

STATIC AND DYNAMIC PROPERTIES OF SIMULATED LIQUID AND AMORPHOUS GeO_2

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ABSTRACT

Static and dynamic properties of liquid and amorphous GeO_2 have been simulated by using Molecular dynamics (MD) method in a model containing 3000 particles under periodic boundary conditions. We have proposed for the first time the new interatomic potentials for liquid and amorphous GeO_2 which have Morse type potential for short range interaction in the system. Structure of liquid and amorphous models is analyzed through the partial radial distribution functions (PRDFs), coordination number distributions, interatomic distances and bond-angle distributions. Calculation data for structure and atomization energy of GeO_2 system agree well with the experimental ones. Further, for the first time the diffusion of particles in liquid GeO_2 has been studied in a wide temperature range from 2000 K to 5000 K. We found that temperature dependence of diffusion constant D shows an Arrhenius law at temperatures above the melting point and with further increasing temperature it shows a power law, $D \propto (T - T_c)^\gamma$. The evolution of structure upon cooling has been observed and presented.

1. INTRODUCTION

GeO_2 is a chemical and structural analog to SiO_2 , both oxides have many similarities in structure and physical properties and they have considerable scientific interest and technological importance [1]. However, while liquid and amorphous SiO_2 have been under intensive investigations for the past decades, it was spent less attention to the liquid and amorphous GeO_2 . In recent years, great interest has focused on vitreous GeO_2 using a number of the experimental methods such as neutron diffraction [2,3], high energy X-ray diffraction [4] and anomalous X-ray scattering at the germanium edge [5,6] or by a combination of neutron diffraction, X-ray diffraction and anomalous X-ray scattering [7]. There is a good agreement between experimental data concerning on the structure of vitreous GeO_2 . It was found that the mean interatomic distances $r_{\text{Ge-Ge}} \approx 3.16 - 3.18 \text{ \AA}$, $r_{\text{Ge-O}} \approx 1.73 \text{ \AA}$ and $r_{\text{O-O}} \approx 2.83 \text{ \AA}$ (see more details in Refs. [2-7]), while the mean bond-angles $\theta_{\text{O-Ge-O}} = 109^\circ$ and $\theta_{\text{Ge-O-Ge}} = 133^\circ$ (see Ref. [8]) and the mean coordination number for the Ge-O and O-

Ge pairs is equal to 4 and 2, respectively [2,9]. This means that at the ambient pressure, vitreous GeO_2 has a slightly distorted tetrahedral network structure like vitreous silica. However, more detailed information about the local structure of vitreous GeO_2 can be provided only by the computer simulation. Due to lacking of good interatomic potentials for liquid and amorphous GeO_2 , there is a few works concerning on the simulation of liquid and amorphous GeO_2 . By using classical MD simulation the structure of densified GeO_2 has been studied [10] in a model containing 768 particles with a Born-Huggins-Mayer type potential which has been fitted to recover the crystalline phases of GeO_2 by Oeffner and Elliot [11]. Calculations showed that the coordination number of Ge changes with increasing density and at the ambient density, amorphous GeO_2 has a tetrahedral network structure like those observed in practice [10]. Comparative numerical study of liquid GeO_2 and SiO_2 has been performed and it was found that the short-range order is identical in liquid and glass phases, made of tetrahedral network while longer range order displays differences with temperature [12]. By using the same interatomic potentials obtained by Oeffner and Elliot, structural properties of liquid germania

were investigated by Gutierrez and Rogan in a model containing 576 particles at 21 different densities [13]. Simulations showed that at ambient density there is a short-range order of slightly distorted tetrahedral network like those obtained in the amorphous state. However, it seems that simulation data in [10,13] agreed not so well with the experimental ones for the mean interatomic distance of Ge-Ge pair, it was found that $r_{Ge-Ge} \approx 3.32 \text{ \AA}$ in [10] and $r_{Ge-Ge} \approx 3.30 \text{ \AA}$ in [13] versus the experimental value of around $3.16 - 3.18 \text{ \AA}$. Moreover, the atomization energy of a model has not been reported in these works.

And therefore, our aim here is to find new interatomic potentials which describe well both structure and atomization energy of liquid and amorphous GeO_2 . We also study the evolution of structure and diffusion of particles in vitreous GeO_2 upon cooling in a large model containing 3000 particles.

2. CALCULATIONS

Simulations were performed at constant volume corresponding to the real density of an amorphous germania of 3.65 g/cm^3 . We use the Verlet algorithm with the MD time step of 1.0 fs. Liquid and amorphous GeO_2 models obtained by cooling from the melt. The initial melt model at the temperature of 5000 K has been relaxed from a random configuration of 3000 particles over 100,000 MD time steps. Temperature of the

system decreases linearly in time as $T = T_0 - \gamma t$, where $T_0 = 5000 \text{ K}$ and cooling rate $\gamma = 5 \times 10^{13} \text{ K/s}$. The so-obtained configurations at finite temperatures by cooling from the melt were subsequently relaxed for 25 ps before calculating static and dynamic properties. In order to calculate the coordination number distributions and bond-angle distributions in liquid and amorphous GeO_2 , we adopt the fixed values $R_{Ge-Ge} = 3.6 \text{ \AA}$, $R_{Ge-O} = 2.2 \text{ \AA}$ and $R_{O-O} = 3.2 \text{ \AA}$. Here R is a cutoff radius which was chosen as a first minimum after a first peak in PRDFs of the amorphous model at the temperature of 300K. We have proposed the interatomic potentials for liquid and amorphous GeO_2 , which have weak electrostatic interactions and the Morse type short-range interactions as follows:

$$U_{ij}(r) = \frac{q_i q_j}{r} + D_0 \{ \exp[\gamma(1 - \frac{r}{R_0})] - 2 \exp[\frac{1}{2}\gamma(1 - \frac{r}{R_0})] \} \quad (1)$$

where q_i and q_j represent the charges of ions i and j , for Ge atom $q_{Ge} = +2.0e$ and for O atom $q_O = -1.0e$ (e is the elementary charge unit), these charges are adopted to be close to those used in [11,13] for the GeO_2 system (i.e. equal to $+1.5e$ and $-0.75e$ for Ge and O, respectively); r denotes the interatomic distance between atoms i and j ; the parameters of the Morse potentials are given below:

Interaction	D_0 (eV)	γ	R_0 (\AA)
Ge-Ge	0.014	15.3700	3.600
Ge-O	3.700	8.6342	1.760
O-O	0.044	10.4112	4.400

The interatomic potentials of such type have been successfully used for simulating of structure and properties of vitreous silica [14,15]. And due to many similarities in structure and properties between vitreous GeO_2 and SiO_2 , we have developed such potentials for our GeO_2 system by modifying parameters of the potentials used in [14,15] to get a good agreement with the experimental data for structure and atomization energy of liquid and

amorphous GeO_2 . The cutoff radius for the short-range interaction is equal to a half of the length of the main cube.

3. RESULTS AND DISCUSSIONS

3.1. Structural properties of liquid and amorphous GeO_2 (a- GeO_2).

Table 1. Structural characteristics of a-GeO₂.

r_{ij} - Positions of the first peaks in PRDFs; θ - The mean bond-angle; Z_{ij} - The average coordination number (numbers 1 and 2 denote Ge and O, respectively).

References	r_{ij} (Å)			Z_{ij}				θ_{O-Ge-O}	$\theta_{Ge-O-Ge}$
	1-1	1-2	2-2	1-1	1-2	2-1	2-2		
Our cal. data for a-GeO ₂ at 300 K	3.21	1.69	2.78	4.06	4.00	2.00	6.44	108°	133°
Cal. data for a-GeO ₂ [10]	3.32	1.72	2.81		4.10				
Exp. data for a-GeO ₂ [8]	3.16	1.73	2.83		4.00			109°	133°
Exp. data for a-GeO ₂ [2,9]	3.18	1.74	2.83		4.00	2.00			130°
Cal. data for a-SiO ₂ [16]	3.16	1.60	2.59		4.00	2.00		108.3°	152°
Exp. Data for a-SiO ₂ [17]	3.12	1.62	2.65		4.00	2.00		109.5°	144°

Structural characteristics of a-GeO₂ model obtained at the temperature of 300 K are in good accordance with the experimental data and with those calculated in [10] (see Table 1). Our calculated mean interatomic distance r_{Ge-Ge} in a-GeO₂ is equal to 3.21 Å and agrees well with the experimental one, the agreement is better than those obtained by simulation in [10,13]. The calculated mean coordination number for Ge-O and O-Ge pairs is equal to 4 and 2, respectively and coincides with the experimental one. Further, for an ideal tetrahedral network structure the O-Ge-O angle is 109.47°, O-O-O is 60° and Ge-O-O is equal to 35.26°. For an amorphous state, our calculated O-Ge-O and

Ge-O-Ge angles are equal to 108° and 133°. And it is in good accordance with the experimental data. Combined such angles with the mean coordination numbers described above, we can conclude that a-GeO₂ has a slightly tetrahedral network structure and almost 99.9% Ge atoms are surrounded by 4 oxygen atoms like liquid and a-SiO₂. The same structure has been obtained for a liquid GeO₂ model at the temperature of 2000 K (not shown). More detailed information about local structure in the system can be found via the coordination number distributions and bond-angle distributions.

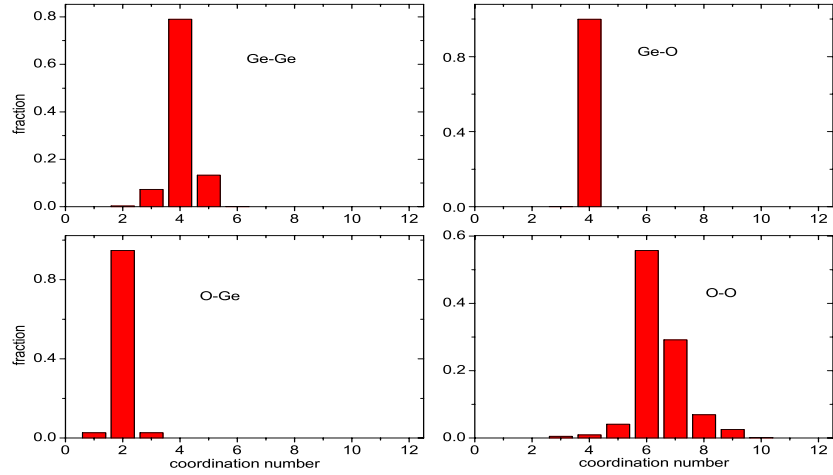


Fig. 1. Coordination number distributions in a-GeO₂ model at the temperature of 300 K.

As shown in Fig.1, coordination number distributions in an amorphous state at the temperature of 300 K are similar to those of liquid one presented in [13] with an exception for the O-O pair, where the peak in our curve is located at value 6 versus 8 in [13]. The discrepancy might be related to the different cutoff radii for the O-O pair used here and in [13]. There is no experimental data for the mean coordination number Z_{O-O} in vitreous GeO₂.

One more thing we would like to discuss here is an atomization energy of the system, which is often ignored in simulation works. The calculated total energy, with respect to free Ge²⁺ and O¹⁻ ions at rest for our a-GeO₂ model at the temperature of 300 K, is $E_{ion} = -4307$ kJ/mol. We can recalculate the atomization energy by the equation: $E_a = -E_{ion} - E_{trans} + E_{kin}$. Here E_{trans} is the energy spent to convert all free neutral atoms to the free ions and E_{kin} is a kinetic energy of particles. The ionization energy of neutral Ge atom to ion Ge²⁺ is of 23.8346 eV/atom, the electron affinity of O atom is of 6.76 eV/atom [18]. Therefore, the atomization energy $E_a \approx 1355$ kJ/mol (per mole of GeO₂ molecules), while the experimental value combined from the experimental data for crystalline GeO₂ is equal to 1455 kJ/mol [18]. This means that the calculated atomization energy of a-GeO₂ is close to the experimental one for crystalline phase. The calculated atomization energy of a-GeO₂ is less than that one of crystalline phase on 100 kJ/mol, which can be considered as a heat of crystallization of a-GeO₂. There is no experimental data for the heat of crystallization of a-GeO₂, however, for amorphous oxides it is often equal to a few

hundreds kJ/mol [19]. The PRDFs for a-GeO₂ model at the temperature of 300 K are close to those presented in [10] (shown in the next subsection). It is interesting to compare the structure of a-SiO₂ and a-GeO₂. Calculations show that structure of these oxides are very similar however, one can see that the mean bond-angle Si-O-Si is much larger than Ge-O-Ge one implied that structure of a-SiO₂ is more looser than that of a-GeO₂. One can check the topological looseness of a system directly via the parameter ρ_1 which is defined as the mean height of the first peaks in PRDFs [19]:

$$\rho_1 = \frac{\sum X_i X_j r_{ij}}{d_0} \quad (2)$$

where X_i and X_j are the atomic parts of components in the system and r_{ij} is the position of the first peak in PRDFs, summation is done over all pairs of particles; and $d_0 = (V/N)^{1/3}$, N is the number of particles in the volume V . Topologically dense systems have $\rho_1 = 1.08 \pm 0.02$ and loose systems have $\rho_1 < 1.05$. From the calculated data shown in

Table 1, for a-GeO₂ the parameter ρ_1 is equal to 0.78. This means that a-GeO₂ is a loose system.

3.2. Evolution of structure of liquid and a-GeO₂ upon cooling.

According to the diffraction and calculated data presented above, liquid and a-GeO₂ have a slightly distorted tetrahedral network structure with the main structural unit GeO₄, the mean coordination number $Z_{Ge-O} = 4$ and $Z_{O-Ge} = 2$. This means that serious defects in this structure are Ge atoms having coordination number $Z_{Ge-O} = 3$ or O atoms having

$Z_{O-Ge} = 1$ or 3. Therefore, it is interesting to study the evolution of coordination number distributions for the Ge-O and O-Ge pairs upon cooling from the melt. As shown in Table 2, the number of defects with $Z_{Ge-O} = 3$ decreases upon cooling and tetrahedral network structure is enhanced upon cooling. The number of defects $Z_{O-Ge} = 1$ decreases upon cooling to T=2500 K and then slightly increases, meanwhile number of defects $Z_{O-Ge} = 3$ decreases upon cooling to T=3750 K and then also slightly increases (not shown).

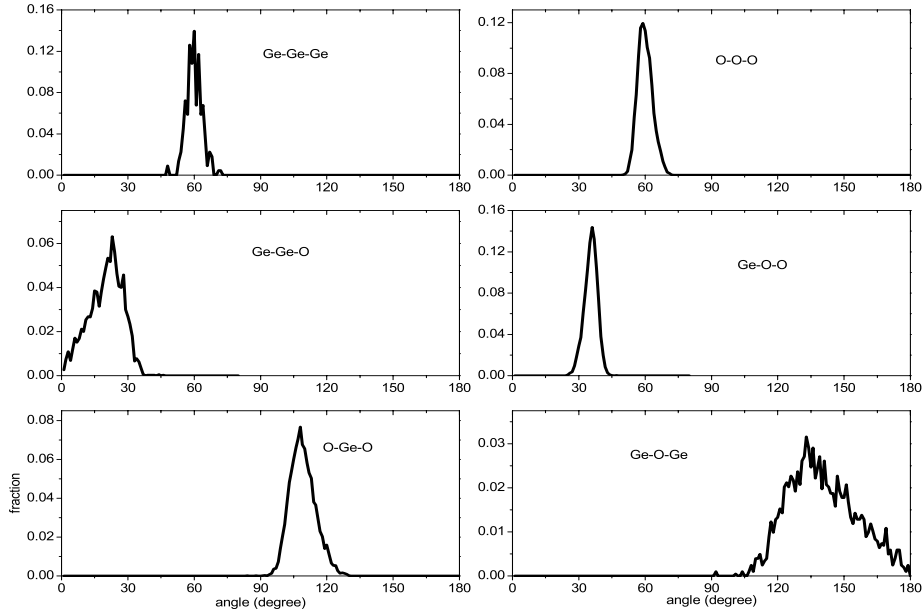


Fig. 2. Bond-angle distributions in the a-GeO₂ model at the temperature of 300K.

Table 2. Temperature dependence of coordination number distribution Z_{Ge-O} for the Ge-O pair in GeO₂ model.

Z_{Ge-O}	1	2	3	4	5
Number of Ge ²⁺ ions (T= 5000 K)	0	1	138	857	4
Number of Ge ²⁺ ions (T= 4500 K)	0	1	96	902	1
Number of Ge ²⁺ ions (T= 4250 K)	0	1	57	939	3
Number of Ge ²⁺ ions (T= 4000 K)	0	0	57	943	0
Number of Ge ²⁺ ions (T= 3750 K)	0	0	43	956	1
Number of Ge ²⁺ ions (T= 3500 K)	0	0	35	965	0
Number of Ge ²⁺ ions (T= 3000 K)	0	0	26	974	0
Number of Ge ²⁺ ions (T= 2500 K)	0	0	4	996	0

Number of Ge^{2+} ions ($T= 2000$ K)	0	0	9	991	0
Number of Ge^{2+} ions ($T= 300$ K)	0	0	1	999	0

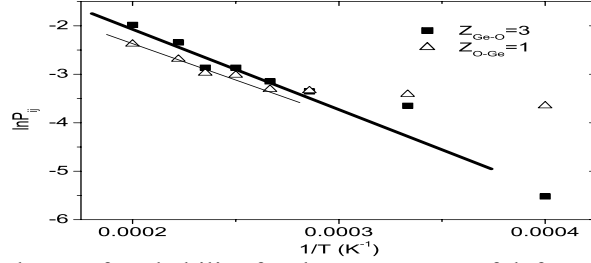


Fig. 3. Temperature dependence of probability for the occurrence of defects, P_{ij} , for the cases of partial coordination numbers $Z_{\text{Ge-O}} = 3$ and $Z_{\text{O-Ge}} = 1$ (for $Z_{\text{O-Ge}} = 3$, there is a small number of points that it has not been presented).

Calculations showed that the probability for the occurrence of structural defects in vitreous SiO_2 is described well by an Arrhenius law [20]:

$$P_{ij} = A_{ij} \exp(-E_{ij} / T) \quad (3)$$

where P_{ij} denotes the probability that a ion of type i has exactly Z nearest neighbors of type j . Fig. 3 presents that such probability for defects with $Z_{\text{Ge-O}} = 3$ and $Z_{\text{O-Ge}} = 1$ also shows an Arrhenius law at temperatures above 3500 K. Prefactors A_{ij} and activation energies E_{ij} were found: $A_{\text{Ge-O}} = 3.139$ and $E_{\text{Ge-O}} = 16,038$ K for $Z_{\text{Ge-O}} = 3$; $A_{\text{O-Ge}} = 0.988$ and $E_{\text{O-Ge}} = 11,632$ K for $Z_{\text{O-Ge}} = 1$. These values differ from those observed for silica melt [20].

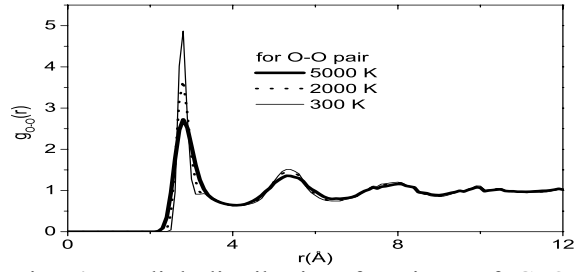
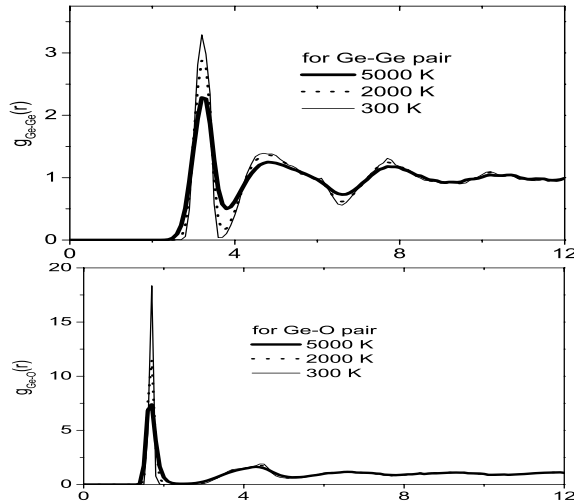


Fig. 4. Radial distribution functions of GeO_2 system upon cooling.

In order to observe an evolution of structure of the system upon cooling, we also display PRDFs, $g_{ij}(r)$, for Ge-Ge, Ge-O and O-O pairs in relaxed models at three different temperatures of 5000 K, 2000 K and 300K. We can see that PRDFs strongly depend on the temperature that the height of the individual peaks and minima become more pronounced upon cooling. And the most prominent changes have been observed for the first peak in $g_{ij}(r)$. The same phenomenon has been observed in vitreous silica [16].

3.3. Diffusion

By using the Einstein relation, $\lim_{t \rightarrow \infty} \frac{\langle r^2(t) \rangle}{6t} = D$, one can calculate the diffusion constant D via the mean-squared atomic displacement $\langle r^2(t) \rangle$ (see Fig. 5). From the temperature dependence of diffusion constant in Fig. 6, we can determined approximately the glass-transition temperature T_g by the extrapolation, which is at around 1000 K. This value is close to the value of 1010 K reported in [10], however, it is larger than those observed in practice $T_g \approx 800$ K [21]. And

according to our calculations, the diffusion constant of Ge and O particles in liquid GeO_2 is smaller than those of Si and O particles in silica melt at the same temperatures (see more details in Ref. [20]). It is essential to notice that the melting temperature of GeO_2 is equal to $T_m = 1378$ K and for silica these values $T_g \approx 1500$ K and $T_m = 1995$ K (see in [13]). The temperature dependence of diffusion constant of particles in germania melt shows an Arrhenius law at temperatures above the melting point with activation energies 1.12 eV and 0.83 eV for Ge and O, respectively. These values are smaller than those for silica (i.e. 4.66 eV and 5.18 eV for Si and O, respectively [20]). At higher temperatures, the curves deviate from an Arrhenius law (see Fig. 7) like those observed in silica melt [20]. And after intensive testing, we found that at high temperatures it shows a power law like those observed in silica melt as given below [20]:

$$D \propto (T - T_c)^\gamma \quad (4)$$

where T_c is the critical Mode-Coupling theory temperature for germania which is estimated about 3500 K. The fitted exponent $\gamma = 1.506$ and 1.525 for Ge and O, respectively. For silica melt, $T_c = 3330$ K and $\gamma = 2.15$ and 2.05 for Si and O, respectively [20].

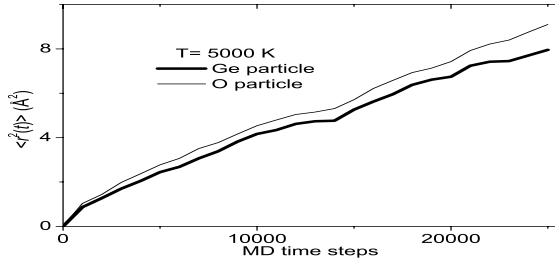


Fig. 5. Time dependence of mean squared atomic displacement $\langle r^2(t) \rangle$ in GeO_2 model at the temperature of 5000 K.

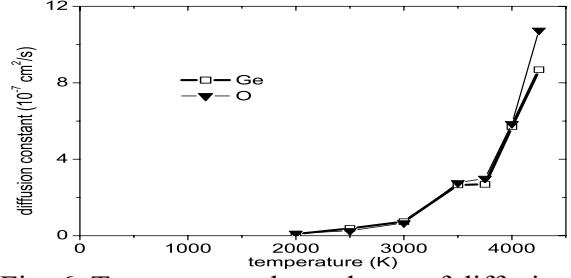


Fig. 6. Temperature dependence of diffusion constant D .

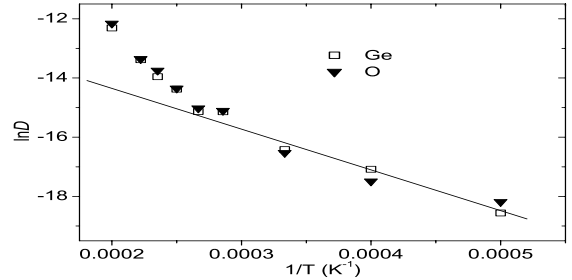


Fig. 7. The $1/T$ dependence of $\ln D$

4. CONCLUSIONS

We would like to make the following conclusions:

- i) For the first time, we have proposed the new interatomic potentials for liquid and amorphous GeO_2 which have weak electrostatic part and short-range Morse type part. These potentials describe well both structure and atomization energy of the system.
- ii) Calculations show that liquid and a- GeO_2 have a slightly distorted tetrahedral network structure like silica.
- iii) For the first time, the diffusion in liquid germania has been calculated and temperature dependence of diffusion constant shows an Arrhenius law at temperatures above the melting point and it shows a power law, $D \propto (T - T_c)^\gamma$, at higher temperatures like silica melt. The critical Mode-Coupling theory temperature T_c for germania was determined equal to 3500K, and the exponent γ is equal to 1.50 for both Ge and O. The glass-transition temperature T_g for the GeO_2 system is at around 1000 K.

REFERENCES

- [1] W. Vogel, *Glass Chemistry* (Springer-Verlag, Berlin, 1994).
- [2] J.A.E. Desa, A.C. Wright, and R.N. Sinclair, *J. Non-Cryst. Solids* **99**, 276 (1988).

- [3] Y. Waseda, K. Sugiyama, E. Matsubara, and K. Harada, *Mater. Trans. JIM* **31**, 421 (1990).
- [4] J. Neufeind and K.D. Liss, *Ber. Bunsenges. Phys. Chem. Chem. Phys.* **100**, 1341 (1996).
- [5] P. Bondot, *Phys. Stat. Sol. A* **22**, 511 (1974).
- [6] D.L. Price, A.J.G. Ellison, M.L. Saboungi, R.Z. Hu, T. Egami, and W.S. Howells, *Phys. Rev. B* **55**, 11249 (1997).
- [7] D.L. Price, M.L. Saboungi, and A.C. Barnes, *Phys. Rev. Lett.* **81**, 3207 (1998).
- [8] O.B. Tsiok, V.V. Brazhkin, A.G. Lyapin, and L.G. Khvostantsev, *Phys. Rev. Lett.* **80**, 999 (1998).
- [9] R. Hussin, R. Dupree, and D. Holland, *J. Non-Cryst. Solids* **246**, 159 (1999).
- [10] M. Micoulaut, *J. Phys.: Condens. Matt.* **16**, L131 (2004).
- [11] R.D. Oeffner and S.R. Elliott, *Phys. Rev. B* **58**, 14791 (1998).
- [12] M. Micoulaut, *Chem. Geology* **213**, 197 (2004).
- [13] G. Gutierrez and J. Rogan, *Phys. Rev. E* **69**, 031201 (2004).
- [14] N.T. Huff, E. Demiralp, T. Cagin and W.A. Goddard III, *J. Non-Cryst. Solids* **253**, 133 (1999).
- [15] A. Takada, P. Richet, C.R.A. Catlow and G.D. Price, *J. Non-Cryst. Solids* **345 & 346**, 224 (2004).
- [16] K. Vollmayr, W. Kob, and K. Binder, *Phys. Rev. B* **54**, 15808 (1996).
- [17] R.L. Mozzi and B.E. Warren, *Appl. Cryst.* **2**, 164 (1969).
- [18] *CRC Handbook of Chemistry and Physics*, Edited by Lide D.R. (CRC Press, NewYork, 1996).
- [19] D.K. Belashchenko, *Russian Chem. Rev.* **66**, 733 (1997).
- [20] J. Horbach and W. Kob, *Phys. Rev. B* **60**, 3169 (1999).
- [21] A. Meyer, H. Schober, and J. Neuhaus, *Phys. Rev. B* **63**, 212202 (2001).