considered in Section 3. The behavior of the particle system and the concentration dependencies of the diffusion coefficients are discussed in Section 4. The summary of the results and conclusions are presented in Section 5. For the interested readers the concise reminder of the known method of the transfer matrix is presented in Appendix.

2. Notations and preliminaries

2.1. Sawtooth lattice

The sawtooth lattice, shown in Fig. 1, is a zigzag 1D array of N sites. There are particles adsorbed in the sites. The adsorption energy equals ε and the energies of the lateral interactions between the NN particles and the NNN particles equal φ and ψ, respectively. The zigzag lattice configuration suggests that one should consider the NNN interaction along with the NN interaction because the distance between the NNN sites a_{NNN} is comparable with the lattice constant a. It changes in the range $[a \div 2a]$.

The particles rest in the sites and occasionally perform stochastic jumps among the NN sites. It resembles the case of metastable walk diffusion on missing-row reconstructed surfaces [11]. It seems natural to include into the consideration the jumps between the NNN sites, which can play an essential role [12]. It can be done in the framework of the approach used in this paper without any principal difficulties, but in this case the model loses its simplicity and the analytical expressions for the diffusion coefficients become cumbersome.

This description of the particle migration is certainly correct at the sufficiently low temperatures. When the duration of jumps is much shorter than the particle sojourn in the sites, the state of the system is completely described by a set of the occupation numbers $\{n_i\}$ with $n_i = 1(0)$ if the ith site is occupied (empty). The double occupancy is excluded.

The energy of the particle system (Hamiltonian) H_a and the particle number N_a are written as

$$H_a = \sum_{i=1}^{N} n_i(\varphi n_{i+1} + \psi n_{i+2} - \varepsilon), \qquad N_a = \sum_{i=1}^{N} n_i. \tag{1}$$

As an example let us consider the well known Lennard–Jones potential, which have been successfully used in the investigations of the particle migration in the low-dimensional systems [13]

$$V_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{2}$$

where ϵ is the depth of the potential well and σ is the distance at which the potential is zero. Then, the NN interaction $\varphi = V_{LJ}(a)$ and the NNN interaction $\psi = V_{LJ}(a_{NNN})$. Depending on the distances between the NN and NNN particles the interaction parameters can assume different values and signs.

2.2. Diffusion coefficients

The particle migration is described by some diffusion coefficients or diffusivities. I briefly recall the main features of these quantities. The center-of-mass (CM) diffusion coefficient (also jump diffusivity), D_{cm}, relates the mean-square displacement of the center of mass of the system with the time

$$D_{cm} = \lim_{t\to\infty} \frac{1}{2tN_a}\left\langle\left[\sum_{k=1}^{N_a} x_k(t)\right]^2\right\rangle. \tag{3}$$