

Mixed mobile ion effect: A numerical study on the basis of a modified two-spin facilitated kinetic Ising model

Beatrix Schulz, Michael Schulz, and Steffen Trimper

Fachbereich Physik, Martin-Luther Universität Halle, 06099 Halle (Saale), Germany

(Received 4 February 1998)

A numerical simulation on the basis of a modified two-spin facilitated kinetic Ising model for the long-standing problem of the mixed mobile ion effect (or mixed alkali effect) in glasses is presented. The essential idea is an internal dynamical interaction between the cation motion and the dynamics of the cooperative regions of the glass. This interaction leads to a strong variation of the dc conductivity versus the composition ratio f of the cations contained in the glass. Both the dependence on temperature and the dependence on the composition ratio can be obtained in good agreement with experimental measurements. [S1063-651X(98)08009-X]

PACS number(s): 64.70.Pf, 66.30.Dn, 72.80.Ng, 81.05.Kf

I. INTRODUCTION

A silicate glass system offering the overwhelming application of glass products consists of randomly arranged SiO_4 tetrahedrons. The network forms an infinitely large cluster of chemical bonds between these structural elements. At sufficiently low temperatures (around or below the glass transition temperature T_g) this lattice is almost fixed, i.e., most of the chemical bonds are closed during the total observation time. The extremely slow glass dynamics is manifested by the destruction of some few bonds, the cooperative motion of the silicate network and by the formation of new bonds.

The inclusion of alkali ions into a pure SiO_2 glass structure leads to a drastic enhancement of the electrical conductivity. If two types of cations, for example Na^\oplus and K^\oplus , are simultaneously substituted into the glass matrix the dc conductivity shows a strong nonlinear dependence on the composition ratio. This effect is usually denoted as a mixed alkali effect (MAE), or more general as mixed mobile ion effect (MMIE), which can be observed in various glasses and for different cations. The reduction of the conductivity is very pronounced. It covers several factors of the order 10^3 – 10^4 . This is in peculiar opposition to the apparent conductivity obtained from a linear superposition of the electrical conductivities observed in glasses containing only one kind of cation. In order to explain this unusual behavior of glasses a variety of models had been developed; for a review see Day [1] or Ingram [2–4].

However, there exists no well elaborated theoretical framework on which all the measured effects can be described in a convincing way. In particular, nearly all models neglect the cooperative dynamics of the underlying glass matrix. For example, recently, the “unified site relaxation model” (USRM) [4] has been proposed that predicts the occurrence of the MMIE if a homogeneously distributed mixture of different cation sites is present. The main idea is that the cation mobility is reduced whenever two different cations are able to create their specific environment by ion-exchange processes. In this model an environment is characterized by their typical bond lengths or coordination numbers of the surrounding oxygen atoms.

Our model considers additionally the fact that the motion of these atoms is strongly correlated with the glass dynamics inside the surrounding cooperatively rearranging region [5]. This assumption suggests a remarkable influence of glass dynamics to the MMIE. To this aim we present the results of a numerical simulation of the mobility in mixed alkali glasses where the mentioned cooperative effects are explicitly taken into account.

In contrast to conventional phase transitions a long range order is not developed at the glass transition. However, the dynamical glass transition is characterized by a remarkable enhanced cooperativity of local processes with decreasing temperature [5]. The cooperativity leads to the well known slowing down in the dynamical behavior (non-Arrhenius), which can be illustrated by a strongly curved trajectory in the Arrhenius plot (relaxation time τ versus the inverse temperature T^{-1}). One possible fit of this curve is given by the Williams-Landel-Ferry (WLF) curve [6] with $\ln \tau \propto (T - T_0)^{-1}$ and a finite Vogel temperature T_0 .

Mode coupling theories [7–10] (MCT) predict the existence of an ergodic behavior (combined by a slow α process and a fast β process) above a critical temperature T_c and a nonergodic behavior (the remaining fast β process) below T_c . Note that T_c is in the range between the melting temperature T_m and the glass temperature T_g , e.g., $T_m > T_c > T_g$. At T_c the system undergoes a sharp phase transition to a state with frozen (density) fluctuations. Within the MCT the α process is obviously related to the actual dynamic glass transition whereas the β process is often identified with a cage rattling process or with the boson peak.

Actually, the α process does exist also below T_c . Such a process leads to a slow decay of apparently frozen structures (i.e., the nonergodic behavior obtained from the MCT is stable approximately only for a large, but finite time interval). The slow decay reveals the typical properties related usually to the dynamics of the main process of the glass transition (WLF-like behavior of the relaxation time, stretched exponential decay of the correlation function). These effects can be partially described in terms of an extended mode coupling theory [11,12] where additional hopping processes are included.

There exists also various alternative descriptions [13,14] that explain the cooperative motion of the particles inside a supercooled liquid below T_c . One of these possibilities is the n -spin facilitated kinetic Ising model [14–17], originally introduced by Fredrickson and Andersen. This model is based on a coarse graining of space and time scales simultaneously coupled with a reduction of the degrees of freedom.

II. MODEL

The glass (or the supercooled liquid) is assumed to consist of a (virtual) lattice with the unit size l . This lattice has no influence on the underlying dynamics of the supercooled liquid. Each cell is characterized by only one trivial degree of freedom, i.e., the cell structure enables us to attach to each cell an observable σ_j that represents the actual dynamic state of particles inside the cell j . The usual realization of the state is given by the local particle density ρ_j of the cell with $\sigma_j = -1$ if $\rho_j > \bar{\rho}$ and $\sigma_j = 1$ if $\rho_j < \bar{\rho}$ where $\bar{\rho}$ is the averaged density of the system. This mapping implies consequently different mobilities of the particles inside such a cell, i.e., $\sigma_j = -1$ corresponds to the immobile solidlike state and $\sigma_j = 1$ to the mobile state of cell j . The set of all observables $\boldsymbol{\sigma} = \{\sigma_j\}$ forms a configuration. The evolution of the statistical probability distribution function $P(\boldsymbol{\sigma}, t)$ obeys a usual master equation

$$\frac{\partial P(\boldsymbol{\sigma}, t)}{\partial t} = \sum_{\boldsymbol{\sigma}'} L(\boldsymbol{\sigma}, \boldsymbol{\sigma}') P(\boldsymbol{\sigma}', t).$$

The dynamical matrix $L(\boldsymbol{\sigma}, \boldsymbol{\sigma}')$ is determined by the dynamics of the supercooled liquid. Obviously, a direct calculation of the dynamical matrix is often very complicated, so that one should use reasonable assumptions on the mathematical structure of L . To make the time evolution of the glass more transparent let us follow the argumentation due to Fredrickson and Andersen [14,15], i.e., we suppose that the basic dynamics is a simple (Glauber) process $\sigma_j = +1 \leftrightarrow \sigma_j = -1$ controlled by the thermodynamical Gibb's measure and by self-induced topological restrictions. In particular, an elementary flip at a given cell is allowed only if the number of the nearest neighbored mobile cells ($\sigma_j = +1$) is equal to or larger than a restriction number n with $0 < n < z$ (z is the coordination number). So, elementary flip processes and geometrical restrictions lead to the cooperative rearrangement within the system and therefore to a mesoscopic model describing a supercooled liquid below T_c . Such models [14] are denoted as n -spin facilitated kinetic Ising model on a d -dimensional lattice SFM[n, d]. In other words, the SFM[n, d] can be classified as an Ising-like model the kinetics of which is confined by restrictions of the ordering of nearest neighbors to a given lattice cell. The self-adapting environments influence in particular the long time behavior of the spin-spin and therefore of the corresponding density-density correlation functions. These models had been studied numerically [18–21] (SFM[2,2]) and recently also analytically [22] (SFM[1,1]). In the present paper we propose an explanation of the MMIE based on a modified SFM[2,2]. We introduce a square lattice and attach to each lattice point a two spin variable $J_i = \sigma_i \otimes c_i$ with the possible states $\sigma_i = \pm 1$ and $c_i = \pm 1$, respectively. In analogy to the original SFM[2,2], the state $\sigma_i = -1$ corresponds to a solidlike re-

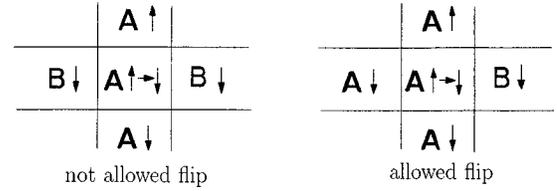


FIG. 1. Examples for an allowed and a forbidden flip process.

gion (low mobility, high density) at the point i , whereas the state $\sigma_i = +1$ corresponds to a liquidlike region (high mobility, low density). On the other hand, $c_i = +1$ is related to a region that contains more cations of type A and consequently $c_i = -1$ characterizes a region predominantly occupied by cations of type B.

The following elementary steps are allowed:

(i) $s_i = -1 \Rightarrow s_i = +1$ (s sector): Such a flip is realized with a transition probability 1 for $+1 \rightarrow -1$ and with $\exp\{-\varepsilon/T\}$ for $-1 \rightarrow +1$ (ε is the energy difference between the liquid and the solidlike state). Additionally we take into account the topological restriction that a flip of that type is only possible if the following condition is satisfied

$$\sum_{j(i)} (1 + \sigma_j) \geq 2n[\mathbf{c}] = (z+1) - \left| \sum_{j[i]} c_j \right|. \quad (1)$$

[$j(i)$ means summation over all z neighbors of the lattice cell i whereas $j[i]$ means a summation over all z neighbors and the lattice cell i and $\mathbf{c} = \{c_i\}$.] Note that this restriction leads to the characteristic hindrance effects; compare also Fig. 1. Furthermore, the glass dynamics is now influenced by the distribution of the cations in the local environment. Physically, it means that a change of the state of a cell is possible if the nearest environment becomes more homogeneous. Further, we argue that there is only a dynamical influence between the distribution of the cations and the local glass processes. This assumption is confirmed by x-ray absorption experiments [23]. The local (Si-O) environment of a cation does not depend on the distribution of adjacent cations, i.e., the cations surrounded by other cations do not change the energy difference between liquidlike and solidlike state within the glass matrix. Thus, it remains as the only possible effect the influence of the cation distribution on the dynamics of the glass matrix.

(ii) Diffusion steps (c sector): An exchange of the kind of the cation between two neighboring cells, e.g., $c_i (= -1) + c_j (= +1) \Rightarrow c_i (= +1) + c_j (= -1)$, is allowed with a temperature dependent probability $p_{ij}(T)$ if (1) both cells are mobile, i.e., $\sigma_i = \sigma_j = +1$, and (2) if the following restriction is satisfied:

$$\sum_{k(i,j)} (1 + \sigma_k) \geq 2m[\mathbf{c}] = 2z - \left| \sum_{k[i,j]} c_k \right| \quad (2)$$

[$k(i, j)$ means all neighbors of the pair (i, j) whereas $k[i, j]$ means all neighbors and the pair (i, j) .] Thus the diffusive dynamics is also influenced by the distribution of the cations within the local environment; compare also Fig. 2.

We take into consideration the general rule that a change of the state within a cell is more easily realized the more the immediate environment becomes homogeneous. The probability $p_{ij}(T)$ is determined by

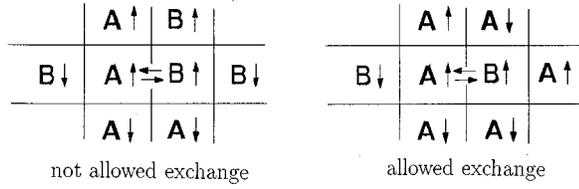


FIG. 2. Examples for an allowed and a forbidden exchange process.

$$p_{ij}(T) = p_0 \exp\left\{-\frac{E_a}{T}\right\} \exp\left\{\frac{\Delta H}{T}\right\}.$$

The first factor represents a thermodynamic activated process, defined by the activation energy E_a . The second term reflects the influence of a possible interaction between the cations of neighboring cells. ΔH is the energy difference before and after realization of the elementary exchange process. The interaction energy is chosen to be conventional by a nearest neighbor coupling

$$H = J \sum_{(i,j)} c_i c_j.$$

$[(i,j)$ denotes a pair of neighbored cells], where $J < 0$ characterizes the ferromagnetic case and $J > 0$ indicates the anti-ferromagnetic case.

Note, the detailed balance is always fulfilled for all elementary flips. Furthermore, the composition ratio of A and B cells is completely conserved. Starting from the initial condition $\sigma_i = +1$ for all lattice sites i and for a given composition ratio $f = [A]/([A] + [B])$ there exists an equilibrium state after a sufficiently long simulation time. It is given by the ratio

$$\frac{N_+}{N_-} = \exp\left(-\frac{\varepsilon}{T}\right). \quad (3)$$

(N_{\pm} are the numbers of cells with σ state $\sigma = +1$ and $\sigma = -1$, respectively.)

It should be remarked that Eqs. (1) and (2) are in a certain sense arbitrary restrictions. But the proposed realizations are reasonable and they will be used for the present calculations.

III. NUMERICAL SIMULATIONS

The numerical simulation of the kinetics of the modified SFM[2,2] is possible by using a simple spin flip dynamics realized by a usual Monte Carlo simulation [21,17] where the elementary steps and the thermodynamic transition probabilities are given above. Following [8,21] we do not expect a long range structure (in contrast to the typical critical phenomena behavior). Consequently, the volume can be chosen to be relatively small. In the following considerations we use a two dimensional square lattice ($d=2$, $z=2d=4$) with $N = L^2$ sites ($L=50$) and periodic boundary conditions. Starting from the nonequilibrium state $\sigma_i = +1$ for all sites (pure liquid state) and a fixed composition ratio f we simulate firstly an equilibrium state, based on the above discussed dynamics and on a usual Metropolis algorithm. After reaching the equilibrium state we determine the diffusion coefficients of the cations using a simple counting of the elementary diffusion steps. By applying the Nernst-Einstein relation (i.e., the dc conductivity is proportional to the diffusion co-

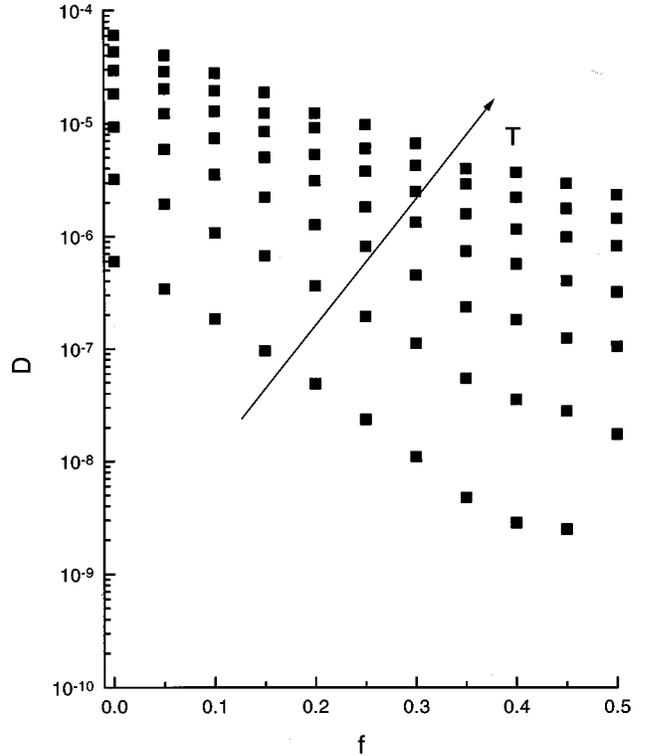


FIG. 3. Diffusion coefficient as a function of composition ratio f and reduced temperature T/ε for the case $J/\varepsilon=0$. Because of the symmetry against and exchange of both components the range of the composition ratio is restricted by $f \in [0, 1/2]$. The temperature increases in the direction of the arrow, $T=0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0$. The diffusion coefficient is given in (lattice unit)² per Monte Carlo step.

efficient) one obtains finally a qualitative relation between the cation composition ratio and the electrical dc conductivity.

The activation energy E_a was assumed to be zero. Hence, the thermodynamical system is controlled by three parameters: the reduced temperature T/ε , the reduced coupling constant J/ε , and the composition ratio f . Because the main interest is the dependence of the conductivity on the composition and the temperature, simulations are realized only for two parameters J/ε . The case $J/\varepsilon=0$ corresponds probably to the experimentally preferred situation [2], i.e., there is no interaction energy between two available cations. The case $J/\varepsilon=1$ corresponds to an antiferromagnetic interaction, which cannot be completely excluded by the experimental measurements. The ferromagnetic case $J/\varepsilon < 0$ has no physical meaning, because such an interaction would imply a long ranged correlation between the cations, which was not observed by experimental measurements.

Figure 3 shows the dependence of the diffusion coefficient and consequently the dc conductivity on the composition and on the temperature for the case $J/\varepsilon=0$. Note that the simulations are realized only for a composition ratio $0 < f < 0.5$ because the underlying system is invariant against an exchange of the components $A \leftrightarrow B$. As expected, there is a relatively strong dependence on the composition ratio [at low temperatures one finds approximately $D(f=0)/D(f=0.5) \approx 10^3$]. Because we have neglected the interaction en-

ergy ($J/\varepsilon=0$) the relatively strong dependence on composition and on temperature can be originated only by the dynamics of the glass matrix. This realization corresponds to the experimental situation [2,24] and it confirms the assumption discussed above that there is a dynamical interaction between the cations inside the glass.

The MMIE increases in the case of an antiferromagnetic interaction (see Fig. 4 for $J/\varepsilon=1$). This result can be attributed to the fact that the nonvanishing interaction energy supports the formation of a chessboardlike distribution of the cations. Apart from that, the characteristic dependence on temperature and on composition is similar to the case $J/\varepsilon=0$.

IV. CONCLUSIONS AND SUMMARY

The main conclusion is that the presented generalization of the SFM[2,2] describes very well the mixed mobile ion effect (MMIE), which was observed in various glasses and for various types of cations. The model studied in this paper reflects essential experimental results. In contrast to other current theories our model takes into account the dynamic interaction between the cations and the glass matrix in contrast to other current theories. The mentioned interaction is realized by a coupling of the glass dynamics and the distribution of the cations. This coupling is given by a dynamically motivated influence of nearest neighbored cations on the cooperativity [see Eq. (1)] and by a dynamical influence of the glass configuration σ on the local exchange processes [see Eq. (2)] and hence on the cation diffusion. From this point of view the main result of the present paper is as follows: the electrical dc conductivity is not a simple linear superposition of the conductivities of the single cations. The strong dynamical interaction between the cations and the dynamics of the underlying glass itself leads to a very pronounced and deep extremum in the conductivity, which is a

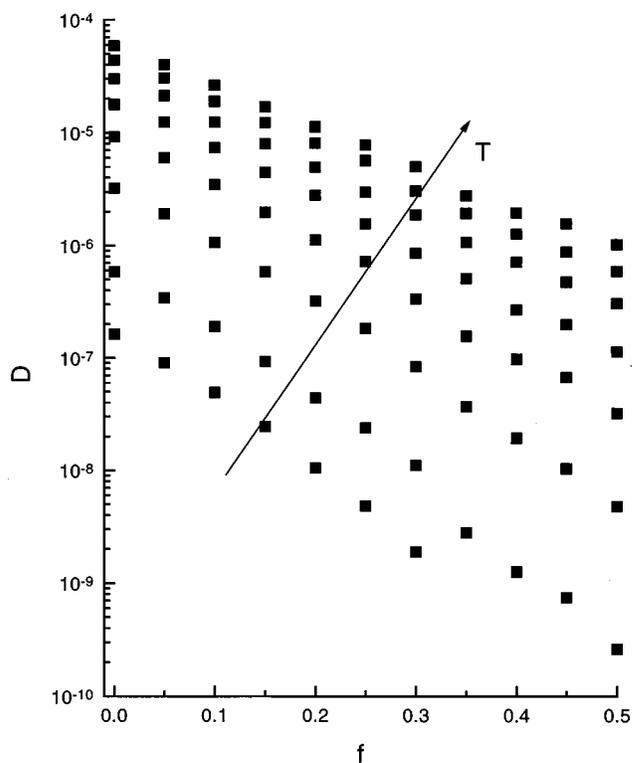


FIG. 4. Diffusion coefficient as a function of composition ratio f and reduced temperature T/ε for the case $J/\varepsilon=1$. The temperature increases in direction of the arrow, $T=0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0$. The diffusion coefficient is given in (lattice unit)² per Monte Carlo step.

result of a characteristic nonlinear superposition of different processes.

ACKNOWLEDGMENTS

This work has been supported by the Deutsche Forschungsgemeinschaft (Grant Nos. SFB 418 and 914/1-3).

-
- [1] D. E. Day, *J. Non-Cryst. Solids* **21**, 343 (1976).
 [2] M. D. Ingram, *Phys. Chem. Glasses* **28**, 215 (1987).
 [3] M. D. Ingram, *Glastech. Ber. Glass Sci. Technol.* **67**, 151 (1994).
 [4] A. Bunde, K. Funke, and M. D. Ingram, *Solid State Ionics* **86-88**, 1311 (1996).
 [5] G. Adam and J. H. Gibbs, *J. Chem. Phys.* **43**, 139 (1965).
 [6] M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.* **77**, 3701 (1955).
 [7] E. Leutheusser, *Phys. Rev. A* **29**, 2765 (1984).
 [8] W. Götze, in *Liquids, Freezing and the Glass Transition*, edited by Hansen *et al.* (North-Holland, Amsterdam, 1991).
 [9] W. Götze and L. Sjögren, *Z. Phys. B* **65**, 415 (1987).
 [10] W. Götze and L. Sjögren, *J. Phys. C* **21**, 3407 (1988).
 [11] T. Franosch, W. Götze, M. R. Mayr, and A. P. Singh, *Phys. Rev. E* **55**, 3183 (1997).
 [12] T. Franosch, M. Fuchs, W. Götze, M. R. Mayr, and A. P. Singh, *Phys. Rev. E* **55**, 7153 (1997).
 [13] J. Jäkle, *Rep. Prog. Phys.* **49**, 171 (1986).
 [14] G. H. Fredrickson and H. C. Andersen, *Phys. Rev. Lett.* **53**, 1244 (1984).
 [15] G. H. Fredrickson and H. C. Andersen, *J. Chem. Phys.* **84**, 5822 (1985).
 [16] G. H. Fredrickson, *Annu. Rev. Phys. Chem.* **39**, 149 (1988).
 [17] G. H. Fredrickson and S. A. Brawer, *J. Chem. Phys.* **84**, 3351 (1986).
 [18] M. Schulz and P. Reinecker, *Phys. Rev. B* **48**, 9369 (1993).
 [19] M. Schulz and P. Reinecker, *Phys. Rev. B* **52**, 4131 (1995).
 [20] M. Schulz, P. R. S. Sharma, and H. L. Frisch, *Phys. Rev. B* **52**, 7195 (1995).
 [21] S. Butler and P. Harrowell, *J. Chem. Phys.* **95**, 4454 (1991).
 [22] M. Schulz and S. Trimper, *Int. J. Mod. Phys. B* **11**, 2927 (1997).
 [23] G. N. Greaves, C. R. A. Catlow, and B. Vessal, *Proc. Int. Physics Conf. Ser. No. III*, 411 (1990).
 [24] C. T. Moynihan, N. S. Saad, D. C. Tran, and A. V. Lesikar, *J. Am. Ceram. Soc.* **63**, 458 (1980).