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ATOMIC DISPLACEMENT ENERGY IN AMORPHOUS COMPOUNDS© **M. I. Ojovan**

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Atomic displacement energy in multicomponent sheet and lead-silicate glasses is calculated from the free activation energy of a viscous flow. The value of $\Delta\varepsilon_c$ is shown to remain constant in a rather wide range of temperatures in the glass transition region. Satisfactory agreement with calculations of displacement energy using the current formula incorporating the glass transition temperature and the fluctuation volume fraction frozen at this temperature is obtained. The validity of the above formula is confirmed not only at the glass transition temperature but also in the temperature region adjacent to it.

Keywords: atomic displacement energy; glass transition region; amorphous compounds; lead-silicate glasses; viscosity; fluctuation of the volume; energy of delocalization of the atom.

Introduction

The development of strict physical theories for disordered structures, based on the first principles of statistical physics and quantum mechanics, encounters serious difficulties [1-3]. Approximate model approaches to liquids and amorphous solids thus remain topical at this stage. Among the developments in recent years for disordered glass-like systems are those with respect to the model of delocalized atoms [4-5] with a certain liquid-glass transition interpretation, an original temperature dependence for the viscosity of glass-forming liquids, and the glass plasticity effect. Further development of the model is associated with the search of different methods for calculating the parameters of this model and ascertaining their physical meaning.

This work is devoted to one way of estimating the atomic displacement energy in amorphous compounds and verifying its constancy in a wide range of temperatures (for examples of sheet and lead-silicate glasses).

Analytical approach

The delocalization of an atom in inorganic glasses and their melts is understood as the critical displacement of a bridging atom (e.g., the oxygen atom in a Si–O–Si bridge) due to the local low-activation viscoelastic strain of a network of valence

bonds. The latter promotes the formation of elementary volume Δv_e required for the delocalization of an atom in its neighborhood. The probability of the delocalization of an active (excited) atom — its displacement from an equilibrium position — is confined to the probability of an elementary fluctuation volume equal to Δv_e or exceeding it forming near this atom. Delocalization energy $\Delta \varepsilon_e$ of an atom is equal to the work needed to displace it from an equilibrium position against internal molecular pressure p_i produced by interatomic (intermolecular) attraction forces:

$$\Delta \varepsilon_e = p_i \Delta v_e. \quad (1)$$

The molecular mobility typical of delocalized atoms is determined by the fluctuation volume fraction in an amorphous compound (ΔV_e) as

$$f = \frac{\Delta V_e}{V}, \quad \Delta V_e = N_e \Delta v_e,$$

where N_e is the number of delocalized atoms, and V is the volume of an amorphous compound.

In the model of delocalized atoms, the glass transition of a liquid is explained by a drop in the fluctuation volume fraction to a certain minimum value f_g , at which the delocalization of an atom is frozen (stopped) [4, 5]:

$$f_g = \left(\frac{\Delta V_e}{V} \right)_{T=T_g} \approx \text{const} \approx 0.020 - 0.030. \quad (2)$$

Here, T_g is the glass transition temperature corresponding to ultimate viscosity $\eta_g \approx 10^{12}$ Pas. The relative number of delocalized (bridging) atoms N_e/N responsible for the viscous flow of glass-forming melts above T_g falls to a negligible value of $\sim 3\%$ in the glass transition range, which is equivalent to freezing. The delocalization of an atom gradually speeds up as the glass is heated in the region of its softening, and the number of delocalized atoms grows from few in the frozen state to their concentration corresponding to a liquid.

The delocalization energy of an atom is normally calculated using the formula (where R is the universal gas constant) [4]

$$\Delta \varepsilon_e = RT_g \ln(1/f_g). \quad (3)$$

For the example of alkali-silicate glasses, for which $T_g \approx 700$ K and $f_g \approx 0.025$, we have

$$\Delta \varepsilon_e \approx 21 \text{ kJ/mol}. \quad (4)$$

At first glance, it appears from Eq. (3) that this value of $\Delta \varepsilon_e$ corresponds only to glass transition temperature T_g , and it must differ from the values at T_g for a different temperature. However, it follows from definition (1) that the delocalization energy of an atom must remain constant in a rather wide range of temperatures, since elementary

volume Δv_e is determined by the volume of a bridging atom ($\Delta v_e \approx \text{const}$), and internal pressure p_i is governed by the short-range order ($p_i \approx \text{const}$).

To reach our objective, let us use the equation for the free activation energy of the viscous flow of a glass-forming liquid $\Delta F_\eta(T)$ [6]

$$\Delta F_\eta = \Delta F_\infty + RT \left[\exp\left(\frac{\Delta \varepsilon_e}{RT}\right) - 1 \right], \quad (5)$$

where ΔF_∞ is the potential for the migration of an atom (a kinetic unit) to a new position, and the second summand represents the local structural transformation potential $\Delta F_s(T)$

The idea of dividing the free activation energy $\Delta F_\eta(T)$ into two components, one of which is constant and the other is a function of the temperature and represents the energy required to change the mutual orientation of groups of atoms, was suggested by Filipovich and Kalinina [3]. This idea has gained further development in the Nemilov valence-configuration theory [3] for the viscous flow of a glass-forming melt. In contrast to Eq. (5), give no explicit form of the temperature dependence of the second summand in the formula for the free flow activation energy. Equation (5) was derived by assuming [6] that the probability of the transition of kinetic unit W from one equilibrium position to another is determined primarily by the probability of a local transformation in the structure of kinetic unit W_1 , and then by probability W_2 that it has sufficient energy ΔF_∞ for migration to a new position; i.e., $W = W_1 W_2$. A local structural transformation upon the activation of the viscous flow of a glass-forming melt is described as the delocalization of an atom due to the displacement of neighboring particles and the transformation of their configuration.

Atomic delocalization energy $\Delta \varepsilon_e$ in Eq. (5) acts as a constant at least in the temperature regions where this relationship describes temperature dependence $\Delta F_\eta(T)$. To confirm this (and thus validate Eq. (5)), we express $\Delta \varepsilon_e$ from Eq. (5) as

$$\Delta \varepsilon_e = RT \ln \left(\frac{\Delta F_\eta - \Delta F_\infty}{RT} + 1 \right) \quad (7)$$

and perform our calculations in a wide range of temperatures. To calculate $\Delta \varepsilon_e$ by this equation, we must know parameters $\Delta F_\eta(T)$ and ΔF_∞ . The free activation energy of a viscous flow can be determined from the familiar Eyring equation and viscosity $\eta(T)$ as

$$\Delta F_\eta = RT [\ln \eta(T) - \ln \eta_0] \quad (8)$$

Preexponential factor η_0 is found by extrapolating viscosity curve $\log \eta - 1/T$ to elevated temperatures $T \rightarrow \infty$ using the Lagrangian polynomial in.

Atom migration potential ΔF_∞ represents the hightemperature limit of free flow activation energy $\Delta F_\infty = \Delta F_\eta(T \rightarrow \infty)$ and does not depend on the temperature. It can be calculated from parameters C_1 and C_2 of the Willams-Landel-Ferry (WLF) equation [7] describing the temperature dependence of viscosity $\eta(T)$ (and the relaxation time) in the glass transition region, i.e.,

$$\Delta F_\infty = RC_1 C_2 \quad (9)$$

The WLF equation parameters for sheet silicate glass are $C_1 = 36.5$ and $C_2 = 305$ K, which yield atom migration potential

$$\Delta F_\infty = 92.6 \text{ kJ/mol}. \quad (10)$$

The error in calculating ΔF_η and ΔF_∞ is $\sim 3\text{--}4\%$ (Table).

Table

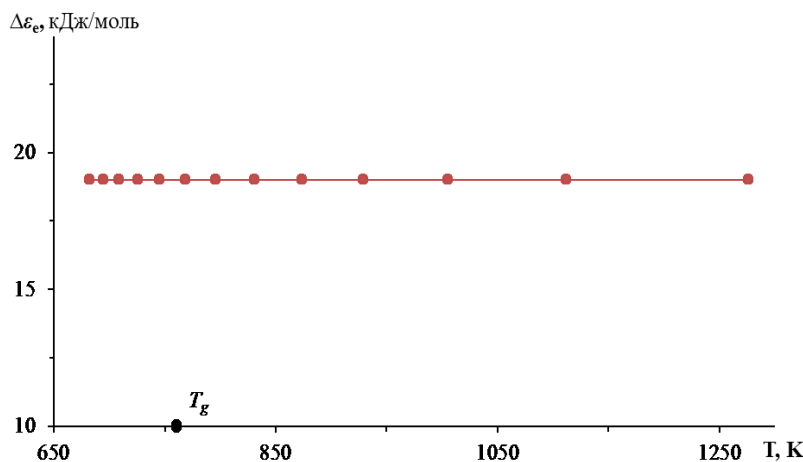
Free viscous flow activation energy and atomic delocalization energy $\Delta \varepsilon_e$
in sheet silicate glass*

T, K	log η [P]	log(η/η_0)	ΔF_η	$\Delta \varepsilon_e$
			kJ/mol	
778	15,5	17,47	262	21
787	15	16,97	257	21
805	14	15,97	247	21
816	13,5	15,47	243	21
825	13	14,97	238	21
846	12	13,97	226	21
873	11	12,97	218	21
906	10	11,97	209	21
944	9	10,97	199	21
988	8	9,97	190	21
1039	7	8,97	180	21
1103	6	7,97	169	20
1191	5	6,97	160	20
1313	4	5,97	152	20
1481	3	4,97	142	20
1578	2,5	4,47	136	19

Free viscous flow activation energy and atomic delocalization energy $\Delta \varepsilon_e$ in sheet silicate glass*

Substituting $\Delta F_\eta(T)$ and ΔF_∞ from Eqs. (8) and (10), respectively, into Eq. (7), we calculated atomic delocalization energy $\Delta \varepsilon_e(T)$ for this glass in the temperature range of 778–1578 K. As can be seen from the table, energy $\Delta \varepsilon_e$ required for the delocalization of an atom proves to be constant ($\Delta \varepsilon_e \approx 21$ kJ/mol) in the glass transition region ($T_g = 807$ K) over a rather wide range of temperatures, in satisfactory agreement with calculations using Eq. (3) (see Eq. (4)). The value of $\Delta \varepsilon_e$ falls slightly, from 21 to 19 kJ/mol, but at much higher temperatures (1100–1160 K) (Table). It seems that the short-range order starts to change at such elevated temperatures, reducing internal pressure p_i in the formula for atomic delocalization energy $\Delta \varepsilon_e$ (Eq. (1)).

Similar results were obtained for PbO–SiO₂ leadsilicate glass with 49.54 mol % of PbO [13]. The atomic delocalization energy for this glass remains constant ($\Delta\varepsilon_e \approx 19$ kJ/mol) over a wide range of temperatures (682–1276 K) (see figure). The characteristics of this glass are $T_g = 676$ K, $\log \eta_g[\text{P}] = 13.8$, $\Delta F_\infty = 50.2$ kJ/mol, $\log \eta_0[\text{P}] = -3.2$, $C_1 = 36.9$ and $C_2 = 163.4$ K.



Atomic delocalization energy in lead-silicate glass as a function of temperature [13]

Conclusions

Atomic delocalization energy $\Delta\varepsilon_e$ in glasses of silicate and its melts is virtually independent of temperature in a rather wide range in the glass transition region. We believe such constancy in the value of $\Delta\varepsilon_e$ is also typical of other amorphous compounds. It follows that energy $\Delta\varepsilon_e$, calculated using the model of delocalized atoms (Eq. (3)), is valid not only at the glass transition temperature, but at other temperatures of the above region as well.

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ЭНЕРГИЯ АТОМНОГО СМЕЩЕНИЯ В АМОРФНЫХ СОЕДИНЕНИЯХ

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Для многокомпонентного листового и свинцовосиликатного стекол проведен расчет энергии делокализации атома по данным о свободной энергии активации вязкого течения. Результаты показали, что величина энергии делокализации атома остается постоянной в достаточно широком интервале температур в области стеклования. Полученные результаты находятся в удовлетворительном согласии с расчетом величина энергии делокализации по используемой в настоящее время формуле, куда входят температура стеклования и доля флуктуационного объема, замороженная при этой температуре. Данный факт подтверждает представление о том, что указанная формула справедлива не только при температуре стеклования, но и в прилегающей к ней области температур.

Ключевые слова: атомная энергия смещения; область перехода стекла; аморфные соединения; свинцовосиликатные стекла; вязкость; флуктуационный объем; энергия делокализации атома.