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Effect of the transition of networks from floppy to rigid on the diffusion coefficient

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We investigate a tracer particle moving on a two-dimensional square lattice created by network formers (NF). The positions of all network formers are randomly displaced by a small amount from the nodes of the network. Each NF can be in a "floppy" or "rigid" state, depending on the number of bonds connecting it to neighboring network formers. The NF that have more than a specified number of m bonds are in rigid state, the remaining ones are in a floppy state. The energy of the tracer particle depends on its distance from those of the four nearest NF that are in "rigid" state. The NF in floppy state do not contribute to the energy. We here demonstrate that the *a priori* increase in the diffusion coefficient with the concentration of the floppy states goes through a crossover point, after which the increase is much sharper.

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I. INTRODUCTION

For multicomponent systems, the chemical composition and hence the structure of the ambient melt is very important for the formation of nanocrystals. This is true, especially if the melt has a composition that is different from that of the newly formed crystals. In highly viscous melts, under conditions near the glass transition temperatures, this leads to the formation of diffusion layers (diffusion of stress deformation energy, as well as diffusion of chemical components).

Recently, a new approach was suggested: this is a combination of percolation theory and the classical nucleation theory [1–4]. This model directly follows from the constraint counting concepts of Phillips [5,6] and Thorpe [7–9]. It was shown in [7–9] that the network becomes rigid if the mean coordination of network formers, $\langle r\rangle$ exceeds a critical value $r_c \geq 2.4$. The exact threshold conditions for the rigid/floppy transition depend on the dimensionality of the space and on the coordination number, and they are summarized in [10].

The main idea of the present report is to simulate diffusion on a multicomponent system. We investigate diffusion of relatively fast moving ions. The network formers are impeding the motion. If a neighboring network former is strongly bonded, it is an obstacle increasing the energy of the investigated tracer. If some of the bonds are "broken," i.e., the number of bonds of the given network former is low enough, it is in a "floppy" state and can retaliate permitting the tracer to move without increasing its energy. Thus, the diffusion coefficient D is expected to depend on the concentration of ion modifiers. We expect a breakpoint concentration, above which the diffusion coefficient will increase sharply with the number of broken bonds.

II. MODEL DESCRIPTION

In the current investigation we consider a tracer particle moving on a two-dimensional (2D) square lattice, which consists of network formers (NF) connected by bonds. In order to move, the tracer has to find open space at the new position. Therefore, if the concentration of the NF is large, this may impede the tracer movement. The bonds of each NF determine how flexible it is in order to yield space for the tracer. The comparison of the tracer energy at the new and old positions determines the probability of each successive jump. If during an attempted move the energy increases, it is more favorable for the particle to remain at its current position, so then the Metropolis algorithm is invoked to decide whether the particle will move or not. If a fraction of the bonds is removed, some of the NF could become more flexible and the new positions of the tracer are easier accepted, resulting in an increase of the mobility. In real systems this is obtained by introducing network modifiers in the lattice. They break the bonds that connect the network formers. As the concentration of the NM increases, it follows that fewer bonds are present in the network and the tracer can move easier through it. The removal of the bonds has a drastic effect on the nature of the network transforming it from rigid to floppy. Therefore, it is anticipated that the diffusion coefficient will be affected by the network transition. In fact, although the increase of the diffusion coefficient could be postulated *a priori*, the exact mode of increase and the presence of a crossover could not have been easily assumed.

Calculations are performed on 2D square lattices, on which the tracer particle moves. The network formers, which are linked with bonds, are initially placed on the sites of the lattice. The network is randomized in two ways. First, at time $t=0$ we introduce a small random perturbation on all NF, so that each one of them is displaced to a new position at a small distance away from the previous one. The orientation is chosen by a random angle $0° \leq \theta \leq 360°$. The distance of the displacement is also chosen randomly, but it is the interval between 0% and 10% of the lattice constant. In this way all particles still remain further apart from each other. We

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consider that the bonds between the network formers remain unchanged. Second, at $t=0$, the network modifiers are introduced to the lattice, breaking a fraction of the bonds. The network modifiers affect in a straightforward manner the concentration of the bonds and, therefore, we consider a removal probability, f, according to which we can estimate the number of the broken bonds, at the beginning of the simulation. If for example, $f=0.4$, this means that 40% of the initial bonds will be removed. As f increases, the lattice transforms from rigid to floppy, and we expect this phenomenon to have a serious effect on the tracer motion. The tracer particle will move through the disordered lattice. We study the dependence of the diffusion coefficient on f. At $t=0$, the tracer particle is placed at a random position on the lattice. Its motion will be regulated by the Metropolis algorithm. At every time step we calculate the energy of the tracer, whose value is defined by the distances R_i to its closest four network formers. At each time step we determine its four closest neighbors and we count the number of the missing bonds each one of these neighbors has. We introduce a dimensionless parameter $0 \leq m \leq 4$, and we compare the number of bonds that a neighboring network former has to the value of m. If this number is equal or greater to m, then the corresponding NF is "rigid" and does not contribute to the energy of the tracer. If the number of bonds is smaller than m, then it is "floppy" and will contribute to the energy by a factor of $1/R$. Here R is defined as the distance between the tracer and the corresponding NF. The tracer particle is not allowed to move to a position occupied by a NF and therefore R cannot be equal to 0. The total energy E_1 of the tracer particle at its current position is defined as a sum of the energy contributions of those of the four neighbors that have at least m bonds. Once E_1 is determined, then the particle moves to a distance equal exactly to one (1) lattice constant and with an orientation randomly chosen, as previously discussed. We then calculate the energy E_2 at the new position, using the same procedure as for E_1. In order to check if the tracer will move, we implement the Metropolis algorithm. We keep track of the tracer position at every time step and determine the mean square displacement. This algorithm is a computer simulation that resembles the shoving model [11].

Earlier [12–15] we had performed Monte Carlo simulations of diffusion in terms of the activation energy. The present approach is quite different from the activation energy models, and rather supplementary to them. This methodology of accepting or rejecting the new position is the basic method to describe crystallization kinetics (see for instance [16] and the literature cited there), where in addition to the activation energy term (viscosity there) an additional term is present accounting whether the step is accepted or rejected, and this determines the mechanism of phase transition kinetics.

III. RESULTS

Calculations are performed on a 2D square lattice of size 1000×1000 for 1000 realizations. The time dependence of the mean square displacement $\langle R^2 \rangle$, for several f values and for $m=2$, is shown in Fig. 1. As f changes within the range $0 \leq f \leq 1$, the network transposes from rigid to floppy, and the slope of the mean square displacement lines increases. In fact, for $f=0$, all bonds are present in the lattice and for $f=1$, there is none, and the tracer executes a simple random walk.

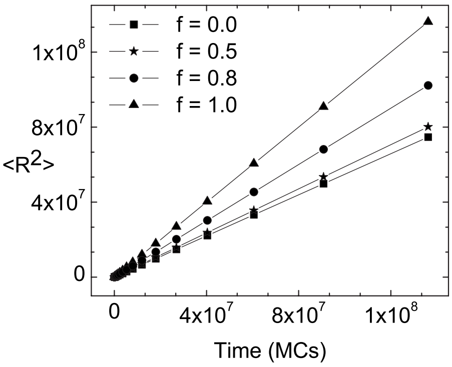

FIG. 1. Mean square displacement $\langle R^2 \rangle$ as a function of time in Monte Carlo steps. In all calculations it is $m=3$, while four f values are shown. The lines are optical guides.

By calculating the slopes of the $\langle R^2 \rangle$ vs time lines, we can determine the corresponding values of the diffusion coefficient

$$D = \frac{\partial \langle R^2 \rangle}{\partial t}. \quad (1)$$

The f dependence of the diffusion coefficient for $m=2$ is shown in Fig. 2. For lower values of f the network is in a rigid state and therefore the tracer particle cannot move easily. It is obvious that up to a critical point f_c, the values of the diffusion coefficients change at a low rate. Beyond f_c, the change is more rapid and the slope is sharper.

Below f_c, the motion of the tracer is impeded by the large number of the existing bonds. The neighboring network formers are expected in this case to have retained most of their bonds and therefore, they will contribute to the particle energy. As f grows this contribution will become weaker,

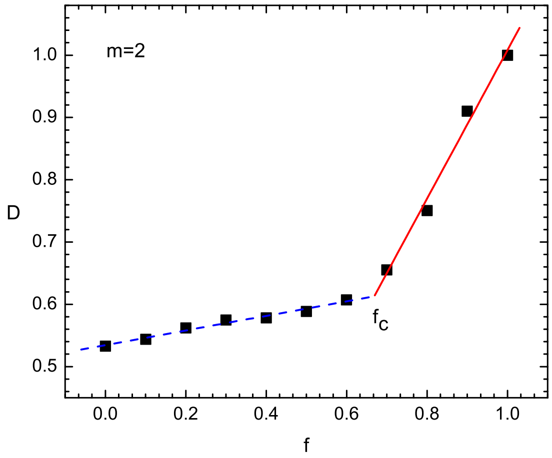

FIG. 2. (Color online) Diffusion coefficient D versus the removal probability f, for the case of $m=2$. The straight lines are optical guides.

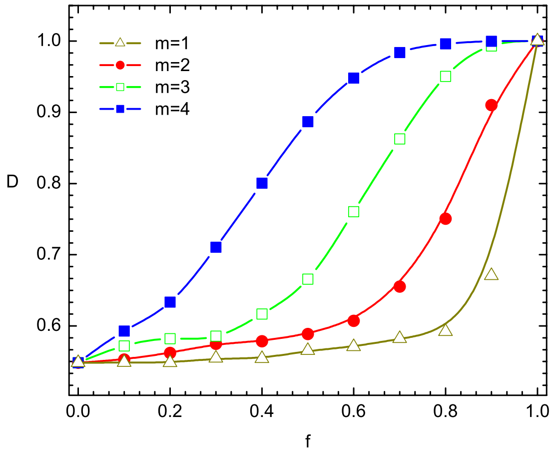

FIG. 3. (Color online) Diffusion coefficient D vs the removal probability f, for several different m values.

allowing the tracer to move easier through the lattice. Although this is evident now from this plot, the quantitative behavior and in particular the appearance of the critical threshold justifies the need for this calculation.

As earlier stated, the parameter m stands for the number of bonds a network former must have, in order to contribute to the tracer energy. In our simulations, we used different values of m, as it can be seen in Fig. 3. In fact if m is large, i.e., $m=4$, then the critical value f_c will appear for lower f values, and therefore, the tracer particle is highly kinetic in a wider range of f values.

It is obvious that at each m value there is a critical concentration of broken bonds (critical f_c value). At this point, the network behavior shifts from rigid to floppy. The diffusion coefficient changes fast in the floppy region and its values are much higher than in the rigid one.

IV. DISCUSSION

The mobility of the tracer particle depends strongly on the probability that some of its first neighbors are in a floppy state, namely, that they have less than m bonds. The main idea is that every monovalent ion "loosens up" one of the otherwise "strong" bridges between the network formers (for example these are Si-O-Si bridges in silicate melts). As the coordination number of Si in silicates is $Z=4$, the number n of "loose" bonds can vary between 0 and 4.

In the case of an ideal solution, the concentration Q_n of the network formers with n bonds is given by the binomial distribution function. It specifies the number of times (n) that an event occurs in Z independent trials

$$Q_n = \frac{Z!}{n!(Z-n)!}(1-f)^n f^{Z-n}. \tag{2}$$

Correspondingly, the concentration of floppy particles is

$$Q(m) = 1 - \sum_{n=m}^{Z} Q_n. \tag{3}$$

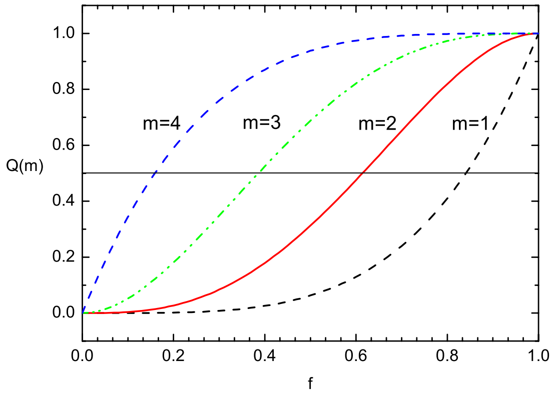

FIG. 4. (Color online) Concentration Q of the broken bonds versus the removal probability f.

The floppy clusters will percolate if their concentration $Q(m)$ exceeds the bond percolation threshold p_c,

$$Q(m) \geq p_c. \tag{4}$$

This is illustrated in Fig. 4, where the m values are indicated on each curve. It is seen that when the m value is low, then the diffusivity is rather low too (as it was also shown in Fig. 4).

The solid line at 0.5 is the percolation threshold p_c for the bond percolation. The intersection points with the corresponding curves give the f_c values at which the diffusion coefficient D changes faster. In Fig. 5 these f_c values are plotted versus m, together with the threshold values determined from Figs. 2 and 3.

It is obvious that there is a coincidence between the theoretical values and the ones acquired by the Monte Carlo simulation.

V. CONCLUSIONS

We study the transition of a network from a rigid state to a floppy one and we investigate how this process affects the diffusion coefficient of a tracer particle. A disordered square lattice is assumed, which consists of network formers that are connected with each other through bonds. The concepts of

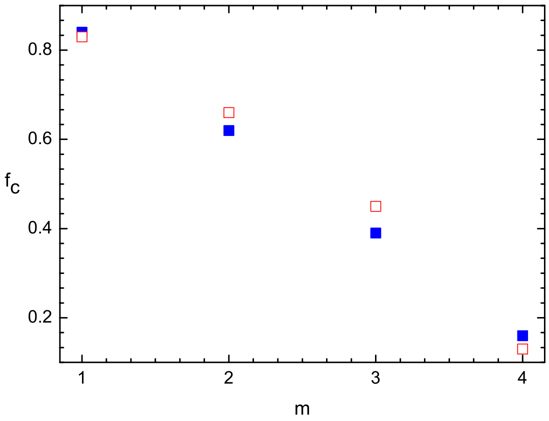

FIG. 5. (Color online) Critical value of the removal probability, f_c, versus the parameter m. The solid squares correspond to the theoretical values from the intersections in Fig. 4, while the open ones to the results of simulations acquired from Figs. 2 and 3.

rigidity and floppiness are examined by means of two parameters, namely, f, which is the bond removal probability, and m, which stands for the upper limit of a number of bonds that a NF must have in order to be treated as floppy. The number of bonds that are present in the system is determined by f, and as f increases the transition of the system from rigid to floppy takes place. This change happens in a sharp tranistion, as shown in Fig. 2, being characterized by a crossover value, f_c. Moreover, the tracer mobility, described by the diffusion coefficient, increases sharply after f_c. Therefore, the tracer particle can move easier as f increases. This pattern is identical for the four different values of m ($m=1,2,3,4$), but it can be easily seen that the threshold concentration f_c strongly depends on each value of m. In fact, the larger the value of m, the lower is the value of f at which the crossover is observed. This result is also theoretically confirmed, by means of the percolation theory.

In real glass forming systems, simulated by network formers and modifiers, it is expected that above the critical concentration f_c, the ions (i.e., Ba^{2+} in a glass with the composition $1.88Na_2O \cdot 15.04K_2O \cdot 7.52Al_2O_3 \cdot 69.56SiO_2 \cdot 6BaF_2$, Ref. [17]) will be extremely kinetic. Therefore, since the system will be in a floppy state, it will be highly improbable to confine the ions in a certain region and hence initialize the crystallization process. Future plans include the simulation of several processes, such as crystallization and nucleation of nanocrystals within a glass material, based on the idea of the rigid/floppy transition. One may need to introduce a large density of particles and to take into account their interactions throughout the whole f range.

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