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Role of energetic disorder on diffusion in one-dimensional systems

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Abstract. The simulation of dynamical process of target particles in one-dimensional lattice is carried out for two types of energetic disorders. The particles are non-interacting except that the double occupancy is forbidden. It is found that the diffusion quantities such as the correlation factor and averaged time between two subsequent jumps are quite different for the lattices of site and transition disorders. However, the diffusion constant of both lattices is close to each other. Closed value of diffusion constant is obtained for the lattice with random distributed barriers. At the wide temperature range the diffusivity follows the Arrhenius law. The blocking effect decreases the correlation factor and activation energy. These two opposite factors lead to appearance of insignificant maximum in the dependence of diffusion constant on concentration of target particles.

Keywords: diffusion, amorphous solid, disordered one-dimension, simulation, blocking effect.

1. Introduction

Migration of particles (atom, molecular and ion) in disordered media is a rather general phenomenon and a list of problems and applications can be found [1-6]. To name, but only a few: the diffusion and conductivity of amorphous alloy, glass, polymer and thin solid film related to the subject. In particular the concentration dependence of diffusion quantities is observed for certain disordered media. For example, the activation energy and diffusion constant for hydrogen in $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ metallic glass noticeably change in the intermediate concentration regime $0.2<H/M<0.9$ [3]. Here H/M is hydrogen-to-metal ratio. In the low concentration regime $H/M<0.2$ insignificant maximum appears on the dependence of diffusion constant on H/M concentration. Besides the hydrogen diffusivity follows the classical over-barrier-hopping mechanism. Authors in ref.[3] interpret this observation by blocking effect and the increasing nearest neighboring distance between metal atoms. However, there is very simple estimation of the contribution of energetic disorder to the dynamic of system and it is not clear how the blocking effect affects on the activation energy and diffusion constant. Moreover, we found only few simulation works on this subject [7-9].

Various theoretical approaches have been applied to study diffusion in disordered media from analytic method based on effective medium theory, master, Fokker-Planck, or Kramers equations to

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simulation techniques based on the molecular dynamic and Monte-Carlo (MC) method [10-13]. The later provides more detail information about specific features as well as the diffusion mechanism of disordered system. It was revealed that the energetic disorder is most important factor affected on the dynamic of the system. Consequently, it is convenient to employ a disordered lattice [8,14-17] where the sites are arranged into regular lattice, but transition and site energies vary from site to site. The basic models studied in this context fall into two classes that of randomly distributed transition and site energies or that of randomly distributed barriers. Obviously, the former represents more general case due to that two nearest neighboring sites have common transition energy. A number of simulations has been done in this direction [7, 18-20] and reveals two specific properties characterized the diffusion in disordered lattice. First one is that the averaged square displacement of target particle is less than one in the case of its migration in ordered lattice by the same number of jumps. Secondary, the averaged duration between two subsequent jumps along diffusion path is significantly less than averaged resident time of particle at a site [18, 19]. Such, the diffusion behavior is well established for migration of single particle in disordered lattice, but the study to the case when many particles hop through disordered lattice is still little. Therefore, the present work is devoted to the study of blocking effect based on MC simulation. Because of the blocking effect concerns mainly the prevention of random movement of particles through sites, hence to simplify, we ignore the particle-particle interacting, e.g. consider only the system with non-interacting particles. The relevant data will be analyzed in accordance with both aspects: the energetic disorder and the blocking effect.

2. Calculation method

The simulation is carried out for a chain consisting of 2000 or 3000 sites with periodic boundary conditions. Several runs have been done for system of 3000 particles in order to test the accuracy of the simulation on a chain with 2000 sites. The energy is assigned to each site in a random way from given distribution. We consider two types of energetic distributions: the uniform distribution in the range from ε_1 to ε_2 ($\varepsilon_1 < \varepsilon_2$) and two-level distribution where the energy for each site is equal to ε_1 or ε_2. The same procedure is used for transition energy between two nearest neighboring sites. In this way the disorder produces only in site and transition energies, but the jump distance and the number of nearest neighboring sites are kept constant. The probability of particle's jump from *ith* to *i+1th* site and the averaged resident time of particle at *ith* site is given as

$$p_{i,i+1} = \frac{\exp(-\varepsilon_{i,i+1}\beta)}{\exp(-\varepsilon_{i,i+1}\beta) + \exp(-\varepsilon_{i,i-1}\beta)} \quad (1)$$

$$\tau_i = \frac{2\tau_0 \exp(-\varepsilon_i\beta)}{\exp(-\varepsilon_{i,i+1}\beta) + \exp(-\varepsilon_{i,i-1}\beta)} \quad (2)$$

Where ε_i and $\varepsilon_{i,i+1}$ are the site and transition energies; τ_0 is frequency period. $\beta = 1/kT$; k is Boltzmann constant and T is temperature.

Consider the diffusion time t_n during n jumps of single particle in a disordered lattice. If n is enough large then the resident time of particle at *ith* site can be approximated by

$$t_i = t_n \frac{\exp(-\varepsilon_i \beta)}{\sum_j^M \exp(-\varepsilon_j \beta)} \tag{3}$$

Here M is number of sites in the system. The number of visiting times of particle for *ith* site is written as

$$n_i = \frac{t_i}{\tau_i} = t_n \frac{\exp(-\varepsilon_{i,i+1}\beta) + \exp(-\varepsilon_{i,i-1}\beta)}{2\tau_0 \sum_j^M \exp(-\varepsilon_j \beta)} \tag{4}$$

The averaged time between two subsequent jumps in this context can be written as

$$\tau_{jump} = \frac{t_n}{\sum_i^M n_i} = \frac{2\tau_0 \sum_j^M \exp(-\varepsilon_j \beta)}{\sum_j^M \exp(-\varepsilon_{i,i+1}\beta) + \exp(-\varepsilon_{i,i-1}\beta)} \tag{5}$$

After the construction of the lattice described before the sites are filled with a number of particles N by randomly choosing their coordinate and by avoiding double occupancy. The number N is set to 1, 20, 40, 80 and 120 which corresponds to the concentration of $5\text{x}10^{-4}$, 0.01, 0.02, 0.04 and 0.06 particles per site. The jump which carries the particle out of site i represents the Poisson process with decay time τ_i. The actual duration of the residence on the current site is given as $-\tau_i \ln R$. Here R is random number in the interval [0,1]. In order to select the particle to jump we determine a list of points (LSP) t_1, t_2.. t_N; here t_i is that point when the jump of *ith* particle occurs, and i = 1, 2, .. N. Let t_{iprev} is moment that *ith* particle jumps at previous step. The point for its next jump is given as

$$t_i = t_{iprev} - \tau_i \ln R \tag{6}$$

From the LSP we select the particle j that has minimum t_j and then move it into neighboring site if this site is empty. Otherwise it remains on the current site. The neighboring site is randomly chosen based on the probability $P_{j,j+1}$, $P_{j,j-1}$ and random number R. Once the event of jump of *jth* particle is happen, the time t_j in the LSP is recalculated using equation (6) and such the diffusion process of target particles is simulated. The total duration after n jumps of *ith* particle can be written as

$$t_{ni} = \sum_{j=1}^{n} t_{ij} \tag{7}$$

In order to improve the statistic we perform 10^6 MC runs for each system with given temperature T_s and number of particles N. For every run the number of jumps per particle is set to about 200-250. The mean square displacement $\langle x_n^2 \rangle$ and diffusion time $\langle t_n \rangle$ is obtained by averaging over 10^6 MC runs. Because of that both site and transition disorders affect on the diffusion and may have very different properties, so we consider two systems with different type of disorder, namely the system that has a random distribution of transition energies and constant site energies (lattice A) and another one with random site energies and constant transition energies (lattice B). The input data is set to ε_2=1, ε_1=0 for lattice A and ε_2=0, ε_1=-1 for the lattice B. This input data provides that both lattices have the same barrier distribution. To account the influence of barrier correlation we also consider lattice of type C that every site is assigned to two barriers of which the value is uniformly distributed in the interval [0, 1], e.g. It has the same barrier distribution as the lattice A and B, but there is not barrier correlations in the lattice C (randomly distributed barriers, see Fig.1).

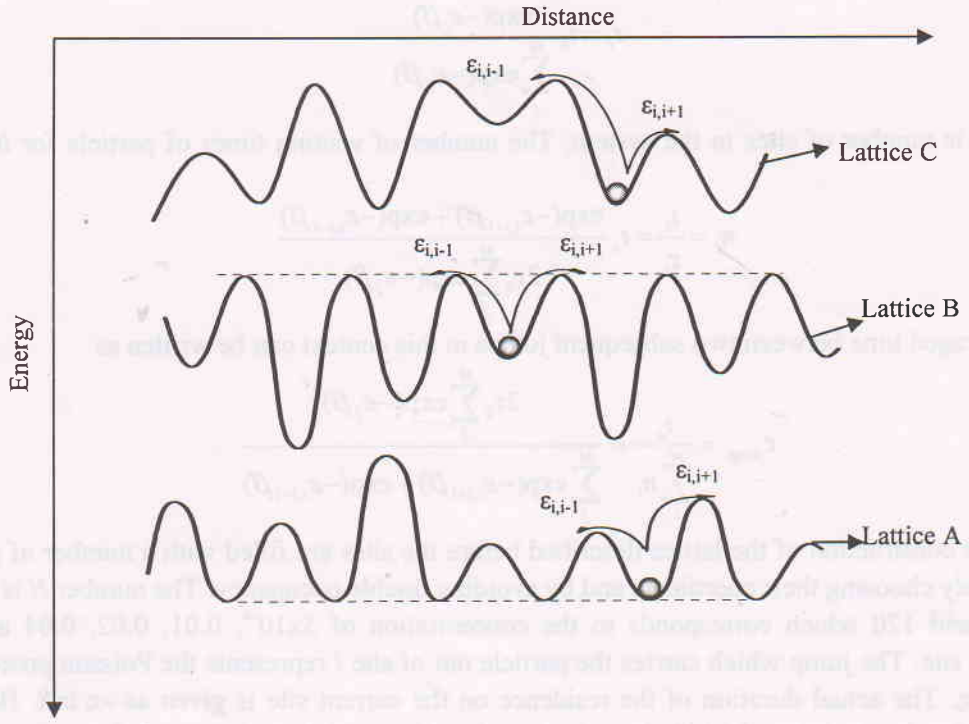

Fig. 1. The variation of energy of particle in lattice A , B and C.

3. Results and discussion

Besides the diffusion constant D two other quantities used here are the correlation factor F and the averaged time between two subsequent jumps of particle along diffusion path t_{jump}. In the case of diffusion of single particle in ordered lattice, e.g. the site and transition energies are kept constant (they are equal to ε_1 or ε_2), the correlation factor F is equal to 1 and the time t_{jump} approaches to mean resident time at a site. In each simulation run the time t_{jump} is determined as $t_{jump}=<t_n/n>$. A typical result for mean square displacement $<x_n^2>$ is shown in Fig.2. Here a is the spacing between two nearest neighboring sites; n is averaged number of jumps per particle; $T_s=(\varepsilon_2-\varepsilon_1)\beta$. For convenient of discussion we employ the parameter t_n^* which is the diffusion time for ordered lattice. Hereafter, the parameters employed with superscript * related to ordered lattice. The data points clearly fall on the straight lines with slope determining the diffusion coefficient D and correlation factor F by following formula

$$< x_n^2 >= Fna^2 \qquad < x_n^2 >= 2Dt_n \tag{8}$$

Fig.3 represents the temperature dependence of correlation factor and averaged time between two subsequent jumps. In the case of transition disorder (lattice A) the factor F monotony decreases with temperature; meanwhile for the site disorder (lattice B) the factor F conversely is almost independent

on temperature. The existence of many particles reflected on the decrease of factor F due to that the number of unsuccessful jumps (blocking effect) increases with number of particles. Regarding the time t_{jump} one can see its value for lattice B is rather bigger than one for lattice A. This effect is essential at low temperature (see Fig.2). It is interesting to note that the time t_{jump} obtained from simulation is very close to τ_{jump} defined by simple formula (5).

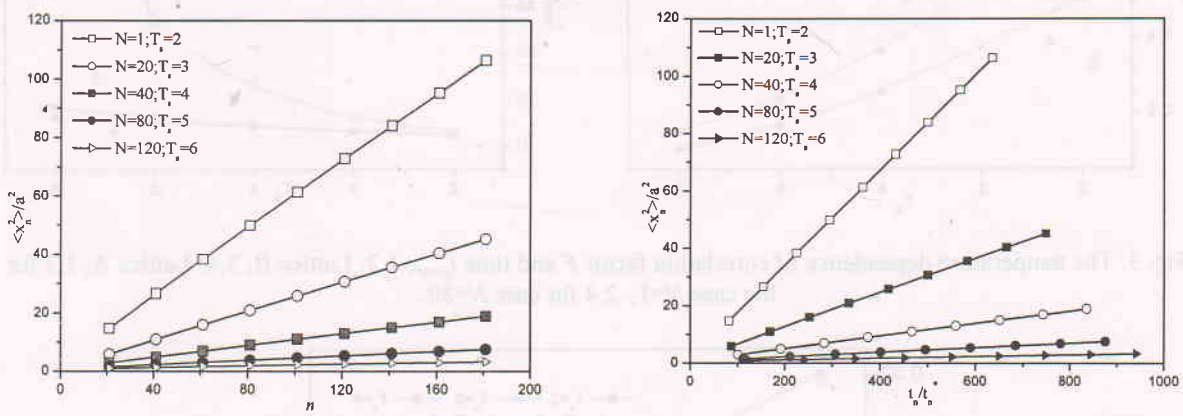

Fig. 2. The mean square displacement for diffusion on the lattice A.

Table 1. The diffusion parameters of lattice A, B and C for energetic uniform distribution and at T_S=3

Number of particles	F			t_{jump}/t_{jump}^*			D/D^*		
	A	B	C	A	B	C	A	B	C
1	0.54	1.00	0.54	3.31	6.26	4.50	0.17	0.16	0.12
40	0.44	0.80	0.47	3.15	6.03	4.26	0.14	0.13	0.11
80	0.38	0.65	0.43	3.15	6.02	4.25	0.12	0.11	0.10
120	0.32	0.53	0.39	3.15	6.01	4.25	0.10	0.09	0.09

As mentioned above, the existence of many particles prevents random movement of particles and gives rise to the decrease of correlation factor F and time t_{jump}. The compensation between F and t_{jump} leads to slight change in diffusion constant D. As shown in Fig.4, the ratio D_{120}/D_1 varies in the interval of 0.54-0.61 depending on temperature. Here D_1, D_{120} correspond to diffusion constant for the case of N=1 and N=120 respectively. It is noticeably that the diffusion constant D for both lattice A and B are close to each other (see Fig.4). The lattice A differ from lattice B in that two nearest neighboring sites in lattice A have the same barrier, meanwhile each site in lattice B attains two identical barriers. It means that for both lattices there are some correlations between barriers in the system. Lattice C has the same barrier distribution as lattice A and B, but no any correlation between the barriers in it. The diffusion parameters of three lattices are listed in Table 1.

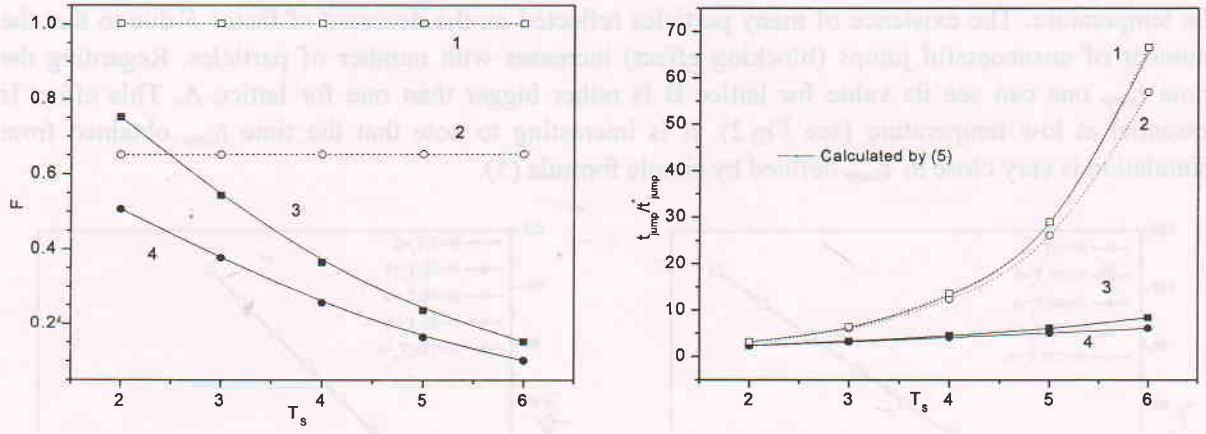

Fig. 3. The temperature dependence of correlation factor F and time t_{jump}; 1,2: Lattice B; 3,4: Lattice A; 1,3 for the case N=1; 2,4 for case N=80.

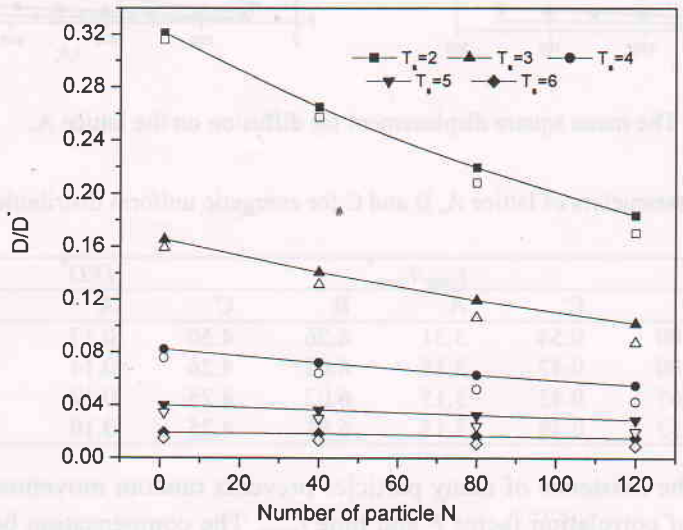

Fig.4 The dependence of diffusion coefficient D on number of particles N for system with energetic uniform distribution; the filled and unfilled symbols represent the case of Lattice A and B, respectively.

We can see that the correlation factor and averaged time between two subsequent jumps varies from one type lattice to another, but their diffusion constants are close to each other. Therefore, the diffusion constant weakly depends on the correlation between the barriers in the system. The diffusion constant D for the lattice B can be approximated by simple formula

$$D = D^* \frac{\eta}{\tau_{jump}} \tag{9}$$

Where η is coefficient in the interval of 0.54-0.61 which characterized the blocking effect. Because of the diffusion constants of three types lattices have a closed value; hence the formula (9) can be applied to estimate quantity D of lattice A as well as lattice C.

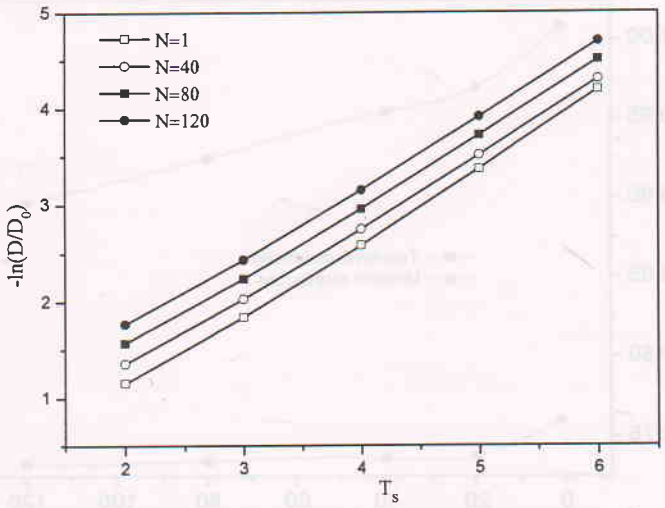

Fig. 5. The Arrhenius plot for diffusion on the lattice A.

Fig.5 shows the Arrhenius plot for the case of transition disorder. The data points fall well on the straight lines and clearly indicates the absence of the compensation effect between site and transition disorders reported in ref.[21]. The reason may be related to three-dimensional lattice used in ref.[21]. Whereby, non-Arrhenius behavior observed for diffusion in some amorphous alloys may be caused by the change in disordered media with temperature, but not due to blocking effect or energetic disorder. This was mentioned in the ref. [22] as the change in short-range order with increasing temperature.

From the Fig.4 the diffusion constant can be derived by

$$D = D_0^* \exp\left(-E^* \beta\right) d \exp\left(-c(\varepsilon_2 - \varepsilon_1)\beta\right) \tag{10}$$

Here the term $d\exp(-c(\varepsilon_2-\varepsilon_1)\beta)$ concern the contribution of energetic disorder. The parameter d is listed in Table 2 and the variation of parameter c as function of N is shown in Fig.6, where the concentration of low level ε_1 is equal to 0.2 for two-level distribution. As shown from Table 2, parameter d may be less or bigger than 1.0 depending on the concentration of particle. It means that the energetic disorder gives rise to increases the pre-exponential factor at the low concentration and to decreases it in high concentration regime. The parameter c in another way varies with the number of particle N. It is monotony decreased as the number of particle enhances due to that all highest barriers are blocked by some particles and other ones have to move along the path with less high barriers. Therefore, the increase of activation energy reported in ref.[3] obviously relates to the change in the disordered media (density, local microstructure, coordination number..), but not due to blocking effect.

Table 2. The parameter d for transition disorder lattice

	d				
	N=1	N=20	N=40	N=80	N=120
Uniform distribution	1.52	1.31	1.17	0.94	0.77
Two-level distribution, α=0.2	1.27	1.08	0.97	0.78	0.64

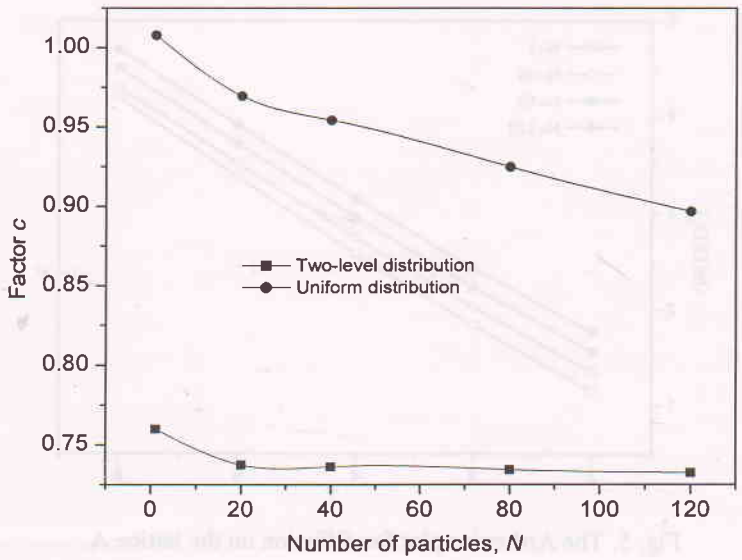

Fig. 6. The dependence of factor c on number of particles N.

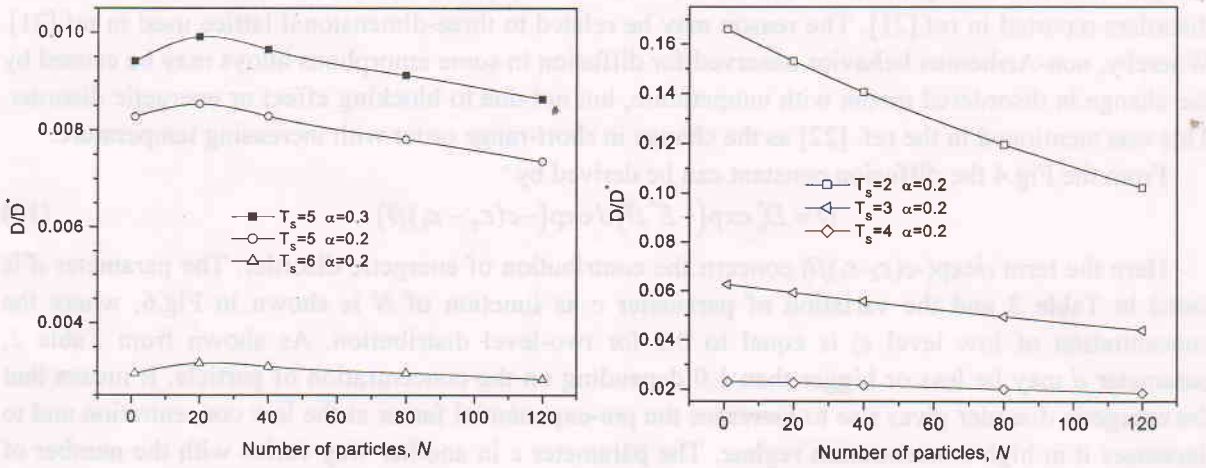

Fig. 7. The dependence of diffusion coefficient D on number of particles N for system of two-level distribution.

Fig.7 shows the variation of diffusion coefficient in the case of two-level distribution as a function of number of particles. Here α is the concentration of low level energy. At high temperature regime the diffusion constant monotony decreases with number of particles, but at low temperature regime there is an insignificant maximum near N=20. It can be interpreted by that the blocking effect leads to two opposite factor. First one decreases the time t_{jump}, e.g. to increases the diffusion coefficient. Second factor decreases correlation factor F which decreases diffusivity. Therefore, due to the action of these factors, at low temperature and in the low concentration regime we observe an insignificant maximum. The relative independence of diffusion constant on the concentration is caused by compensation of two factors just mentioned. As such, the experimental data reported in [1, 3, 23] may be interpreted as result of blocking effect.

4. Conclusions

MC simulation shows that the site and transition disorder lattices attain a quite different value of the correlation factor F and the averaged time between two subsequent jumps t_{jump}. In the case of transition disorder the correlation factor F is monotony decreased with temperature. Meanwhile, in converse the factor F is independent of temperature for lattice with site disorder. Regarding the diffusion time t_{jump} its value of site disorder lattice is significantly larger than one of transition type. However, the diffusion constant of both type lattices is very close to each other upon identical temperature and energetic distribution form. Closed value of diffusion constant is obtained for the lattice with random distributed barriers. This evidences the weak influence of barrier correlation on the diffusion constant. For one-dimensional lattice the diffusion constant can be satisfactory approximated by simple formula derived from site disorder lattice. In the wide temperature range we observe the Arrhenius behavior of diffusion on all considered lattices. The contribution of energetic disorder to pre-exponential factor D_0 is varied by factor d larger or less than 1.0 depending on the concentration of diffusing particles. The blocking effect caused by unsuccessful jumps of diffusing particles decreases the activation energy and correlation factor F. These two opposite factors lead to appearance of an insignificant maximum in the dependence of diffusion constant on the concentration.

Reference

[1] Y. Sakamoto, K. Baba, W. Kurahashi, K. Takao, S. Takayama, *J.non-cryst. solids*, 61&62 (1984) 691.
[2] Y.S. Su, S.T. Pantelides, *Phys. Rev. Lett.* 86 (16) (2002)165503.
[3] T. Apih, M. Bobnar, J. Dolinsek, L. Jastrow, D. Zander, U. Koster, *Solid State Comm.* 134 (2005) 337.
[4] V.V. Kondratyev, A.V. Gapontsev, A.N. Voloshinskii, A.G. Obukhov, N.I.Timofeyev, *Int. J. Hydrogen Energy* 24 (1999) 819.
[5] S. Havlin, D. Ben Avraham, *Adv.Phys.* 36 (1987) 695.
[6] N. Eliaz, D. Fuks, D. Eliezer, *Materials Letters* 39 (1999) 255.
[7] P. Argyrakis, E. Arapaki, S.V. Dubinin, Y.G. Groda, V.S. Vikhrenko, *Solid State Ionics* 179 (2008) 143.
[8] S.H. Payne, H.J. Kreuzer, *Phys.Rev.* B 75 (2007) 115403.
[9] Hen van Beijeren, K.W. Kehr. R. Kutner, *Phys. Rev.* B 28 (10) (1983) 5711.
[10] J.W. Haus, K.W. Kehr, *Phys. Rep.* 150 (1987) 263.
[11] Li shi Luo, George D.J. Philies, *Phys. Rev.* E 51 (1) (1995) 43.
[12] Panos Argyrakis, Andrey Milchev, Victor Pereyra, Klaus W. Kehr, *Phys. Rev.* E 52 (4) (1995) 3623.
[13] R. Kirchheim, U. Stolz, *Acta Metal* 35 (2) (1987) 281.
[14] A. Tarasenko, L. Jastrabik, *Applied Surface Science* 256 (2010) 5137.
[15] D.A. Laurens, Siebbeles, Yuri A. Berlin, *Chem. Phys. Lett.* 265 (1997)460.
[16] A. Tarasenko, L. Jastrabik, T. Muller, *Phys. Rev.* B 75 (2007) 085401.
[17] A. Tarasenko, L. Jastrabik, T. Muller, *Phys. Rev.* B 76 (2007) 134201.
[18] P.K. Hung, T.V. Mung, L.T. Vinh, *Phys. Lett.* A 373 (2009) 2077.
[19] D.K. Belashchenco, P.K. Hung, Izv. Akad. Nauk. SSSR, *Metally* 2 (1986) 57.
[20] Y. Limoge, J.L. Bocquet, *Acta Metal* 36 (1988) 1717.
[21] Y. Limoge, J.L. Bocquet, *Phys.Rev.Lett.* 65 (1) (1990) 60.
[22] N. Eliaz, D. Fuks, D. Eliezer, *Materials Letters* 39 (1999) 255.
[23] Y.S. Lee, D.A. Stevenson, *J. non-crysl. Solids* 72 (1985) 249.