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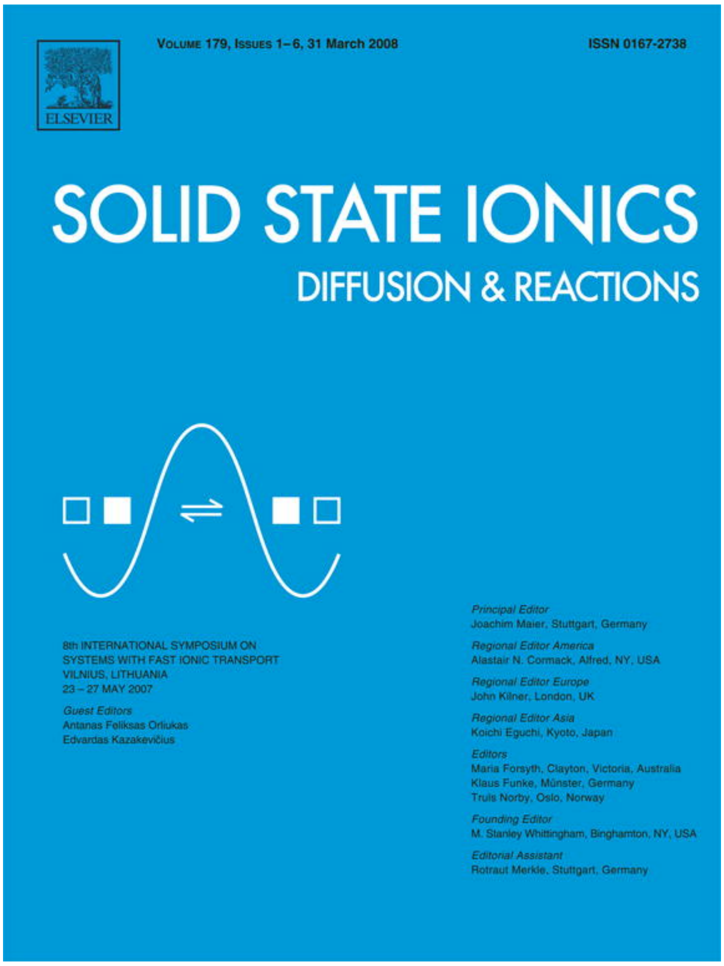

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Diffusion characteristics of particles on energetically disordered lattices

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Abstract

The barrier model with random distribution of barrier energies is considered at nonzero particle concentrations. The statistical mechanics expressions for the jump diffusion coefficient that takes into account interparticle interactions are derived for dynamic and static disorder. For the former case the analytical expression for the barrier energy contribution is calculated, while for the latter case the limiting low and high temperature contributions are obtained. The derived expressions are tested by Monte Carlo simulations for uniform and exponential barrier energy distributions for one- and square, triangular and honeycomb two-dimensional lattices.

Keywords: Disordered barrier lattice gas model; Monte Carlo simulation; Diffusion coefficient; Activation energy; Electric conductivity

1. Introduction

Widely used real materials such as intercalation compounds, solids with fast ionic transport, semiconductors with electron hopping transport etc. require to consider random character of energy landscape where mobile particles move [1–4]. At present, influence of particle concentration, temperature and the type of interparticle interaction on diffusion and electric transport over regular lattices is well known [5–7]. However, random character of energy landscape in real materials brings important peculiarities in migration characteristics of particles. It was experimentally shown that alternative current (ac) conductivity can be scaled on a master plot that is almost independent on the type of material or charge carriers [8–10].

Several models were proposed to understand these peculiarities. Ngai et. al. [11,12] introduced on phenomenological level the coupling model and investigated the problem of near constant loss, Funke and coworkers [3,13,14] suggested more microscopic jump relaxation model and the concept of mismatch and relaxation. In Ref. [15] the completely microscopic model of charged particles on a lattice was simulated and it was shown that the combined effect of disorder of site energies and Coulomb interactions can explain the universal dynamic response of the system, while Dyre and Schrøder [4,16,17] on the basis of percolation arguments has argued that the universality of ac conductivity can be achieved in the extreme disorder limit without interparticle Coulomb interactions to be taken into account. Effective medium approximation was used for investigating the influence of barrier disorder on particle migration characteristics [18,19] as well.

Probably, a variety of different mechanisms can result in scaling behavior of ac conductivity [20,21]. Thus, it is worth to consider the consequences for particle migration characteristics that follow from microscopic models on regular basis. In Refs. [16–19] hopping barrier model was considered in fact at the limit of zero concentration of mobile particles. Thus, important features of the model that are connected with correlated motion of particles and their interactions at non-zero concentration were not investigated. In this paper the direct current characteristics of particles for the barrier model are considered. The model with site energy disorder at low concentrations was considered in Ref. [22], however, the properties of models with barrier and site energy disorder are substantially different.

2. Statistical mechanics of particle migration for random barrier model

A system of particles on a periodic one-, two- or three-dimensional lattice with uniform site energies is considered. Particle jumps to nearest neighbor vacant sites are thermally activated

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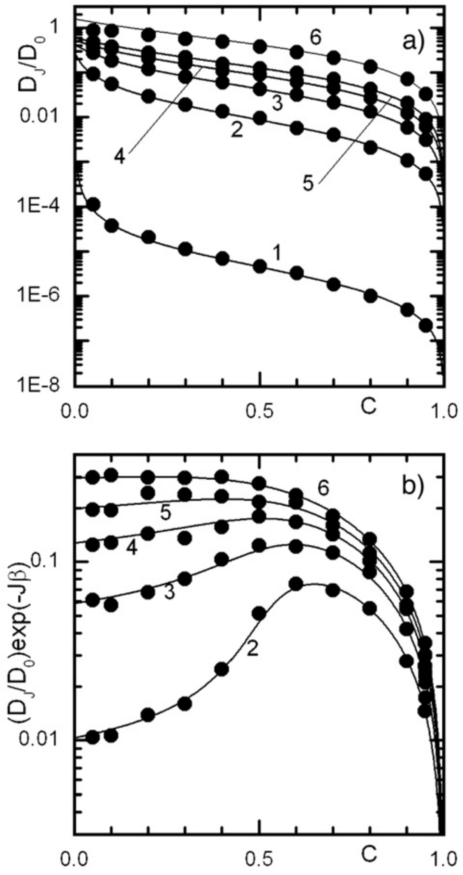

Fig. 1. The jump diffusion coefficient for the lattice gas on dynamically disordered 1d-lattice with the uniform distribution of barrier energies ($\varepsilon_0=|J|/2$) and attractive (a) or repulsive (b) interaction. MC simulation results are shown by circles, the curves represent analytical results [Eqs. (6), (8)], $k_BT/|J|=0.1$ (1); 0.3 (2); 0.5 (3); 0.7 (4); 0.9 (5); 1.2 (6).

with randomly distributed intersite barriers. The jump rate from site j to a vacant nearest neighbor site i is given by the expression

$$w_{ij} = v\exp\left[\beta\left(u_j - \varepsilon_{ij}\right)\right], \quad u_j = u_0 + J\sum_{k(j)} n_k, \tag{1}$$

where v is a frequency factor of the order of vibrational frequency of a particle that determines the time scale of the model, $\beta=1/(k_BT)$ is inverse temperature, k_B is the Boltzmann constant, $u_0<0$, u_j and J are the site energy, the energy of a particle at site j and the nearest neighbor interparticle interaction constant, respectively, $n_k=0$ or 1 is the occupation number of site k (double occupancy of a site is forbidden), summation in Eq. (1) is carried out over nearest neighbor sites of site j, ε_{ij} are energies of randomly distributed barriers between sites i and j. It should be mentioned that although the lattice site energies u_0 are the same for all sites u_j fluctuates due to interparticle interaction. $J>0$ for repulsive and $J<0$ for attractive interactions.

Two barrier energy distributions are considered. The uniform distribution in the range $[0,2\varepsilon_0]$ and the exponential distribution

$$P(\varepsilon) = \varepsilon_0^{-1}\exp(-\varepsilon/\varepsilon_0), \quad \varepsilon \geq 0. \tag{2}$$

The mean value of barrier energies is equal to ε_0 in both cases.

The energetic barriers can be stationary distributed over lattice bonds (static disorder) or the barrier energies are taken from their distribution continuously in time (dynamic disorder).

The general statistical mechanics derivation of the diffusion coefficient was given in Ref. [23]. The result for the collective jump diffusion coefficient takes the form given by Reed and Ehrlich [24]

$$D_j = zwa^2/2\mathrm{d}, \tag{3}$$

where z and a are the coordination number and intersite distance of the lattice, d is the dimensionality of space, and the mean transition rate [23]

$$w = c^{-1}\langle w_{ij}n_j(1-n_i)\rangle, \tag{4}$$

c is a lattice concentration, the angle brackets $\langle\ldots\rangle$ mean equilibrium ensemble averaging.

Thus, the problem of diffusion coefficient calculation is reduced to evaluation of the mean transition rate.

The jump diffusion coefficient is a multiplier at the chemical potential gradient when the Stefan–Maxwell (or Onsager) formulation for the particle flux is used. Alternatively, this coefficient can be calculated through the mean square displacement of the center of mass of particles [25]

$$D_J = \lim_{t\to\infty}\frac{1}{2tnd}\left\langle\left(\sum_{i=1}^{n}\Delta r_i\right)^2\right\rangle, \tag{5}$$

where n is a number of particles, t is time that is usually calculated in Monte Carlo steps (MCS).

Replacement of the chemical potential in the particle flux expression by the electrochemical one shows that the electric conductivity is proportional to the jump diffusion coefficient [26]. Thus, it is sufficient to consider the latter one.

In accordance with Eqs. (1) and (4) it is necessary to average the product of two factors one of which depends on distribution of neighboring particles through the interparticle interaction energy and the other is defined by the barrier distribution. These factors are not independent because the possibility for the particle to jump

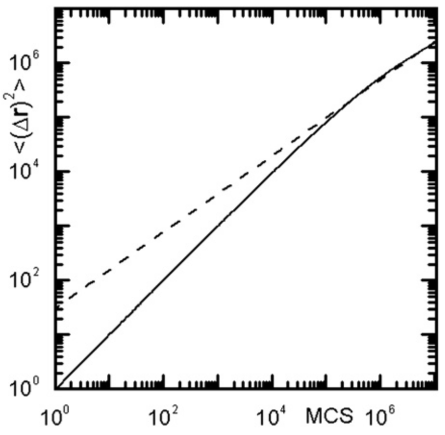

Fig. 2. The TMSD versus time (MC steps) for the Langmuir gas on a regular 1d lattice at $c=0.001$. The dashed line corresponds to the square root subdiffusion regime.

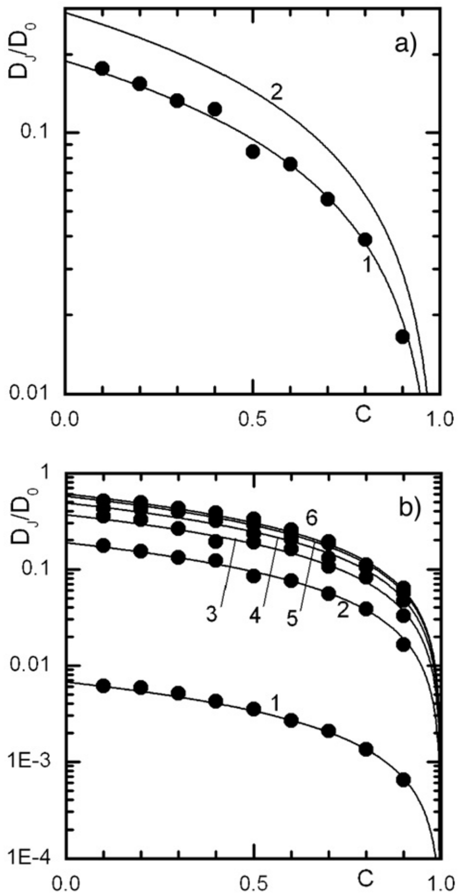

Fig. 3. The jump diffusion coefficient for the Langmuir gas on a square lattice versus concentration at static disorder with the uniform distribution of barrier energies. (a) $k_BT/\varepsilon_0=0.6$. MC simulation results are shown by circles. The solid curves represent analytical results (the lines 1 and 2 correspond to expressions (11) and (8), respectively). (b) $k_BT/\varepsilon_0=0.2$ (1); 0.6 (2); 1.0 (3); 1.4 (4); 1.8 (5); 2.0 (6).

a special arrangement of the neighboring particles is necessary. However, for the barrier model the barrier distribution does not influence the equilibrium distribution of particles over lattice sites because the system energy does not depend on barrier energies. Then in accordance with Ref. [23] after averaging over equilibrium distribution of particles the jump diffusion coefficient takes the form

$$D_J = D_0\langle\exp(-\beta\varepsilon_{ij})\rangle\frac{\exp(\beta\mu)}{c}P(0;0), \quad D_0=\frac{za^2}{2d}\nu\exp(\beta u_0), \tag{6}$$

where μ is the chemical potential, $P(0,0)$ is the probability for two nearest neighbor lattice sites to be vacant. These quantities can be either evaluated in the course of equilibrium Monte Carlo simulations or calculated on the basis of approximate theoretical expressions (see e.g. Ref. [27]). D_0 is the diffusion coefficient of particles in the limit of low concentration on a regular lattice with site energies u_0.

For the lattice gas without lateral interactions ($J=0$, Langmuir gas) $P(0,0)=(1-c)^2$ and the jump diffusion coefficient

$$D_J = D_0\langle\exp(-\beta\varepsilon_{ij})\rangle(1-c). \tag{7}$$

Eqs. (6), (7) show that the concentration dependence of the jump diffusion coefficient can readily be calculated. The main problem concerns with evaluation of the random barrier contribution to the diffusion coefficient because it requires taking into account geometrical structure of the lattice.

At dynamical disorder the sequence of barriers that are overcame by particles corresponds to the distribution of barrier energies and can be easily calculated. For the uniform and exponential distributions it consecutively follows

$$\langle\exp(-\beta\varepsilon_{ij})\rangle = \exp(-\beta\varepsilon_0)\frac{\sinh(\beta\varepsilon_0)}{\beta\varepsilon_0}, \tag{8}$$

$$\langle\exp(-\beta\varepsilon_{ij})\rangle = (1+\beta\varepsilon_0)^{-1}. \tag{9}$$

In the former case at $\beta\varepsilon_0 <\approx 1$ particles overcome the energetic barriers of the order of the mean barrier energy ε_0, while at $\beta\varepsilon_0>1$ the enhancement of diffusion occurs due to that particles prefer to wait lower barriers instead to jump over higher barriers. In the latter case the temperature dependence of the mean transition rate is rather weak because of high density of barriers in the low energy region.

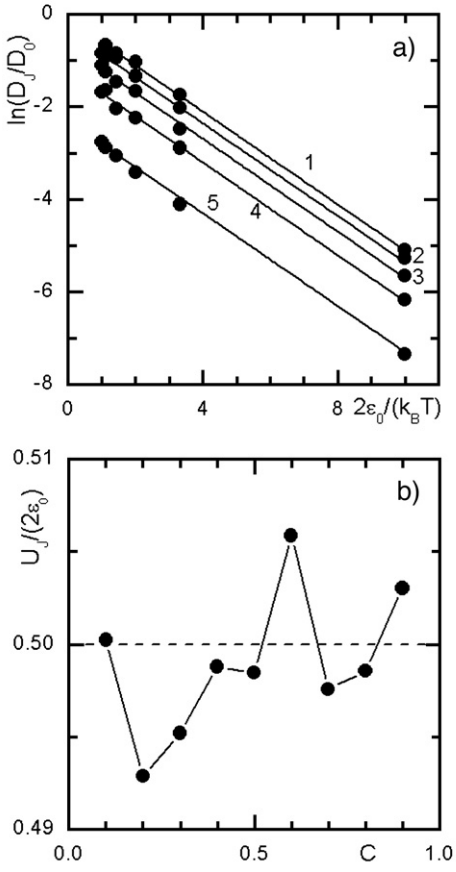

Fig. 4. MC simulation results for the Langmuir gas on a square lattice at static disorder with the uniform distribution of barrier energies. (a) The jump diffusion coefficient versus inverse temperature at $c=0.1$ (1), 0.3 (2), 0.5 (3), 0.7 (4), 0.9 (5). (b) The activation energy for the jump diffusion coefficient versus concentration.

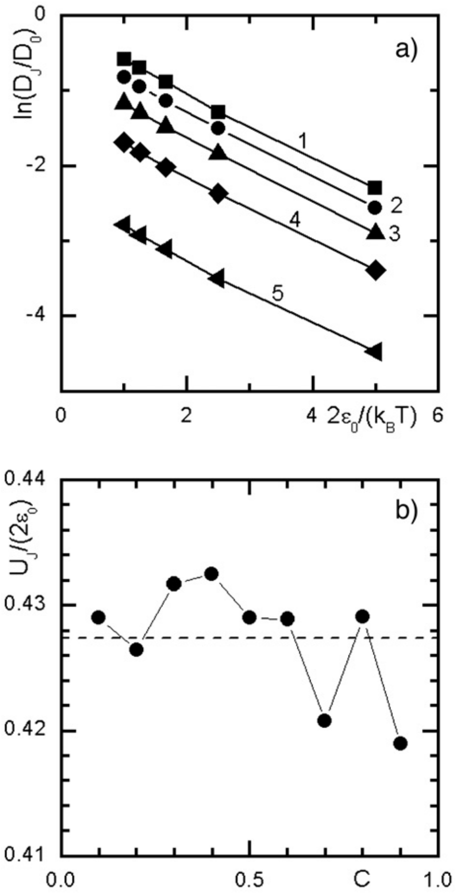

Fig. 5. MC simulation results for the Langmuir gas on a triangular lattice at static disorder with the uniform distribution of barrier energies. (a) The jump diffusion coefficient versus inverse temperature at $c = 0.1$ (1), 0.3 (2), 0.5 (3), 0.7 (4), 0.9 (5). (b) The activation energy for the jump diffusion coefficient versus concentration.

At static disorder it is possible to calculate the limiting values only. In the low temperature limit ($\beta\varepsilon_0$»1, the extreme disorder limit [4,16,17])

$$\langle \exp(-\beta\varepsilon_{ij}) \rangle = c_p \exp(-\beta\varepsilon_p), \tag{10}$$

where c_p and ε_p are the particle concentration and the energy barrier that correspond to the percolation threshold in the problem of bonds. In the high temperature limit ($\beta\varepsilon_0$<≈ 1) Eq. (8) takes the form

$$\langle \exp(-\beta\varepsilon_{ij}) \rangle = \exp(-\beta\varepsilon_0). \tag{11}$$

At intermediate temperatures the interpolation expression

$$\langle \exp(-\beta\varepsilon_{ij}) \rangle = \exp[-\beta(\xi\varepsilon_p + \varsigma\varepsilon_0)], \quad \xi + \varsigma = 1 \tag{12}$$

can be suggested. At low temperature $\xi \approx 1$, at high temperature $\xi \approx 0$. The multiplier c_p in Eq. (10) becomes equal to one at elevated temperature.

3. Analytical and Monte Carlo simulation results and discussion

The standard procedures were used [23] performing Monte Carlo (MC) simulation of particle jumps over lattice sites in accordance with the master equation and the transition rates given by Eq. (1). For static disorder in each simulation run barriers were distributed over bonds between nearest neighbor sites and frozen during the run, while for dynamic disorder the barrier heights were continuously taken from the corresponding distribution for each particle attempting to jump.

In Fig. 1 the simulation and analytical results for the jump diffusion coefficient are represented for dynamically disordered one-dimensional lattice gases with the uniform barrier energy distribution and attractive or repulsive lateral interaction between nearest neighbors at $\varepsilon_0 = |J|/2$. Equilibrium properties of the systems were calculated in the quasichemical approximation that is exact in the one-dimensional case. It is evident that Eqs. (6), (8) exactly reproduce the simulation results. A small scatter of the simulation results can be removed by improving statistics. The increase of the diffusion coefficient in Fig. 1b at intermediate concentrations is explained by repulsive interparticle interactions, while at large concentrations the deficit of vacancies dominates.

The tracer mean square displacement (TMSD) in one-dimensional systems show subdiffusion behavior [28] and in the long time limit it is proportional to square root of time

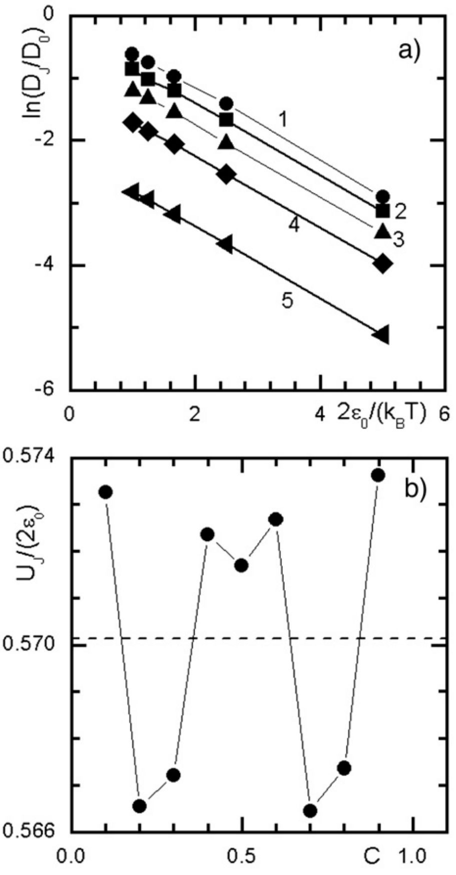

Fig. 6. (a) MC simulation results for the Langmuir gas on a honeycomb lattice at static disorder with the uniform distribution of barrier energies. The jump diffusion coefficient versus inverse temperature: $c = 0.1$ (1), 0.3 (2), 0.5 (3), 0.7 (4), 0.9 (5). (b) The activation energy for the jump diffusion coefficient versus concentration.

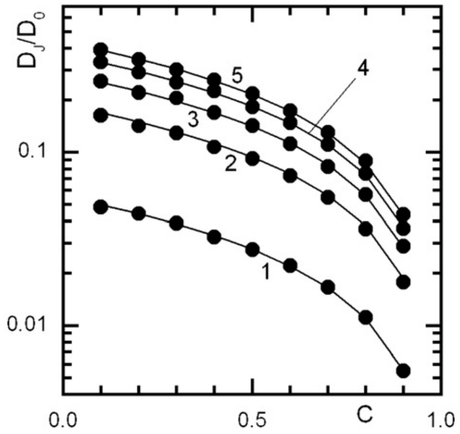

Fig. 7. The jump diffusion coefficient of the Langmuir gas on a triangular lattice at exponential distribution of barrier energies versus concentration at k_BT/ε_0= 0.2 (1); 0.4 (2); 0.6 (3); 0.8 (4); 1.0 (5).

instead to be linear in higher dimensions. However, at very small concentrations the TMSD must be linear in time at not too long times. As the mean interparticle distance is $1/c$ (in units of the lattice parameter) the crossover time from tracer diffusion to subdiffusion regimes should occur at approximately $(1/c)^2$ MC steps. In Ref. [28] this conclusion was made on the basis of more rigorous and considerably more involved calculations. Fig. 2 demonstrates such a behavior of the TMSD at concentration as small as $c=10^{-3}$. Moreover, true linear behavior is observed only at $t<1/c$ because at $c=10^{-3}$ on time segment (0, 10^4 MC steps) the exponent is already equal to 0.94 instead of 1.0 for diffusion behavior.

The plane square lattice is characterized by that the percolation energy and the mean barrier energy at uniform barrier distribution are equal, $\varepsilon_p=\langle\varepsilon_{ij}\rangle=\varepsilon_0$ and then Eq. (11) due to Eq. (12) holds at arbitrary temperature. Indeed, Fig. 3 demonstrates that Eqs. (7), (11) well represent the simulation data at all temperatures considered. At low temperature (Fig. 3a) Eq. (8) overestimates the transition rates. Fig. 4 proves that the jump diffusion coefficient obeys Arrhenius behavior with activation energy $U_J=\varepsilon_p=\varepsilon_0$ at arbitrary concentration. The scatter of the simulation data is around one per cent due to restricted statistics.

For the triangular ($\varepsilon_p=0.343\varepsilon_0$) and honeycomb ($\varepsilon_p=0.657\varepsilon_0$) lattices the percolation energy is not equal to the mean barrier energy. However, in the temperature range considered ($T=0.4\ldots2.0\varepsilon_0/k_B$) it was found that $\xi\cong\zeta\cong0.5$ (Figs. 5 and 6) and the deviation of the simulation data from the theoretical value $U_J=0.5(\varepsilon_p+\varepsilon_0)$ is around of one per cent for both lattices.

For the exponential barrier energy distribution Eq. (9) shows no Arrhenius type contribution to the mean transition rate. Thus, for the Langmuir gas the jump diffusion coefficient does not show Arrhenius temperature dependence as well and when it is approximated by Eq. (7) with activation type dependence on temperature the activation energy strongly depends on temperature changing from $0.58\varepsilon_0$ at $T=0.2\varepsilon_0/k_B$ to $0.84\varepsilon_0$ at $T=1.0\varepsilon_0/k_B$ while the concentration dependence is well reproduced by Eq. (7) (Fig. 7).

4. Conclusion

The comparison of analytical and simulation results shows that the low temperature percolation path approximation [4,16,17] remains valid for non-zero particle concentrations and probably for interacting particles as well. For the Langmuir lattice gas the influence of concentration results in the multiplier $(1-c)$, for interacting particles additional contributions can be estimated from equilibrium statistics of the system on regular lattices. For intermediate temperatures interpolation coefficients have to be calculated.

References

[1] J. Haus, K.W. Kehr, Phys. Pep. 150 (1987) 263.
[2] S. Havlin, D. Ben Avraham, Adv. Phys. 36 (1987) 695.
[3] K. Funke, Prog. Solid State Chem. 22 (1993) 111.
[4] J.C. Dyre, T.B. Schrøder, Rev. Mod. Phys. 72 (2000) 873.
[5] C. Uebing, R. Gomer, J. Chem. Phys. 95 (1991) 7626 (7636, 7641, 7648).
[6] A. Danani, R. Ferrando, E. Scalas, M. Torry, Int. J. Mod. Phys. B11 (1997) 2217.
[7] Ya.G. Groda, P. Argyrakis, G.S. Bokun, V.S. Vikhrenko, Eur. Phys. J. B32 (2003) 527.
[8] J.O. Isard, J. Non-Cryst. Solids 4 (1970) 357.
[9] R.A. Roling, B.A. Happe, K. Funke, M.D. Ingram, Phys. Rev. Lett. 78 (1997) 2160.
[10] D.L. Sidebottom, Phys. Rev. Lett. 82 (1999) 3653.
[11] K.L. Ngai, Comments Solid State Phys. 9 (1979) 127.
[12] K.L. Ngai, R.W. Rendell, C. Leon, J. Non-Cryst. Solids 307–310 (2002) 1039.
[13] K. Funke, D. Wilmer, Solid State Ionics 136–137 (2000) 1329.
[14] K. Funke, R.D. Banhatti, S. Brükner, C. Cramer, C. Krieger, A. Mandanici, C. Martiny, I. Ross, PCCP 4 (2002) 3155.
[15] P. Maass, J. Petersen, A. Bunde, W. Dieterich, H.E. Roman, Phys. Rev. Lett. 66 (1991) 52.
[16] J.C. Dyre, T.B. Schrøder, Phys. Rev. B54 (1996) 14884.
[17] J.C. Dyre, T.B. Schrøder, PCCP 4 (2002) 3173.
[18] J.C. Dyre, Phys. Rev. B49 (1994) 11709.
[19] A. Hörner, A. Milchev, P. Argyrakis, Phys. Rev. E52 (1995) 3570.
[20] K. Funke, R.D. Banhatti, S. Brükner, C. Cramer, PCCP 6 (2004) 157.
[21] J.R. Dygas, Solid State Ionics 176 (2005) 2065.
[22] M. Porto, P. Maass, M. Meyer, A. Bunde, W. Dieterich, Phys. Rev. B61 (2000) 6057.
[23] G.S. Bokun, Ya.G. Groda, C. Uebing, V.S. Vikhrenko, Physica A296 (2001) 83.
[24] D.A. Reed, G. Ehrlich, Surf. Sci. 102 (1981) 588 (105 (1981) 603).
[25] R. Gomer, Rep. Prog. Phys. 53 (1990) 917.
[26] G.S. Bokun, Ya.G. Groda, C. Uebing, V.S. Vikhrenko, Tech. Phys. 45 (2001) 1375.
[27] V.S. Vikhrenko, Ya.G. Groda, G.S. Bokun, Phys. Lett. 286 (2001) 127.
[28] R. Kutner, H. Van Beijeren, K.W. Kher, Phys. Rev. B30 (1984) 4382.