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THEORETICAL INTERPRETATION OF ACTIVATION ENERGIES ASSOCIATED WITH THE GLASS TRANSITION, OBTAINED FROM TD OR DSC EXPERIMENTS

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Thermodilatometry (TD) and differential scanning calorimetry (DSC) experiments in the glass-transition region of different kinds of glasses have been simulated on a computer by means of a previously proposed theoretical free volume model. From the results obtained, the empirical procedures often used to obtain the values of "activation energies" associated with the glass transition are theoretically justified. Moreover, these "activation energies" are interpreted, in the framework of the model used, as average energies for the structural rearrangements in the glass.

The activation energy for structural rearrangement in a glass is generally widely distributed [1–3]. However, it is possible to define an average energy characteristic of these processes, starting from macroscopic measures such as those of viscosity. Like other physical magnitudes, this energy changes strongly in the region of temperature known as the glass transition. This region, which can be characterized by a temperature T_g, separates two possible states of the material. For temperatures higher than T_g the glass is in a metastable supercooled liquid state, while for temperatures lower than T_g a recently formed glass is in a solid-like unstable state. The former state is characterized by an excess of enthalpy and volume in relation to the metastable supercooled liquid state at the same temperature. The solid-like state can therefore undergo relaxation phenomena towards the metastable state corresponding to the supercooled liquid.

In the supercooled liquid state, structural rearrangements have a marked cooperative character, which is typical of the liquid state in general. Further, the temperature-dependence of magnitudes such as viscosity, η, the diffusion coefficient, D, or the characteristic time for structural rearrangements, τ, defined from η or D, are fitted by the Vogel–Fulcher [4] or Doolittle [5] expressions, i.e.

$$\eta(T) = \eta_0 \exp\left\{\frac{B}{T-T_0}\right\} \tag{1}$$

where η_0, B and T_0 are appropriate empirical parameters.

Expressions of form (1) allow us to define an apparent activation energy as

$$\langle E\rangle = \frac{\mathrm{d}\ln\eta(T)}{\mathrm{d}\,1/T} \tag{2}$$

which varies with temperature.

This kind of behaviour can be explained theoretically in the framework of free volume theories for molecular transport in dense liquids [6–9]. This theory predicts a behaviour for viscosity or for rearrangement time given by

$$\eta(T) = \eta_0 \exp\left(\frac{1}{f}\right) \tag{3}$$

where η_0 is a pre-exponential factor and f the average fractional free volume (for definition, see [7]), whose behaviour with temperature can be taken to a first approximation as

$$f = \alpha_f(T-T_0) \tag{4}$$

Here, α_f is the expansion coefficient for the average free volume and T_0 the temperature where f vanishes. With these idea, expression (3) becomes the Doolittle or Vogel–Fulcher empirical expressions.

Well below T_g, the material is in a solid-like state, so the motion of structural units would be localized and therefore thermally activated (constant activation energy) as in crystalline solids. These predictions are in good agreement with the results obtained in this temperature range ($T \ll T_g$) [10]. However, it is at temperatures near T_g that we may expect some cooperativity to take place in the structural motion, given that the material begins to relax towards the supercooled liquid state. This fact would explain the high apparent activation energy values that are generally obtained in this temperature region [11, 12].

On the other hand, TD and DSC are techniques widely applied to characterize the glass behaviour around T_g. From TD measurements the expansion coefficient $\alpha(T)$ can readily be obtained, while the parameter directly measured by DSC is the specific heat $C_p(T)$. Both $\alpha(T)$ and $C_p(T)$ show an increase in the glass transition region, T_g usually being defined as the temperature of the inflection point of the $\alpha(T)$ or $C_p(T)$ curve (see Fig. 2). Sub-T_g structural relaxation processes are commonly studied by means of the difference between two consecutive scans of TD or DSC, performed at the same heating rate but with different thermal histories [1, 13]. By this procedure, the difference between the expansion coefficients or the

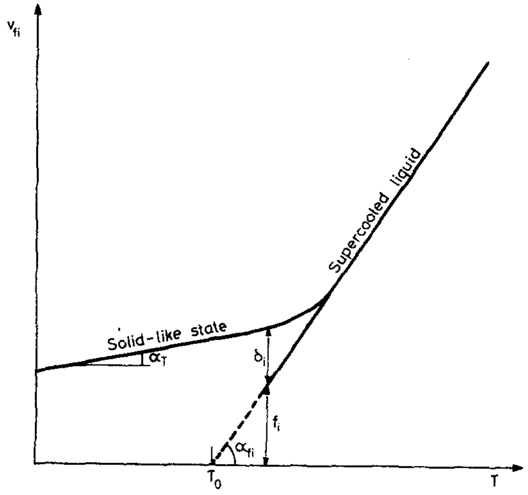

Fig. 1 Schematic plot of the temperature variation of the free volume in the *i*-region, showing the main parameters of the used model

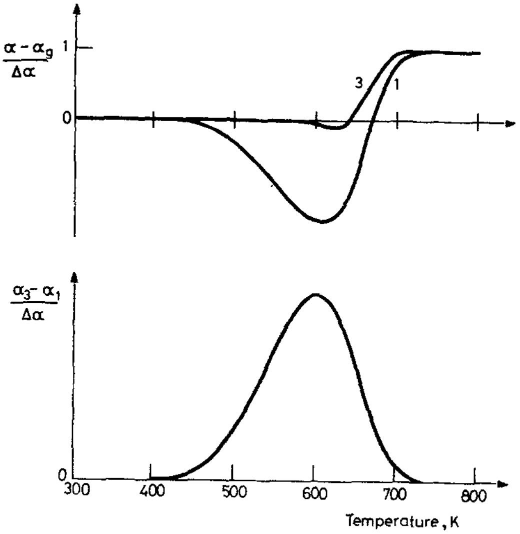

Fig. 2 Simulated curves obtained starting from metallic glass parameters with $\sigma = 0.2$, $q_c = 1$ K s^{-1} and $q_h = 0.1$ K s^{-1}. (a) Simulated scans of normalized expansion coefficient corresponding to steps 1 and 3 (see the text). (b) Curve obtained as the difference between the two scans of (a)

specific heats corresponding to the two experimental scans can be obtained. The resulting curves show a widely spread peak (see Fig. 2), which can easily be characterized by the temperature of the maximum, T_m. The shifts in the characteristic temperatures T_g and T_m when the heating rate is varied are habitually used empirically to obtain the "activation energy" corresponding to the glass transition or sub-T_g processes [14, 15]. Such a procedure however, is, seldom justified in the frame of any kinetic model for processes of structural rearrangements in glasses near T_g. Moreover, these processes are characterized by involving a wide distribution of relaxation times [1–3] and consequently of activation energies. This fact renders it even more difficult to interpret "activation energies" obtained empirically.

The aim of this work is to justify, from a theoretical point of view, the empirical procedures for obtaining the "activation energies", and also to find a physical meaning for the obtained values of these parameters.

For this purpose, typical TD or DSC experiments have been simulated on a desk computer by means of a theoretical model for structural rearrangements in glasses around T_g. This model has previously been proposed and successfully used for the interpretation of dielectric relaxation around the glass transition of polymeric glasses [16–18].

Theory

Free volume model for structural relaxation in glasses around the glass transition

The proposed model [16, 17] considers the glass as composed of N different kinds of infinitesimal, but macroscopic regions, understanding by macroscopic that each of these regions contains a large number of structural units. At temperatures higher than T_g, each of these regions has a volume and also a free volume, both depending only on the temperature at constant pressure. In this sense, the metastable supercooled liquid state can be considered a kind of equilibrium state, the problem of crystallization being disregarded. As a consequence, the free volume of the i-th region at temperatures higher than T_g will be referred to as the free volume at equilibrium, V_{eqi}. At temperatures below T_g, however, the free volume of this i-th region depends not only on the temperature at constant pressure, but also on the thermal history of the sample (annealing time even at room temperature, rate of glass formation, etc.). Hence, the unstable solid-like state of the i-th region can be considered an out-of-equilibrium state. The free volume of this i-th region at temperatures below T_g can therefore be expressed as $V_{\mathrm{fi}} = V_{\mathrm{exi}} + V_{\mathrm{eqi}}$. Here, V_{exi} is the excess free volume of the i-th region in relation to the supercooled liquid state extrapolated to this range of temperatures.

By using as normalization volume the total volume at equilibrium of the i-th region, $V_{\infty i}$, the fractional free volume at equilibrium can be defined as $f_i = V_{\mathrm{eqi}}/V_{\infty i}$. The variation with temperature of f_i is taken to a first approximation as:

$$f_i = \alpha_{fi}(T-T_0) \tag{5}$$

where α_{fi} is the expansion coefficient of free volume at equilibrium corresponding to the i-th region and T_0 is the temperature at which this volume vanishes (the model assumes that T_0 has the same value for all regions). In a similar way, we can define the fractional excess free volume of the i-th region as:

$$\delta_i = \frac{V_{\mathrm{exi}}}{V_{\infty i}} \tag{6}$$

This parameter will be one characterizing the out-of-equilibrium state of each region. The total fractional free volume of the i-th region is now expressed by $v_{fi} = f_i + \delta_i$. A schematic plot of the temperature behaviour of v_{fi} around the glass transition is shown in Fig. 1.

The model assumes that δ_i behaviour is described by the well-known kinetic equation of Kovacs and coworkers [19]:

$$\frac{\mathrm{d}\,\delta_i}{\mathrm{d}t} = -\frac{\delta_i}{\tau_i} - (\alpha_{fi} - \alpha_T)q \tag{7}$$

where q is the rate of temperature variation, α_T is the non-configurational component of the expansion coefficient of the free volume (equal to a first approximation for all the regions) and τ_i is the structural rearrangement time. The model takes τ_i as dependent on the free volume of the i-th region following the expression:

$$\tau_i = \tau_0 \exp\left\{\frac{1}{\alpha_{fi}(T-T_0)+\delta_i}\right\} \tag{8}$$

Under equilibrium conditions, $\delta_i = 0$ and τ_i takes after the Vogel–Fulcher or Doolittle expressions.

The distribution of relaxation times arises from the different values taken by the expansion coefficient of the free volume α_f in the different regions. The model assumes $1/\alpha_f$, which has energy dimensions, as distributed parameter. In this work, a Gaussian distribution function $\varphi(1/\alpha_f)$ has been used. As a consequence, a Gaussian-like distribution function of relaxation times $\varphi(\ln \tau)$ is obtained through expression (8). Under these conditions, the average fractional free volume at each temperature can be obtained as

$$\langle v_f(T)\rangle = \sum_{i=1}^{N} g_i\{\alpha_{fi}(T-T_0)+\delta_i\} \tag{9a}$$

where $g_i = \Phi(1/\alpha_{fi})\cdot\left(\frac{1}{\alpha_{fi+1}} - \frac{1}{\alpha_{fi}}\right)$ is the weight corresponding to discretization of the distribution function $\Phi\left(\frac{1}{\alpha_f}\right)$. Taking into account expression (8), $v_f(T)$ can also be expressed as

$$\langle v_f(T)\rangle = \sum_{i=1}^{N} g_i/\ln\frac{\tau_i}{\tau_0} \tag{9b}$$

The viscosity, the diffusion coefficient and the characteristic time for structural rearrangement mentioned in the introduction are defined in this model by expressions of the form

$$\tau = \tau_0 \exp\left\{\frac{1}{\langle v_f(T)\rangle}\right\} \tag{10}$$

where τ is related with τ_i through expression (9b). Expression (10) is similar to expression (3), but is now valid even out of equilibrium ($T < T_g$). Equation (10) allows us to define a mean activation energy

$$\langle E\rangle = K_B\frac{\mathrm{d}\ln\tau}{\mathrm{d}1/T} \tag{11}$$

So we have

$$\langle E\rangle = \frac{K_BT^2}{\langle v_f(T)\rangle^2}\frac{\mathrm{d}\langle v_f(T)\rangle}{\mathrm{d}T} \tag{12}$$

This equation can be written for the two different regions: equilibrium ($T > T_g$) and out-of-equilibrium ($T < T_g$). In the equilibrium region $\delta_i = 0$ and, in according with Eq. (9a), expression (12) becomes

$$\langle E\rangle = \frac{K_BT^2}{\langle\alpha_f\rangle(T-T_0)^2} \tag{13}$$

depending only on temperature.

In the out-of-equilibrium region, and according to expression (9a), we obtain

$$\frac{\mathrm{d}\langle v_f(T)\rangle}{\mathrm{d}T} = \sum_{i=1}^{N} g_i\left(\alpha_{fi} + \frac{\mathrm{d}\delta_i}{\mathrm{d}T}\right) \tag{14}$$

Making use of expression (7), this becomes

$$\frac{\mathrm{d}\langle v_f(T)\rangle}{\mathrm{d}T} = \sum_{i=1}^{N} g_i\left(\alpha_T - \frac{\delta_i}{\tau_i\cdot q}\right) \tag{15}$$

At temperatures well below T_g, where $\tau_i q \gg \delta_i$, expression (15) can be approximated by

$$\frac{\mathrm{d}\langle v_f(T)\rangle}{\mathrm{d}T} \simeq \alpha_T \tag{16}$$

and consequently

$$\langle E\rangle = \frac{K_B T^2 \alpha_T}{\langle v_f(T)\rangle^2} \tag{17}$$

In this case, $\langle v_f(T)\rangle$ and hence $\langle E\rangle$ depend not only on temperature, but also on the thermal history through the δ_i values (see expression 9a)).

Numerical simulation of DT or DSC measures

Starting from Eqs (7) and (8) with appropriate parameters and given a distribution function $\Phi\left(\frac{1}{\alpha_f}\right)$, it is possible to simulate TD experiments numerically near the glass transition for a glass. It is possible to describe DSC experiments, due to the fact that Eq. (7) remains valid on replacing δ_i by δ_{Hi} (defined as $\delta_{Hi} = H_i - H_\infty$ where H_∞ is the enthalpy of the glass at equilibrium) α_{fi} by C_{pi} and α_T by C_{pT}. In this case δ_{Hi} is a parameter with dimensions (cal. g^{-1}), related with δ_i by means of the following expression (see [20]):

$$\delta_{Hi} = \frac{\Delta C_p}{\Delta\alpha}\delta_i \tag{18}$$

where $\Delta\alpha$ and ΔC_p are, respectively, the configurational components of the expansion coefficient and the specific heat of the glass at equilibrium.

In the simulations performed in this work, data corresponding to volume parameters have been used and, consequently, the experiments actually simulated are TD experiments. Nevertheless, the results have been expressed in terms of normalized magnitudes $(\alpha-\alpha_g)/\Delta\alpha$, where α_g is the expansion coefficient of the material at temperatures well below T_g (glassy state). Accordingly, these results can also be considered valid for DSC experiments.

A numerical procedure of simulation has previously been described in [16, 17]. In this work, Gauss-like distribution functions $\Phi\left(\frac{1}{\alpha_f}\right)$ have been considered around a central value $\frac{1}{\alpha_{fm}}$ in the following way:

$$\Phi\left(\frac{1}{\alpha_f}\right) = \frac{1}{\sqrt{\pi}\sigma}\exp\left\{-\frac{1}{\sigma^2}\left(1-\frac{\alpha_{fm}}{\alpha_f}\right)^2\right\} \tag{19}$$

Simulations have been made for different values of distribution width given by σ. Standard values, similar to those reported in [13, 19, 21], corresponding to covalent semiconductor, organic polymer and metallic glasses, have been used as parameters of the model. These values are shown in Table 1.

Table 1 Characteristic values of the parameters of the model used in the simulations

Glass	α_{fm}, K^{-1}	α_T, K^{-1}	T_0, K	τ_0, s
Metallic	$2.8 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$	500	10^{-7}
Covalent semiconductor	$1.0 \cdot 10^{-4}$	$0.7 \cdot 10^{-4}$	200	10^{-13}
Organic polymer	$7.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$	350	10^{-13}

Table 2 Results obtained from simulation with parameters corresponding to a metallic glass. Relaxation times, τ_m and τ_g, are in seconds

σ	q_h, K/s	T_m, K	$\ln(\tau_m q_h)$	E_m, eV	$\langle E_m \rangle$, eV	T_g, K	$\ln(\tau_g q_h)$	E_g, eV	$\langle E_g \rangle$, eV
0	1	619	4.5	3.0	3.3	699	1.9	5.0	4.6
	0.32	605	4.5			688	1.8		
	0.1	593	4.6			678	1.7		
	0.032	582	4.6			669	1.6		
	0.01	571	4.7			661	1.5		
	0.0032	561	4.7			654	1.4		
0.1	1	630	4.4	3.7	3.4	689	2.4	5.2	5.0
	0.32	618	4.4			679	2.3		
	0.1	607	4.5			669	2.2		
	0.032	597	4.5			661	2.1		
	0.01	589	4.5			653	2.0		
	0.0032	581	4.5			646	1.9		
0.2	1	628	4.9	3.4	3.6	679	2.5	5.4	5.3
	0.32	615	5.0			669	2.4		
	0.1	603	5.2			660	2.3		
	0.032	593	5.3			655	2.0		
	0.01	584	5.4			644	2.2		
	0.0032	575	5.5			641	1.8		
0.3	1	618	6.0	3.2	3.5	672	2.5	5.5	5.4
	0.32	603	6.4			663	2.4		
	0.1	591	6.8			655	2.3		
	0.032	580	7.1			647	2.1		
	0.01	571	7.4			640	2.0		
	0.0032	562	7.8			634	1.9		

Table 3 Results obtained from simulation with parameters corresponding to a covalent semiconductor glass. Relaxation times, τ_m and τ_g, are in seconds

σ	q_h, K/s	T_m, K	$\ln(\tau_m q_h)$	E_m, eV	$\langle E_m \rangle$, eV	T_g, K	$\ln(\tau_g q_h)$	E_g, eV	$\langle E_g \rangle$, eV
0	1	487	4.1	1.5	1.7	515	1.1	2.6	2.5
	0.32	471	4.2			505			
	0.1	457	4.3			495	1.0		
	0.032	444	4.5			486	1.0		
	0.01	432	4.6			477	1.0		
	0.0032	420	4.6			469	1.0		
0.1	1	489	3.5	1.4	1.7	506	2.2	2.6	2.6
	0.32	471	3.9			496	2.1		
	0.1	455	4.2			486	2.0		
	0.032	441	4.5			477	1.9		
	0.01	429	4.6			468	1.9		
	0.0032	417	4.8			460	1.8		
0.2	1	475	4.2	1.4	1.7	499	2.2	2.5	2.5
	0.32	458	4.7			488	2.1		
	0.1	447	4.9			479	2.0		
	0.032	432	5.4			470	1.9		
	0.01	418	5.8			461	1.8		
	0.0032	407	6.2			454	1.7		
0.3	1	463	4.7	1.3	1.7	483	2.7	3.0	2.5
	0.32	445	5.4			476	2.3		
	0.1	430	6.1			470	2.0		
	0.032	415	6.8			464	1.6		
	0.01	403	7.4			454	1.6		
	0.0032	392	8.0			448	1.3		

The simulation has been performed in the following steps:

0 Formation of glass by cooling from the melt at a formation rate $q_f = 10^5$ deg s^{-1} for metallic glass, $q_f = 10^2$ deg s^{-1} for covalent glass and $q_f = 10$ deg s^{-1} for polymeric glass.

1 Heating up to $T > T_g$ at a constant rate q_h.

2 Cooling at a constant rate q_c down to room temperature.

3 Second heating at the same rate q_h.

The values q_h and q_c used in the three last steps are the same for the three kinds of glasses considered here.

The heating rates q_h employed are within the typical range of standard TD or DSC apparatus (0.1 up to 60 deg s^{-1}). These rates are always lower than those used in the simulation of the formation process (step 0).

By means of this procedure we obtain $\alpha_1(T)$ in step 1 and $\alpha_3(T)$ in step 3. Starting from these values, we may calculate $\alpha_3(T) - \alpha_1(T)$. The temperature T_g is

Table 4 Results obtained from simulation with parameters corresponding to a polymeric glass. Relaxation times, τ_m and τ_g, are in seconds

σ	q_h, K/s	T_m, K	$\ln(\tau_m q_h)$	E_m, eV	$\langle E_m\rangle$, eV	T_g, K	$\ln(\tau_g q_h)$	E_g; eV	$\langle E_g\rangle$, eV
0	1	384	4.1	3.1	3.3	398	1.1	9.8	10.0
	0.32	379	4.2			396	1.0		
	0.1	375	4.3			395	1.0		
	0.032	370	4.5			393	1.0		
	0.01	366	4.6			392	1.0		
	0.0032	362	4.6			390	0.9		
0.1	1	384	4.1	3.1	3.3	396	1.3	10.3	10.6
	0.32	379	4.2			394	1.2		
	0.1	375	4.4			393	1.1		
	0.032	370	4.5			391	1.0		
	0.01	366	4.6			390	1.0		
	0.0032	362	4.7			389	0.9		
0.2	1	383	4.3	3.2	3.4	394	1.1	10.6	11.4
	0.32	378	4.5			393	0.9		
	0.1	374	4.6			391	0.9		
	0.032	370	4.7			390	0.7		
	0.01	364	4.9			388	0.7		
	0.0032	362	5.0			387	0.6		
0.3	1	—	—	3.2	3.5	392	0.6	10.5	12.0
	0.32	378	4.4			390	0.6		
	0.1	374	4.7			389	0.4		
	0.032	369	5.0			388	0.0		
	0.01	365	5.2			386	0.2		
	0.0032	361	5.4			385	0.0		

calculated from the first scan as the inflection point of the curve $\alpha_1(T)$ in the region of transition. Temperature T_m is the temperature of the maximum of the curve, $\alpha_3(T)-\alpha_1(T)$. Figure 2 shows this procedure schematically by means of the normalized magnitudes $\left(\frac{\alpha-\alpha_g}{\Delta\alpha}\right)$ mentioned previously.

Results and conclusions

The results obtained by means of the simulation are given in Tables 2, 3 and 4. In these Tables, T_m and T_g are shown as "experimental" data (obtained from simulated curves) as functions of the heating rate q_h and for different widths of the distribution function $\Phi\left(\frac{1}{\alpha_f}\right)$ (different values of σ) within the range of values which

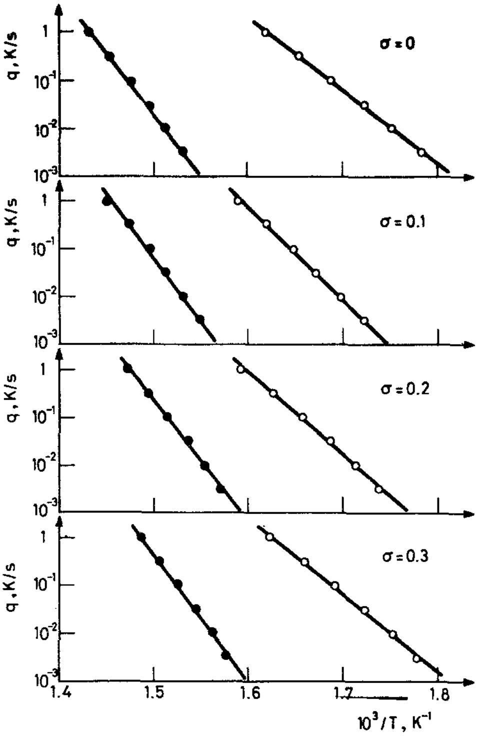

Fig. 3 Ozawa plots obtained by simulation from metallic glass parameters for the indicate σ values. Full points correspond to T_g while empty points correspond to T_m

may be expected in glasses. The Tables also give the values corresponding to $\ln(\tau_g q_h)$ and to $\ln(\tau_m q_h)$, where τ_g and τ_m are the average relaxation times in T_g and T_m, respectively. These values are calculated theoretically, starting from different values of $\langle v_f \rangle$ at points T_g and T_m, and from Eq. (10). $\langle E_g \rangle$ and $\langle E_m \rangle$ are the average theoretical values for the structural rearrangements in T_g and T_m, respectively (calculated from expressions (13) and (17)). Finally, E_m and E_g are the values for the "activation energy" obtained from the typical Ozawa plot [22] ($\ln q_h$ *vs.* $1/T_m$ or $1/T_g$).

From the values shown in Tables 2, 3 and 4, we may point out the following conclusions:

— The values of $\ln(\tau_g q_h)$ and $\ln(\tau_m q_h)$ are reasonably constant for each value of σ, being nearly independent of the value of q_h. This constancy weakens as the distribution width, σ, increases. It must be mentioned, however, that the value of the σ parameter $= 0.3$ can be taken as an extreme case.

— The condition expressed in the former point leads to Ozawa-like plots, approximately linear, even for extreme values of σ. These representations are shown in Fig. 3 for the metallic glass case. The "experimental" values of E_m and E_g in the Tables have been obtained from these plots.

— It may be noted that the values of E_m and E_g obtained of this procedure agree (within an error of about 10%) with the calculated average theoretical values $\langle E_m \rangle$ and $\langle E_g \rangle$. Moreover, the values hardly vary in the range of σ considered.

These points allow us finally to conclude that, within the validity of the proposed theoretical model, empirical procedures for obtaining "activation energy" in the neighbourhood of the glass transition are justified. Further, the physical meaning of these energies is that of average energy for the structural rearrangements in the glass. The values of $\langle E \rangle$ or E however, are, too high to correspond to independent thermally activated processes. Accordingly, these parameters should be considered as apparent activation energies characteristic of the cooperative molecular motions in the glass-transition region.

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Zusammenfassung — Thermodilatometrische (TD) und differential-scanningkalorimetrische (DSC) Experimente mit verschiedenen Arten von Gläsern im Glastransitionsbereich werden unter Verwendung eines Computers mittels des kürzlich vorgeschlagenen theoretischen Modells des freien Volumens simuliert. Aus den erhaltenen Ergebnissen geht hervor, daß die oft benutzten empirischen Prozeduren zur Bestimmung der sich auf die Glastransition beziehenden „Aktivierungsenergien" theoretisch gerechtfertigt sind. Diese „Aktivierungsenergien" werden im Rahmen des benutzten Modells als mittlere Energien für die strukturellen Umordnungen im Glas interpretiert.

Резюме — Термодилатометрические и ДСК измерения различных стекол в области температур стеклообразования были промоделированы на ЭВМ с помощью ранее предложенной модели теоретически свободного объема. Полученные результаты дали возможность теоретически обосновать эмпирические методы определения «энергий активации» процесса стеклообразования. Кроме того, в рамках использованной модели, такие «энергии активации» интерпретированы как средние энергии структурных преобразований в стекле.