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Glass Formation in Amorphous SiO_2 as a Percolation Phase Transition in a System of Network Defects

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Thermodynamic parameters of defects (presumably, defective SiO molecules) in the network of amorphous SiO_2 are obtained by analyzing the viscosity of the melt with the use of the Doremus model. The best agreement between the experimental data on viscosity and the calculations is achieved when the enthalpy and entropy of the defect formation in the amorphous SiO_2 network are H_d = 220 kJ/mol and S_d = 16.13R, respectively. The analysis of the network defect concentration shows that, above the glass-transition temperature (T_g), the defects form dynamic percolation clusters. This result agrees well with the results of molecular dynamics modeling, which means that the glass transition in amorphous SiO_2 can be considered as a percolation phase transition. Below T_g, the geometry of the distribution of network defects is Euclidean and has a dimension d = 3. Above the glass-transition temperature, the geometry of the network defect distribution is non-Euclidean and has a fractal dimension of d_f = 2.5. The temperature T_g can be calculated from the condition that percolation arises in the defect system. This approach leads to a simple analytic formula for the glass-transition temperature: $T_g = H_d/(S_d + 1.735R)$. The calculated value of the glass-transition temperature (1482 K) agrees well with that obtained from the recent measurements of T_g for amorphous SiO_2 (1475 K). © *2004 MAIK "Nauka/Interperiodica".*

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Percolation transitions attract considerable interest, because they offer an explanation for a wide class of phenomena [1–3]. For example, the glass transition in spin glasses is explained on the basis of the percolation theory [4]. At the same time, the nature of glass transition in oxide systems is not yet clearly understood [5–8]. Amorphous SiO_2, as the simplest glass-forming material, is suitable for use in the model studies in this area of research. At temperatures higher than T_g = 1475 K, amorphous SiO_2 transforms to the supercooled liquid state, whereas, below T_g, it is in the glassy solid state. The changes occurring in the atomic system as the temperature passes through T_g have been much investigated. According to the concept proposed by Hunt, the material at temperatures above T_g is in the percolative transport regime, while at low temperatures, it is in the diffusive transport regime [5]. Major progress in the understanding of the structural changes of an amorphous material passing through T_g was achieved with the help of the molecular dynamics (MD) modeling [6] and, in particular, by studying the Voronoi polyhedra (analogues of the Vigner–Seitz cell) [7, 8]. The MD experiments showed that, in the liquid state, percolation clusters composed of Voronoi coordination polyhedra with low-density atomic configurations are formed in the material, while no such clusters occur in the solid (glassy) state [7]. However, in the solid state, percolation clusters of Voronoi coordination polyhedra with high-density (compact) atomic configurations are formed [7, 8]. Since the percolation clusters of Voronoi coordination polyhedra with low-density atomic configurations exist in the liquid state only, it is possible to distinguish between the liquid and solid (glassy) states of amorphous materials on the basis of the MD experiments [7]. At the same time, the MD experiments show that, near the glass-transition temperature, the geometry of an amorphous material changes because of the formation of the fractal percolation clusters [2].

This paper shows that, as the temperature passes through T_g in amorphous SiO_2, a percolation transition occurs in the system of the network defects presumably consisting of defective SiO molecules. The transition can be traced analytically, making it possible to derive a simple expression for the glass-transition temperature. The analytic calculation is based on the Doremus viscosity model (D model) relating the viscosity of the amorphous material to the thermodynamic parameters of the network defects [9–11].

An amorphous material can be represented by a topologically disordered network. The three-dimensional network of amorphous SiO_2 consists of SiO_4 tetrahedra bridged by oxygen atoms. A perfect network of an amorphous material has no defects at absolute zero, but defects arise at finite temperatures T. The formation of defects depends on the Gibbs free energy of a defect:

$$G_d = H_d - TS_d, \quad (1)$$

where H_d is the enthalpy and S_d is the entropy of formation of one mole of defects. Doremus assumed that the diffusion and viscous flow in silicates proceed through the formation of defective SiO molecules. The formation of these defects favors the appearance of five-coordinate Si and O atoms, which was confirmed experimentally in [9]. The formation of defects in the network of amorphous SiO_2 can be represented by the reaction

$$\begin{aligned}&(\text{–Si–})_{\text{net}} + (\text{–O–Si–})_{\text{net}}\\ &\longleftrightarrow (\text{–Si–})_{\text{defect}} + (\text{–O–Si–})_{\text{defect}},\end{aligned} \tag{2}$$

where $(\text{–Si–})_{\text{net}}$ and $(\text{–O–Si–})_{\text{net}}$ refer to the network and $(\text{–Si–})_{\text{defect}}$ and $(\text{–O–Si–})_{\text{defect}}$ are the bond-rupture defects. Let the concentration of the elementary blocks of the network be C_0 and the defect concentration be $[(\text{–Si–})_{\text{defect}}] = [(\text{–O–Si–})_{\text{defect}}] = C_d$. Then, $[(\text{–Si–})_{\text{net}}] = [(\text{–O–Si–})_{\text{net}}] = (C_0 - C_d)$. The equilibrium reaction constant for (2) depends on the change in the Gibbs energy $G = 2G_d$:

$$K = \exp(-\Delta G/RT). \tag{3}$$

Hence, the equilibrium content of defects is determined as (see also [11, 12])

$$C_d = C_0\frac{\exp(-G_d/RT)}{1 + \exp(-G_d/RT)}. \tag{4}$$

To calculate the concentration of network defects in amorphous SiO_2, it is necessary to know the numerical values of the enthalpy H_d and entropy S_d of defect formation. Both these quantities, H_d and S_d, are involved in the expression for the viscosity in the D model [10, 11]:

$$\begin{aligned}\eta(T) &= \frac{kT}{6\pi r D_0}\exp\left(-\frac{S_m}{R}\right)\\ &\times \exp\left(\frac{H_m}{RT}\right)\left[1 + \exp\left(-\frac{S_d}{R}\right)\exp\left(\frac{H_d}{RT}\right)\right],\end{aligned} \tag{5}$$

where k is the Boltzmann constant, r is the defect radius, $D_0 = f\alpha\lambda^2\nu$, f is the correlation factor, α is the symmetry parameter, λ is the hopping distance, ν is the frequency, and S_m and H_m are the entropy and enthalpy of defect motion. By processing the experimental data on viscosity, it is possible to obtain the exact values of H_d and S_d. The results of this analysis are shown in Fig. 1, which displays the viscosity of amorphous SiO_2 calculated from Eq. (5) and the experimental data on viscosity from [13, 14]. The best agreement between the viscosity calculated from Eq. (5) and the experimental data [13, 14] is achieved with $H_d = 220$ kJ/mol and $S_d = 16.13R$, where R is the universal gas constant. Note that the value $H_d = 220$ kJ/mol is practically equal to half the strength of one bond for Si in SiO_2 (443 kJ/mol [15]), which agrees with the physical meaning of this quantity.

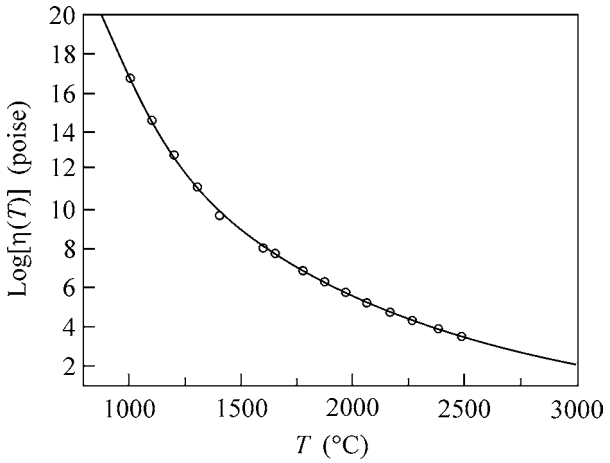

Fig. 1. Viscosity of amorphous SiO_2: the curve is calculated from Eq. (5), and the experimental data are taken from [13, 14].

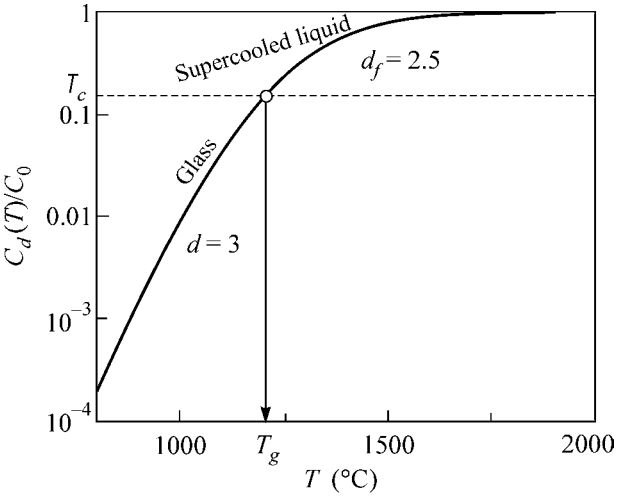

Fig. 2. Concentration of network defects in amorphous SiO_2. Above T_g, the defect geometry becomes fractal with the dimension $d_f = 2.5$.

Now, let us consider the evolution of the network defect concentration in amorphous SiO_2 with increasing temperature. The results of calculating the relative concentration $\rho = C_d/C_0$ of defects by Eq. (4) are shown in Fig. 2.

The defect clusterization is unlikely as long as the defect concentration is small. As the defect concentration increases, the formation of clusters becomes more and more probable. The relative defect concentration is a function of temperature, $\rho(T) = C_d/C_0$, and increases with temperature T. A percolation cluster of network defects is formed when the relative defect concentration $\rho = C_d/C_0$ reaches the critical value:

$$\rho(T) = \rho_c. \tag{6}$$

For a three-dimensional space, the critical density value is determined by the Scher–Zallen invariant $\vartheta_c = 0.15 \pm 0.01$ [1, 16]. Hence, one can determine from Eq. (6) the percolation transition temperature. Taking into account that $\rho(T)$ in equilibrium can be determined from Eq. (4), we obtain for the glass-transition temperature

$$T_g = \frac{H_d}{S_d + R\ln[(1-\vartheta_c)/\vartheta_c]}. \quad (7)$$

At temperatures $T < T_g$, no percolation clusters occur in the material and the geometry of the network defects remains Euclidean ($d = 3$). When $T > T_g$, a percolation cluster is formed with the fractal geometry of dimension $d_f = 2.5$ [2]. The network defects are mobile, and, hence, the percolation cluster is dynamic in character (from the viscosity data and from Eq. (5), it follows that the enthalpy of the network defect motion is H_m = 525 kJ/mol). Dynamic percolation clusters with the dimension $d_f = 2.6$ were experimentally observed in emulsions [17]. It is also significant that the relaxation processes near the percolation threshold are nonexponential and described by the Kohlrausch law [2–5]. At temperatures $T > T_g$, amorphous SiO_2 is a supercooled liquid, while below T_g, it transforms to the glassy state. Formula (7) for amorphous SiO_2 yields T_g = 1482 K. This value is only slightly higher than the known value of T_g = 1450 K (see, e.g., [6]). However, it virtually coincides with the recent data of scanning calorimetric measurements: $(T_g)_{exp}$ = 1475 K [18].

Thus, the glass formation in amorphous SiO_2 can be considered as a percolation transition in the system of network defects (presumably, defective SiO molecules) with a change in the geometry of the defects from fractal in the liquid state to Euclidean in the glassy state.

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