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Viscosity in Disordered Media

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SUMMARY

The paper addresses the properties of glassforming melts in an attempt to predict the dependence of viscosity on temperature and on pressure. A review on the main viscosity models (free volume model, the Adam & Gibbs model etc.) is given. It is demonstrated that the activation energy can be expressed through the glass transition temperature T_g . The main attention is concentrated on the *jump frequency model* of Avramov & Milchev, the **AM** model. According to it, viscosity \mathbf{h} depends on the entropy S of the system and through it on temperature and on pressure. The viscosity

equation $\mathbf{h}(P,T) = \mathbf{h}_\infty \exp \left[2.3(13.5 - \lg \mathbf{h}_\infty) \left(\frac{T_g(P)}{T} \right)^a \right]$, derived in the framework of this

approach, describes the plethora of experimental data, summarized in the article, with an accuracy, superior to that of the other models. It is demonstrated that the fragility power \mathbf{a} depends on heat capacity. Therefore, the composition dependence of \mathbf{a} is in agreement with Deby-Neumann law.

1. Introduction

Viscosity, or the internal friction during the motion of liquid, appears because various layers flow with different velocities and glide with respect to each other. Due to the attractive forces, the faster moving layers tend to carry with them the layers, which move at lower rate. In this way a friction between the adjacent layers appears, giving rise to irreversible conversion of a part of the energy of motion to heat, *i.e.* to dissipation of energy.

For a laminar flow, the Newton's law relates the frictional force f the surface undergoing friction A and the velocity gradient du/dx in direction perpendicular to flow direction through viscosity coefficient \mathbf{h} as follows:

$$f = \mathbf{h}A \frac{du}{dx} \quad (1)$$

where \mathbf{h} the dynamic viscosity is measured in [Pa.s] units, more popular is the old unity [Poise] = [dPa.s]. There is no time in Thermodynamics, therefore viscosity cannot be a pure thermodynamic variable and cannot be determined by pure thermodynamic methods, instead of this it is always determined in the framework of certain models. This rule is valid also for diffusion coefficients, for characteristic times etc. The use of models leads to some uncertainty. Thus, at least one order of magnitude difference appears between particular expressions relating viscosity, diffusion coefficient

and relaxation time. According to Stokes the friction coefficient F of particle of diameter d is related to viscosity as:

$$F = 3\boldsymbol{\rho}d\mathbf{h} \quad (2)$$

This equation gives the background for experimental determination of absolute value of viscosity. The self-diffusion coefficient D can be derived considering diffusion of molecules as a particular case of Brownian motion. Applying the Einstein's approach [1] the following relation is obtained

$$D = \frac{k_B T}{3\boldsymbol{\rho}d_o\mathbf{h}} \quad (3)$$

where d_o is the size of the building unit and k_B is Boltzmann constant. Hereafter we call the building units responsible for the motion "molecules", although strictly speaking, they could be sometimes different from molecules in chemistry notation. The absolute rate [2] theory gives:

$$D = \frac{k_B T}{d_o\mathbf{h}} \quad (4)$$

Similarity between Eqs.(3 and 4) is evident. However, the two models predict about one order of magnitude difference in the value of the self-diffusion coefficient. Further, one can use the Einstein's relation, connecting the mean square displacement and time

$$\bar{X}^2 = 2Dt \quad (5)$$

to determine the Frenkel's time [3] \mathbf{t}_R for the average displacement to distance d_o of one molecule

$$D = \frac{d_o^2}{\mathbf{t}_R} \quad (6)$$

The relationship between Frenkel's time and viscosity is easily obtained combining Eqs.(3, 6)

$$\mathbf{h} = \frac{k_B T}{3\boldsymbol{\rho}d_o^3} \mathbf{t}_R = \frac{RT}{3\boldsymbol{\rho}V_m} \mathbf{t}_R \quad (7)$$

where R is the ideal gas constant and V_m is the molar volume. A similar result

$$\mathbf{h} = \frac{k_B T}{d_o^3} \mathbf{t}_R = \frac{RT}{V_m} \mathbf{t}_R \quad (8)$$

is obtained if Eq.(4) is used instead of Eq.(3). It is a common assumption that relaxation proceeds as spatial rearrangement of molecules. Therefore, it is supposed that Frenkel's time is equivalent to relaxation time.

Maxwell law establishes relation between \mathbf{t}_R and \mathbf{h} through the elasticity modulus G as

$$\mathbf{h} = G_\infty \mathbf{t}_R \quad (9)$$

It is not clear what is elasticity modulus of a liquid. The experimental data on solid glassy state near the glass-transition temperature T_g give for elasticity modulus

$$G_\infty \sim 10^{10} [Pa]. \quad (10)$$

The value of $\frac{RT}{V_m}$ is about $10^8 Pa$. So, a discrepancy of about two orders of magnitude appears

between the expected values of $\frac{RT}{V_m}$ and G_∞ . It seems, this is because G of the liquid is lower than

that of the glass. Some typical viscosity values (see for instance Ref.[4]) are listed in Table 1 and compared to relaxation time.

Table 1: viscosity of some substances (see [4])

Substance	Viscosity h in [dPa.s]	Relaxation time t in [s]
Air at room temperature	$2 \cdot 10^{-4}$	
Water at room temperature	10^{-2}	
Motor Oil at room temperature	10	
Honey	10^2	
Andesite Lava	10^7 to 10^8	
Rhyolite Lava	10^{12} to 10^{13}	
Glass working point	10^4	
Glass flow point	10^5	
Glass softening point	$10^{7.6}$	
Glass dilatometric softening point	$10^{11.3}$	
annealing point	10^{13}	15 min = 900 s
Glass at glass-transition temperature	$10^{13.5}$	100 min = $6 \cdot 10^3$ s
Glass strain point	$10^{14.5}$	15h $\approx 5.4 \cdot 10^4$ [s] (initial strain is relaxed to 10%)
Solid like behaviour	$>10^{15}$	

According to Table 1 the value of $\frac{h}{t_R}$ varies between $5 \cdot 10^8$ and 10^9 [Pa]. To summarize: viscosity is proportional to relaxation time

$$h = G t_R \quad (11)$$

where the proportionality coefficient G , varying between 10^8 and 10^9 [Pa], is determined by different models as follows:

$$G = \begin{cases} \frac{RT}{3pV_m}, & \text{Frenkel's model} \\ \frac{RT}{V_m}, & \text{absolute rate theory model} \\ G_\infty, & \text{Maxwell's model} \end{cases} \quad (12)$$

Equation (11) reflects the first set of models in determining the relationship between the thermodynamic variables and viscosity. As soon as the time t_R depends on thermodynamic variables (like temperature T and pressure P) much stronger than G , a second set of models is needed in determining t_R while G is assumed a constant.

2. The temperature dependence of viscosity

The mode coupling theory [5-9] reveals the influence of the density fluctuations modes on viscosity. The motion of a particle transfers some energy to be redistributed among the surrounding

particles. It results in a density fluctuation modes with a given wave vector. The density correlation function $\mathbf{F}(t)$ is determined by the equation of motion

$$\ddot{\Phi} + \Omega^2 \Phi + \Omega^2 \int_0^t m(t-t') \dot{\Phi}(t') dt' = 0 \quad (13)$$

where \mathbf{W} is frequency. The memory kernel $m(t)$ reflects the collective effects arising from the cooperative motion of a particle and its surrounding. Some prove of the model comes from the molecular dynamic simulation of Roe [10]. He investigates the short time motion in polymer glass forming liquid. Unlike the small molecule liquids, no hopping is observed in this case.

Although the mode-coupling theory predicts properly the occurrence of the glass transition it still has long way to go in order to be become applicable in quantitative description. More successful are models considering viscosity as a thermally activated process, i.e. its temperature dependence is given [2] by the expression:

$$\mathbf{h} = \mathbf{h}_\infty \exp\left(\frac{E}{RT}\right) \quad (14)$$

Viscosity of glass-forming melts increases sharply when temperature T decreases. If the activation energy E of the viscous flow is temperature independent, the experimental data should give a straight line when plotted in Arrhenius coordinates, $\lg \mathbf{h}$ vs $1/T$. An example (according to Mazurin et al [11]) is shown in Fig.(1) for viscosity of a standard soda-lime silicate glass NBS710. Solid points represent equilibrium viscosity. Non-equilibrium viscosity, measured below the glass-transition temperature is given by the open points. If sample is annealed long time, viscosity steadily increases from that of the open points towards that of the solid points. Two important features are readily seen: first, below the glass transition temperature there appears a pronounced difference in the viscosity behavior of the non-equilibrium system and second: the experimental point do not give in Arrhenius coordinates a straight line even for equilibrium system. Therefore, one has to assume that, in general, the activation energy depends on temperature

$$E = E(T) \quad (15)$$

It seems that most of the contemporary models [8,9,12-14] are devoted to determination of the temperature dependence of the average value of the activation energy. Authors proposed a number of equations for the temperature dependence of viscosity. The best of them have three adjustable parameters, two of which are used to adjust $E(T)$ while the third one is for the preexponential constant \mathbf{h}_∞ .

One of the best known expressions is the empirical equation of Vogel-Fulcher –Tamman (VFT):

$$\mathbf{h} = \mathbf{h}_\infty \exp\left(\frac{B}{T - T_\infty}\right) \quad (16)$$

It is capable to describe viscosity data, varying over 10 orders of magnitude, with accuracy better than 10%. A similar expression is known, in polymer science, as equation of Williams-Landel-Ferry with an “universal” constant characteristic of the activation energy for chain motion (reptation) in the melt 6.280 kJ/mol and $T_\infty \approx T_g - 50K$. It is well known [15,16] that a single VFT equation cannot accurately describe viscosity at all temperatures. According to this equation, viscosity diverges for temperatures approaching T_∞ . Although viscosity is certainly finite, this is a minor problem because at low temperatures viscosity is very high and out of practical interest.

Cohen and Turnbull [12] developed the “*free volume*” model according to which the flow occurs by motion of molecules into some voids. Within certain approximation this approach leads to Eq.(16).

Macedo and Litovitz [13] determine the average activation energy from the probability of forming a hole. The values of parameters needed to fit the viscosity data were found [17] to be unrealistic.

It is logical to consider the motion as a cooperative process involving a simultaneous rearrangement of a large number of molecules. The Adam–Gibbs model [14] is based on the idea that motion occurs by internal cooperative rearrangement of independent regions of n molecules. When temperature decreases, the motion of one molecule disturbs an increasingly larger number n of its neighbors. Adam and Gibbs (**AG** model) assumes that the barrier of rearrangement is proportional to n , and determined the temperature dependence of n in terms of the configurational entropy, ΔS as follows:

$$\mathbf{h} = \mathbf{h}_\infty \exp\left(\frac{B}{T\Delta S}\right) \quad (17)$$

i.e. (see Eqs.(14,15) $\frac{E(T)}{R} = \frac{B}{\Delta S}$.

Although the Adam-Gibbs model fits well a large number of viscosity data on glassforming melts, it fails for others [9].

To move, the building units meet always the same activation energy barrier in the perfect crystal. In amorphous state there is a more or less broad distribution of the activation energy heights E . We already mentioned that motion occurs by cooperative rearrangement of several molecules. It seems that this is the reason why most of the models of viscosity determine the average value of the activation energy for a given set of parameters T , P , *etc.* However, this is a fallacy because the average jump frequency is not determined by the average value of the activation energy.

The Avramov & Milchev [18-21] model (**AM** model) determines the temperature dependence of the average jump frequency of molecules and, through it, the viscosity. For the details of the model see Appendix 1. The main assumption is that, because of the existing disorder, the activation energy barriers of different height appear. The width ΔS of the distribution function barriers heights depends on entropy. Therefore viscosity is a function of entropy S of the system according to equation

$$\lg \mathbf{h} = \lg \mathbf{h}_\infty + \left(\lg \frac{\mathbf{h}_g}{\mathbf{h}_\infty} \right) \exp\left[-\frac{2(S - S_g)}{ZR} \right] \quad (18)$$

where a certain reference state is denoted with subscript g . We choose as reference state the glass transition temperature T_g . It is well known that the experimentally determined glass transition temperature depends on the measured property as well as on the heating (or cooling) rate. Here, for T_g , we adopt the temperature at which viscosity is $\mathbf{h}_g = 10^{13.5}$ [dPa.s]. Therefore, in Eq.(18) S_g is the equilibrium entropy at T_g while $Z/2$ is the number of escape channels available for the moving particle. Note that T_g is always in the glass-transition interval and, therefore, it has a value close to that of the experimentally determined glass-transition temperature (within $\pm 2\%$ of accuracy). Equation (18) relates viscosity to the entropy of the system. Unlike most of the recent approaches (see [20-22] and literature cited there) \mathbf{h} depends on the whole entropy, not on the configuration entropy only. Therefore, the viscosity does not diverge at the Kauzmann temperature T_K , although it is becoming extremely high. Eq.(18) is a double exponential function on entropy. This, quite

unpleasant situation, is surmounted by taking into account that entropy is a logarithmic function on temperature. Therefore the temperature dependence of equilibrium viscosity (see Attachment 1) is given by

$$\mathbf{h} = \mathbf{h}_\infty \exp \left[2.3(13.5 - \lg \mathbf{h}_\infty) \left(\frac{T_g}{T} \right)^a \right] \quad (19)$$

where the "fragility" parameter α in stands for:

$$\mathbf{a} = \frac{2C_p}{ZR} \quad (20)$$

Here C_p is the average molar heat capacity in $\left[\frac{J}{K.mol} \right]$ units. Note that $\lg \frac{\mathbf{h}_g}{\mathbf{h}_\infty} = 13.5 - \lg \mathbf{h}_\infty$

3. Activation energy and glass-transition temperature.

The main advantage in defining T_g as the temperature at which $\mathbf{h}_g = 10^{13.5} [dPa.s]$ is that the activation energy $E(T_g)$ is a simple function of T_g . Thus, from the general expression given by Eqs.(14,15) one obtains

$$E(T_g) = 2.3(13.5 - \lg \mathbf{h}_\infty) RT_g \quad (21)$$

Equation (21) permits to resolve only the value of activation energy at T_g . Determination of the activation energy in the whole temperature range requires a detailed model of viscosity, for instance this is possible using one of the **VFT**, **AG** or **AM** approaches. On the other hand, Eq.(21) is valid for all these models since they are particular cases of Eqs.(14,15). This permits us to determine, in terms of T_g , both the temperature dependence of the activation energy and the temperature function of viscosity. In the case of the **VFT** equation(16) they are:

$$E(T) = 2.3(13.5 - \lg \mathbf{h}_\infty) \frac{T_g - T_\infty}{T - T_\infty} RT \quad (22)$$

and

$$\lg \mathbf{h} = \lg \mathbf{h}_\infty + 2.3(13.5 - \lg \mathbf{h}_\infty) \frac{T_g - T_\infty}{T - T_\infty} \quad (23)$$

In the case of the **AG** model (Eq.(17)) the corresponding expressions become:

$$E(T) = 2.3(13.5 - \lg \mathbf{h}_\infty) \frac{T_g \mathbf{DS}_g}{T \mathbf{DS}} RT = 2.3(13.5 - \lg \mathbf{h}_\infty) \frac{\ln \frac{T_g}{T_\infty}}{\ln \frac{T}{T_\infty}} RT_g \quad (24)$$

respectively

$$\mathbf{h} = \mathbf{h}_\infty \exp \left(2.3(13.5 - \lg \mathbf{h}_\infty) \frac{T_g \mathbf{DS}_g}{T \mathbf{DS}} \right) = \mathbf{h}_\infty \exp \left(2.3(13.5 - \lg \mathbf{h}_\infty) \left(\frac{T_g}{T} \right)^{\left(\frac{\ln \frac{T_g}{T_\infty}}{\ln \frac{T}{T_\infty}} \right)} \right) \quad (25)$$

In the case of the **AM** model, Eq.(19) gave already the temperature dependence of viscosity in T_g terms. As for the activation energy, it becomes

$$E(T) = 2.3(13.5 - \lg \mathbf{h}_\infty) \left(\frac{T_g}{T} \right)^a RT \quad (26)$$

Note that Eq.(19) always describe the experimental data with equal or superior accuracy as compared to Eqs.(23,25) (see for instance [23]).

Empirically, Angell et al separate glasses to strong one and fragile one (see for instance [24]). The “strong” glasses do not change structure with increasing temperature. Therefore, these systems have relatively low heat capacity and the activation energy for viscous flow is not sensitive to temperature changes. On the other side are “fragile” glasses with a “weak” structure that easily changes with temperature. They have high heat capacity and the activation energy changes with temperature. To account for the fragility the authors [24] formulated the steepness index or fragility index m as follows

$$m = \left. \frac{d \log \mathbf{h}}{d(T_g / T)} \right|_{T_g} \quad (27)$$

It is a popular fallacy that the activation energy in the glass transition region can be determined experimentally as equal to $E(T_g) = mRT_g$ because the slope m depends on $E(T)$ as well as on its first derivative $\frac{\partial}{\partial(T_g / T)} E(T)$. Thus in the case of **AM** model, Eq.(19), the slope m is

$$m = a2.3(13.5 - \lg \mathbf{h}_\infty) \quad (28)$$

A comparison with Eq. (21) (see also Eq.(26)) yields

$$E(T_g) = \frac{mRT_g}{a} \quad (29)$$

3. Viscosity of nonequilibrium systems

In the glass-transition region the experimental time scale becomes comparable with the time scale for structural rearrangements. The relaxation time increases sharply upon further cooling. In this way, the structure is fixed so that the system turns into a nonequilibrium state. Therefore, an additional internal parameter is needed to describe it. For this reason Tool and Eichlin [25] introduced the so-called "fictive" or "structural" temperature T_f . This is the temperature at which the system with a given structure will be in equilibrium. At temperatures lower than T_f the configurational entropy \mathbf{DS} is fixed (i.e. the configurational part \mathbf{DC}_p of the heat capacity vanishes)

Eqs.(17,18) give the dependence of viscosity on the entropy. Therefore, both the **AG** approach as well as the jump frequency **AM** model are capable to describe the temperature dependence of viscosity of both equilibrium and nonequilibrium glasses (see Fig.1).

Basically, the entropy of undercooled melts splits into two parts: configuration entropy \mathbf{DS} , and vibration entropy S_{vibr} . Respectively, the heat capacity of undercooled melts is $C_p = \mathbf{DC}_p + C_{gl}$. According to Eq.(17) in Arrhenius coordinates the slope L_e of $\log \mathbf{h}$ against $1/T$ is

$$L_e = \frac{B}{2.3\mathbf{DS}} \left(1 + \frac{\mathbf{DC}_p}{\mathbf{DS}} \right) \quad (30)$$

If configurational entropy is fixed the nonequilibrium viscosity will have, in the same coordinates, a slope L_g equal to

$$L_e = \frac{B}{2.3DS} \quad (31)$$

so that the ratio of the two slopes should be

$$\frac{L_e}{L_g} = 1 + \frac{DC_p}{DS}. \quad (32)$$

A similar logic can be applied and for the **AM** model. At temperatures under T_f the entropy S can be determined as

$$S(T) = S_g + C_p \ln\left(\frac{T_f}{T_g}\right) + C_{gl} \ln\left(\frac{T}{T_f}\right) \quad (33)$$

Taking into account Eqs.(18,33) the nonequilibrium viscosity is given by:

$$\mathbf{h} = \mathbf{h}_\infty \exp\left[2.3(13.5 - \lg \mathbf{h}_\infty) \left(\frac{T_g}{T_f}\right)^a \left(\frac{T_f}{T}\right)^g\right] \quad (34)$$

The dimensionless power \mathbf{g} is proportional to the ratio of the heat capacity C_{gl} of the glass and the heat capacity of the undercooled melt C_p .

$$\mathbf{g} = \mathbf{a} \frac{C_{gl}}{C_p} \quad (35)$$

In agreement with experimental evidence, the model predicts that in Arrhenius coordinates (see Fig.1), the ratio between the slopes of the lines of nonequilibrium and equilibrium viscosity, is equal to the ratio $\frac{C_{gl}}{C_p} = \frac{C_p - DC_p}{C_p}$ at the break point T_f . In Fig.1, lines are drawn according to Eq(34)

with $\lg \mathbf{h}_\infty = 1.28$; $T_g = 801$ K; $T_f = 806$ K; $\mathbf{a} = 3.7$ and $\mathbf{g} = 1.7$, i.e. $\frac{C_{gl}}{C_p} \approx 0.46$.

4 Correlation between adjustable parameters of viscosity equations

The power \mathbf{a} serves as a measure for the “fragility” of glasses. “Strong” are glasses with $\mathbf{a} \gg 1$. “Fragility” increases simultaneously with \mathbf{a} . Moreover, it was demonstrated (see Eq.(20)) that \mathbf{a} is proportional to heat capacity. In terms of the **AM** model the effective value of activation energy responsible for the viscous flow is accounted for by T_g . In terms of the **VFT** model, fragility could be accounted for by the $\frac{T_\infty}{T_g}$ value. For $\frac{T_\infty}{T_g} \rightarrow 0$ the systems are strong while for $\frac{T_\infty}{T_g} \rightarrow 1$ they become very fragile. It is a popular fallacy that, in the **VFT** model, the activation energy is accounted for by the parameter B . We already demonstrated (see Eq.(30)) that B is a complicated parameter accounting for “fragility” to much greater extent. Actually, the parameter that accounts for the activation energy in all models is the glass-transition temperature.

In all models the preexponential constant, if viscosity is measured in $[dPa.s]$ units, is given (see Eq.(12)) by

$$\mathbf{h}_\infty = 10G\mathbf{t}_\infty \quad (36)$$

where the vibration time $\mathbf{t}_\mathbf{v}$ is equal to relaxation time at extremely high temperatures. The vibration frequency of a single atom is about $\frac{k_B T}{h} \approx 10^{13} \text{ s}^{-1}$, predicting $\lg \mathbf{h}_\mathbf{v} \gg -4$ [dPa.s]. However, the building unit responsible for relaxation process consists of a number of atoms and, therefore, it has much larger vibration time (resp. lower vibration frequency). Therefore the rule could be reformulated as $\lg \mathbf{h}_\mathbf{v} \approx -4$. Table 2 summarizes data for the values of adjusting parameters, for many glassforming melts. Parameters are determined to describe, by means of Eq.(19) the existing experimental data ([23,26-34] and literature cited there). It is seen that $\lg \mathbf{h}_\mathbf{v} = 0 \pm 1.6$ [dPa.s].

Although T_g is considered as free parameter in both **AM** and **VFT** models, it can vary in a limited range as it must be equal to the glass-transition temperature within 2% of accuracy. It is frequently assumed that the third adjustable parameter, T_p , of the **VFT** model has a value close to the Kauzmann temperature T_0 (see chapter 2). As for the third adjustable parameter in the **AM** model (Eq.(19)), it was demonstrated [28] that $\mathbf{a} \approx \frac{C_p}{10}$ if C_p is measured in [cal/K.mol], i.e. the number of escape channels is $Z=10$. This is seen well in Fig.2 where existing experimental data (see Table 2) of α are plotted against heat capacity.

The ability of **AM** model to describe temperature dependence of viscosity is illustrated in Fig.3 where data on temperature dependence of viscosity of lead silicates [29] are compared with the theory. The lines are a fit to each set of data according to Eq.(19) with the values of adjustable parameters given in Table 2.

In general, the value of α increases simultaneously with the concentration of modifying oxides in the glass. This can be explained easily in terms of Eq.(20) by taking into account that heat capacity depends on composition. According to Deby-Neumann law the heat capacity $C_p(x)$ of composition with molar fraction x of modifying oxides is

$$C_p(x) = C_p(0) + 3RxZ \quad (37)$$

where $C_p(0)$ is the heat capacity of the pure network former. Considering Eq.(37) remember that the number of escape channels Z is in fact the degeneracy of the system. Accordingly, the fragility parameter $\mathbf{a}(x)$ can be expressed through the fragility parameter of the pure network former $\mathbf{a}(0)$ as follows:

$$\mathbf{a}(x) = \mathbf{a}(0) + \frac{2 \cdot 3RxZ}{RZ} = \mathbf{a}(0) + 6x \quad (38)$$

Fig.4 shows the data for α against the molar fraction x of modifying oxides in glasses. Note that data on each α value are obtained as adjustable parameters to the corresponding viscosity data, independent on the other ones. The straight line with a slope of 6 is a good prove for the model.

Table 2 Viscosity parameters

Substance	$h = h_{\infty} \exp \left(2.3(13.5 - \lg h_{\infty}) \left(\frac{T_g}{T} \right)^{\alpha} \right)$		
	$\lg h_{\infty} [dPas]$	T_g (K)	α
SiO ₂	-3.85	1425	1.22
Li ₂ O.2SiO ₂	0.96	719	3.43
2 Li ₂ O.8 SiO ₂	0	734	2.25
3Li ₂ O.7 SiO ₂	0 .53	708	3
0.05Na ₂ O.0.95SiO ₂	-3.8	911	1.3
0.13Na ₂ O.0.875SiO ₂	-2.7	839	2
Na ₂ O. 3SiO ₂	0.5	706	2.5
Na ₂ O.2SiO ₂	0.6	731	2.5
15Na ₂ O. 85SiO ₂	0	776	2.15
2 Na ₂ O.8 SiO ₂	0 .1	735	2.27
3Na ₂ O.7SiO ₂	0.65	711	2.85
3.3Na ₂ O.6.7SiO ₂	0.4	705	2.8
4 Na ₂ O.6 SiO ₂	0.57	678	3
44Na ₂ O.56SiO ₂	0.28	655	2.9
Na ₂ O. SiO ₂	0.25	825	4
2 K ₂ O.8SiO ₂	0 .84	751	2.5
3 K ₂ O.8SiO ₂	1.37	703	3
BaO.2SiO ₂	-1.5	962	3.25
3 PbO.7SiO ₂	0 .66	743	3
3.5 PbO.6.5SiO ₂	0.53	754	3.25
4 PbO.6SiO ₂	0 .24	712	3.5
4.6 PbO.5.4SiO ₂	0.32	673	3.8
PbO. SiO ₂	-0.03	659	4
5.5 PbO.4.5SiO ₂	-0.2	635	4.3
6PbO.4SiO ₂	-0.3	627	4.9
97 8B ₂ O ₃ 2 17SiO ₂	1.38	520	3.25
94B ₂ O ₃ 5 95SiO ₂	1.29	525	3
89 3B ₂ O ₃ 10 7SiO ₂	1.45	527	3
51 6B ₂ O ₃ 48 4SiO ₂	0.6	582	1.5
44 6B ₂ O ₃ 55 4SiO ₂	-0.02	682	1
B ₂ O ₃	0.95	511.5	2.75
13 5Na ₂ O.86 5B ₂ O ₃	-0.7	695	4.25
33 3Na ₂ O 66 7B ₂ O ₃	-1.5	744	4.5
6Li ₂ O.94B ₂ O ₃	0.1	612	4
13.9Li ₂ O.86.1B ₂ O ₃	-0.2	695	4.7
33.5Li ₂ O.66.5B ₂ O ₃	-1.6	754	4.7
19.5K ₂ O.80.5B ₂ O ₃	-0.16	675	4
24.4K ₂ O.75.6B ₂ O ₃	0	677	4
18BaO.82B ₂ O ₃	-0.97	790	4
23.9BaO.76B ₂ O ₃	-0.9	826	4.5
33PbO. 67 B ₂ O ₃	-2.9	718	4

PB ₂ :PbO.2 B ₂ O ₃	0.09	780	9.5
P ₂ O ₅	-4.87	522	1
Li ₂ O. P ₂ O ₅	0.14	580	5.4
Na ₂ O. P ₂ O ₅	0.43	544	5.5
GeO ₂	1.34	923	1.4
5Na ₂ O.95GeO ₂	0.11	695	2.25
10Na ₂ O.90GeO ₂	-0.13	743	4.5
29.6Na ₂ O.70.4GeO ₂	0.43	710	6.5
20PbO.80GeO ₂	0.33	716	4.25
30PbO.70GeO ₂	0.66	679	6.25
40PbO.60GeO ₂	0.25	715	5
50PbO.50GeO ₂	0.33	626	5.25
20.96Na ₂ O.9CaO.70SiO ₂	0.22	775	2.83
21Na ₂ O.9CaO.70SiO ₂	0.8	777	3.2
19Na ₂ O.9CaO.72SiO ₂	0.4	784	2.9
21Na ₂ O.7CaO.72SiO ₂	0.5	769	2.9
Na ₂ O.2CaO.3SiO ₂	-2.57	821	2.77
2Na ₂ O.1CaO.3SiO ₂	-4.54	742	3.2
CaO. Al ₂ O ₃ . 2SiO ₂	-2.06	1105	3.5
(CaO) _{0.423} (Al ₂ O ₃) _{0.083} (SiO ₂) _{0.494}	-0.7	1043	4.18
(CaO) _{0.439} (Al ₂ O ₃) _{0.083} (SiO ₂) _{0.456}	-0.7	1057	4.36
(CaO) _{0.461} (Al ₂ O ₃) _{0.105} (SiO ₂) _{0.413}	-0.7	1065	4.4
(CaO) _{0.479} (Al ₂ O ₃) _{0.127} (SiO ₂) _{0.373}	-0.7	1075	4.61
(CaO) _{0.505} (Al ₂ O ₃) _{0.147} (SiO ₂) _{0.330}	-0.7	1084	4.62
(CaO) _{0.351} (Al ₂ O ₃) _{0.164} (SiO ₂) _{0.498}	-0.7	1066	3.83
(CaO) _{0.385} (Al ₂ O ₃) _{0.151} (SiO ₂) _{0.441}	-0.7	1075	4.05
(CaO) _{0.405} (Al ₂ O ₃) _{0.174} (SiO ₂) _{0.395}	-0.7	1089	4.25
(CaO) _{0.427} (Al ₂ O ₃) _{0.225} (SiO ₂) _{0.348}	-0.7	1093	4.4
(CaO) _{0.459} (Al ₂ O ₃) _{0.247} (SiO ₂) _{0.294}	-0.7	1104	4.56
(CaO) _{0.428} (Al ₂ O ₃) _{0.143} (SiO ₂) _{0.428}	0.88	1056	4.77
Na ₂ O. Al ₂ O ₃ . 6SiO ₂	-8.58	1012	1
2Na ₂ O.1CaO.3SiO ₂	-5.54	742.3	3.2
5Na ₂ O.10MgO.10Al ₂ O ₃ .75 SiO ₂	-1.77	1016	1.85
10Na ₂ O.10MgO.10Al ₂ O ₃ .70 SiO ₂	0.21	979	2.5
15Na ₂ O.10MgO.10Al ₂ O ₃ .65 SiO ₂	1.26	961	3.5
20Na ₂ O.10MgO.10Al ₂ O ₃ .60 SiO ₂	1.27	899	3.5
10Na ₂ O.10MgO.5Al ₂ O ₃ .75SiO ₂	0.4	933	2.42
10Na ₂ O.10MgO.80SiO ₂	-0.43	828.5	2
Albite	-1.7	1051	1.9
Haplogranite	-4.6	1081	1.36
Diopside CaMgSi ₂ O ₆	-1.07	974	3.5
Diopside 80 Anortite 20	-0.66	997	3.82
Diopside 64 Anortite 36	-0.03	1011	4.25
Diopside 40 Anortite 60	0.27	1034	4.31
Diopside 20 Anortite 80	0.23	1079	4.32

Anortite $CaAl_2Si_2O_8$	0.26	1126	4.53
Polystyrene	2.3	370	7
Glycerine	-2.2	177	3.2

5 The pressure dependence of viscosity

There are some cases when pressure dependence of viscosity is very important, although most of the glasses are processed at no or at moderate pressure. For instance, it could answer the question what is viscosity of Earth mantle. According to [35], mantle viscosity near 2000 km depth is 10^{21} [dPa.s]. The extremely high pressure there causes this. **If viscosity is that high, then is the mantle a glass?** If it is considered as solid amorphous body the answer is yes. On the other hand, the relaxation time, corresponding to 10^{21} [dPa.s], is about 10^4 years, a period quite large in comparison with the human lifetime but quite short in comparison with the age of the Earth. However, any distortion of the mantle appearing within the time of human history has not relaxed yet.

In order to find the pressure and temperature dependence of viscosity we have to introduce into Eq.(19) the explicit form of the pressure P dependence of entropy. According to Maxwell's law one has:

$$-\left(\frac{\mathcal{H}S}{\mathcal{H}P}\right)_T = \left(\frac{\mathcal{H}V}{\mathcal{H}T}\right)_P = \mathbf{k}V \quad (39)$$

where \mathbf{k} is the volume expansion coefficient. Although there are no data in the literature, it is reasonable to assume that at extremely high pressures \mathbf{k} will reduce in a somewhat inversely proportional to pressure P way, namely:

$$\mathbf{k} = \frac{1}{V} \left(\frac{\mathcal{H}V}{\mathcal{H}T}\right)_P \approx k_o \frac{P}{P+P} \quad (40)$$

where P is a constant and k_o is the volume expansion coefficient at no pressure. It follows (for details see Appendix 1) that pressure dependence of viscosity is given by

$$\mathbf{h} = \mathbf{h}_\infty \exp \left\{ 2.3(13.5 - \lg \mathbf{h}_\infty) \left(\frac{T_r}{T}\right)^a \left(\frac{\Pi + P}{\Pi + P_1}\right)^b \right\} \approx \mathbf{h}_\infty \exp \left\{ 2.3(13.5 - \lg \mathbf{h}_\infty) \left(\frac{T_r}{T}\right)^a \left(1 + \frac{P}{\Pi}\right)^b \right\} \quad (41)$$

where $\mathbf{b} = \frac{k_o V_m}{ZR} P = \mathbf{a} \frac{k_o V_m}{2C_p} P$. The value of \mathbf{k} , (and respectively the value of \mathbf{b}) could be

positive as well as negative. Water is the classical example of substance with negative thermal expansion coefficient (between $0^\circ C$ and $4^\circ C$). Many glasses are known with temperature independent density. Therefore, there are certain compositions for which viscosity does not increase with pressure (e.g. anhydrous andesitic melts viscosity is independent of pressure [30,31]). In terms of Eq. (41) this corresponds to zero or even negative thermal expansion coefficient (resp. $\mathbf{b} \leq 0$).

The glass transition temperature depends on pressure as follows:

$$T_g(P) = T_{g0} \left(1 + \frac{P}{\Pi}\right)^{b/a} \quad (42)$$

In Eq.(42) T_{g0} stands for the glass transition temperature at no pressure. With this notation the pressure and temperature dependence of viscosity keeps the form of Eq.(19)

$$\mathbf{h}(P,T) = \mathbf{h}_\infty \exp \left[2.3(13.5 - \lg \mathbf{h}_\infty) \left(\frac{T_g(P)}{T} \right)^a \right] \quad (43)$$

The model could become more sophisticated if the temperature dependence of compressibility coefficient is taken into account. So far, only the **AM** model describes the pressure dependence of viscosity. There are certain attempts to adapt the **AG** model to explain the pressure dependence of viscosity (see [32,33]). Still, there remains a problem because the Maxwell's law, i.e. Eq.(39), is valid for the whole entropy S , not necessarily for the configurational entropy DS .

There are just a few reliable experimental data concerning the pressure dependence of viscosity. The reason is that it is very difficult to construct an instrument capable to measure viscosity simultaneously at extremely high pressure and extremely high temperature for sufficiently long time to avoid non-equilibrium effects. Therefore, most of the data on the pressure dependence of viscosity are on organic materials as reported in Refs.[36-43]. Fig. 5 gives the pressure dependence of viscosity of *orto therphenyl* for temperatures given as parameter to each curve. The solid lines are according to Eq.(41) with values of \mathbf{b} and \mathbf{P} listed in Table 3. The experimental points are from Refs. [30,31,36-40]. It is seen that the ratio $\frac{\mathbf{b}}{\mathbf{a}} = \frac{k_o V_m \mathbf{P}}{2C_p}$ varies in a limited region. The temperature is given at each line. Note that after the \mathbf{P}, \mathbf{b} parameters were determined for the first of the curves, data at remaining temperatures were successfully described with not a single adjustable parameter.

Recently, an unexpected correlation was discovered (see Ref. [44]) between the extent of fragility and the Poisson ratio of the resulting glass. This finding could play an important role in better understanding the properties of undercooled systems.

It was demonstrated that the **AM** model is capable to describe with accuracy, superior to that of the other models, both the temperature and the pressure dependence of viscosity. Therefore, it is natural to ask: can it describe viscosity in the Earth bowels. There are experimental indications [45] hat viscosity of the mantle varies between 10^{21} and 10^{23} [Pa.s]. In addition, there is a pronounced low viscosity channel at about 250 km depths. The ability of the AM model (respectively Eq.(43) to describe the existing experimental data on viscosity of mantle deep in the Earth bowels was confirmed [46] when known [47] dependencies of pressure and of temperature on the depth in the Earth was introduced. Note that, with the values of viscosity experimentally observed [45], the relaxation time of the mantle is about 32 000 years, time suspiciously close to the period during which the direction of magnetic poles changes.

Table 3

Substance	\mathbf{P} MPa	\mathbf{b}	$\mathbf{b/a}$
glycerol	900	0.7	0.26
di-butyl phthalate	200	0.87	0.26
orto therphenyl	300	2.35	0.37
polymethylphenylsiloxane	499	4.33	0.58
andesite	--	0	0

APPENDIX 1

1 Detailed derivation of Avramov & Milchev (jump frequency) model

The Avramov & Milchev [18-21] model (**AM** model) determines the temperature dependence of the average jump frequency of molecules and, through it, the temperature dependence of viscosity. If the probability of appearance of energy barrier of height E_i is $\mathbf{j}(E_i)$ then the mean jump frequency is given as:

$$\langle \mathbf{n} \rangle = \sum \mathbf{n} \mathbf{j}(E_i) \quad (44)$$

Note that v_i decays exponentially with the activation energy.

$$\mathbf{n}_i = \mathbf{n}_\infty \exp\left(-\frac{E_i}{kT}\right) \quad (45)$$

At first site it seems that one problem is replaced with another: instead of creating a model for determining the average energy barrier $\langle E \rangle$ the model deals with the determination of $\mathbf{j}(E_i)$. However, there is one very important advantage: Because v decays exponentially with the activation energy, of significance for the summation is only the low energy part of the probability distribution function $\mathbf{j}(E_i)$ as illustrated in Fig.(6) where the thin solid line represents the dependence of the jump frequency on the activation energy (according to Eq.(14)). The dotted line is a schematic representation of the continuous distribution function $\mathbf{j}(E)$; it depends on the dispersion of the activation energy σ and on the value of E_{max} . An appearance of higher barriers is unlikely because the molecules cannot get closer. Although the native distribution function is not known, a sufficiently accurate result can be obtained. This is because most of the probability distribution functions differ in the vicinity of the maximum but are getting together away from the maximum (for $E \ll E_{max}$). Therefore, the tail of this unknown curve can be approximated with a sufficient accuracy with a Poissonian law. The final result, the product of $\mathbf{j}(E)$ and $v(E)$, is represented by the thick solid line.

In continuous case, Eq.(44) transforms to:

$$\langle \mathbf{n} \rangle = \int_0^{E_{max}} \mathbf{j}(E) \mathbf{n}(E) dE \quad (46)$$

This equation can be solved for any special choice of the $\mathbf{j}(E)$ distribution function. It was shown [18-22] that the solution of Eq.(46), under the assumption that $\mathbf{j}(E)$ is described as Poissonian distribution (i.e. the jump probability is considered as a flow of independent events).

$$\mathbf{j}(E) = \frac{\exp\left(\frac{E - E_{max}}{\mathbf{s}}\right)}{\mathbf{s} \left(1 - \exp\left(-\frac{E_{max}}{\mathbf{s}}\right)\right)} \quad (47)$$

is given by the expression:

$$\langle \mathbf{n} \rangle = \frac{\left[1 - e^{-E_{max} \left(\frac{1}{RT} - \frac{1}{s} \right)} \right]}{\left(\frac{s}{RT} - 1 \right) \left(1 - e^{-\frac{E_{max}}{s}} \right)} \mathbf{n}_{\infty} e^{-\frac{E_{max}}{s}} \quad (48)$$

For $RT < s < E_{max}$, the term to the left of \mathbf{n}_{∞} , as compared to the exponential term on the right-hand side, is a weak temperature function of the order of unity. Therefore, one can use the approximation:

$$\langle \mathbf{n} \rangle \approx \mathbf{n}_{\infty} e^{-\frac{E_{max}}{s}} \quad (49)$$

Eq.(49) is of little use, unless dispersion s is expressed through some known and easily measurable variable. There is a strong relationship between the dispersion σ and the entropy S of the system:

$$s = s_g \exp \left[\frac{2(S - S_g)}{ZR} \right] \quad (50)$$

Here s_g is the dispersion at the reference state with entropy S_g and $Z/2$ is the degeneracy of the system, i.e. Z is the number of escape channels available for the moving particle and each channel can be used in two directions. Taking into account that viscosity is inversely proportional to the mean jump frequency the viscosity can be expressed through Eqs.(49 and 50) as:

$$\mathbf{h} = \mathbf{h}_{\infty} \exp \left\{ \mathbf{e} \exp \left[-\frac{2(S - S_g)}{ZR} \right] \right\} \quad (51)$$

where $\mathbf{e} = \frac{E_{max}}{s_g}$.

The entropy depends on temperature T as:

$$S(T) = S_g + \int_{T_g}^T C_p d \ln T \quad (52)$$

In the following we apply the most frequently used approximation that heat capacity is temperature independent, i.e. C_p is the average value for the interval between T_g and T . Under this assumption the entropy of a melt in metastable equilibrium is becoming:

$$S(T) = S_g + C_p \ln \left(\frac{T}{T_g} \right) \quad (53)$$

Eq.(51) together with Eq.(48) determines the dispersity as:

$$s = s_g \left(\frac{T}{T_g} \right)^a \quad (54)$$

where the "fragility" parameter α in stands for:

$$a = \frac{2C_p}{ZR} \quad (55)$$

In terms of α , Eqs.(49) and (51-53) give:

$$\mathbf{h} = \mathbf{h}_{\infty} \exp \left[\mathbf{e} \left(\frac{T_r}{T} \right)^a \right] \quad (56)$$

pressure dependence of viscosity

The entropy can be expressed by means of volume expansion coefficient $\mathbf{k} = \frac{1}{V} \left(\frac{\mathcal{V}}{\mathcal{T}} \right)_P$ in the form:

$$S - S_o = V_m \int_{P_0}^P \mathbf{k} dp \quad (57)$$

where V_m is the molar volume. An explicit form of the dependence of \mathbf{k} on P is needed to solve Eq.(57). Although there are no data in the literature, it is reasonable to assume that at extremely high pressures \mathbf{k} will reduce in a somewhat inversely proportional to pressure P way, namely:

$$\mathbf{k} = \frac{1}{V} \left(\frac{\mathcal{V}}{\mathcal{T}} \right)_P \approx k_o \frac{P}{P + P} \quad (58)$$

where P is a constant and k_o is the volume expansion coefficient at no pressure. In this case the solution of Eq. (57) leads to:

$$S = S_g + C_p \ln \frac{T}{T_g} - k_o V_m \Pi \ln \left(\frac{\Pi + P}{\Pi + P_o} \right) \quad (59)$$

So that, for $P_o \ll \Pi$, the viscosity Eq. (51) yields:

$$\mathbf{h} = \mathbf{h}_\infty \exp \left\{ \mathbf{e} \left(\frac{T_r}{T} \right)^a \left(\frac{\Pi + P}{\Pi + P_o} \right)^b \right\} \approx \mathbf{h}_\infty \exp \left\{ \mathbf{e} \left(\frac{T_r}{T} \right)^a \left(1 + \frac{P}{\Pi} \right)^b \right\} \quad (60)$$

or

$$\mathbf{h} = \mathbf{h}_\infty \exp \left\{ \mathbf{e} \left(\frac{T_g(P)}{T} \right)^a \right\} \quad \text{where} \quad T_g(P) = T_{g_o} \left(1 + \frac{P}{\Pi} \right)^{b/a} \quad (61)$$

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Figure captions

Fig.1 Viscosity of a standard soda-lime silicate glass NBS710. Solid points represent equilibrium viscosity. Non-equilibrium viscosity is given by the open points.

Fig.2 Dependence of parameter α on average heat capacity. The solid line has a slope 0.1

Fig.3 Temperature dependence of viscosity of silicates: - $(Na_2O)_{0.25}(SiO_2)_{0.75}$;
 ■- $(PbO)_{0.4}(SiO_2)_{0.6}$; Δ - $(PbO)_{0.5}(SiO_2)_{0.5}$; \blacktriangledown - $(PbO)_{0.6}(SiO_2)_{0.4}$

Fig.4 Composition x , dependence of parameter α . - two-component silicates; ■- three component silicates. A solid line with a slope equal to 6 is drawn.

Fig.5 Pressure dependence of viscosity of OTP (orto therpenyl) at temperatures given as parameter at each curve. Solid lines are according to Eq.(41).

Fig.6 The thin solid line represents the dependence of the jump frequency $\nu(E)$ on the activation energy (according to Eq.(14)). The dotted line is a schematic representation of the continuous distribution function $\nu(E)$. The product $\nu(E) \cdot j(E)$ is presented by the thick solid line.

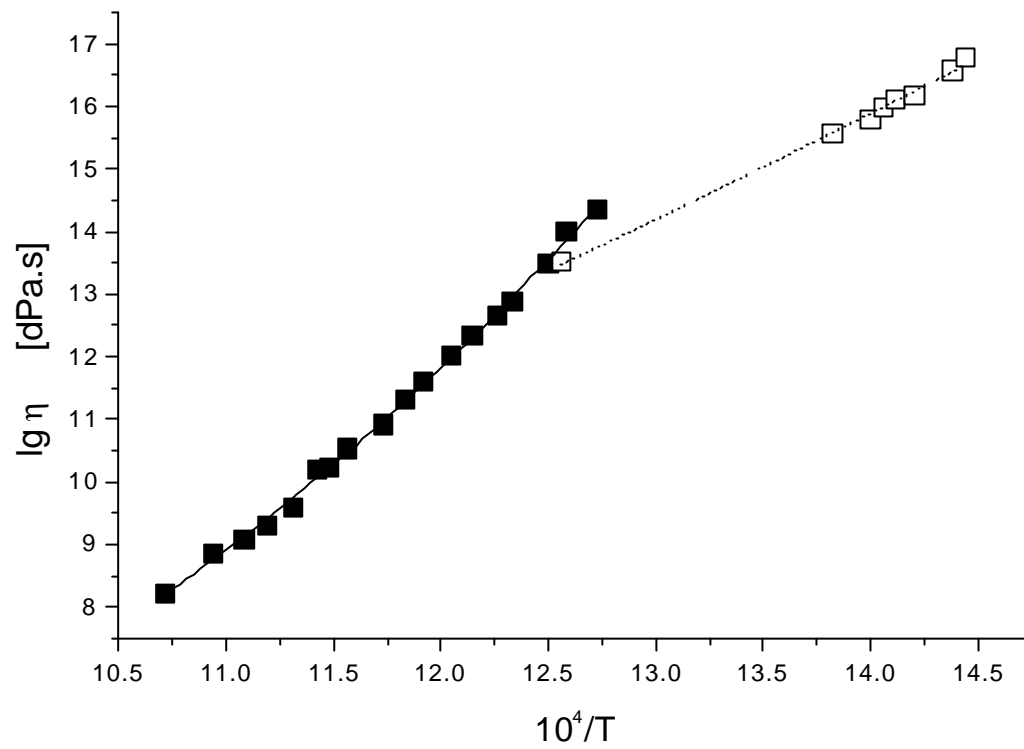


Fig.1

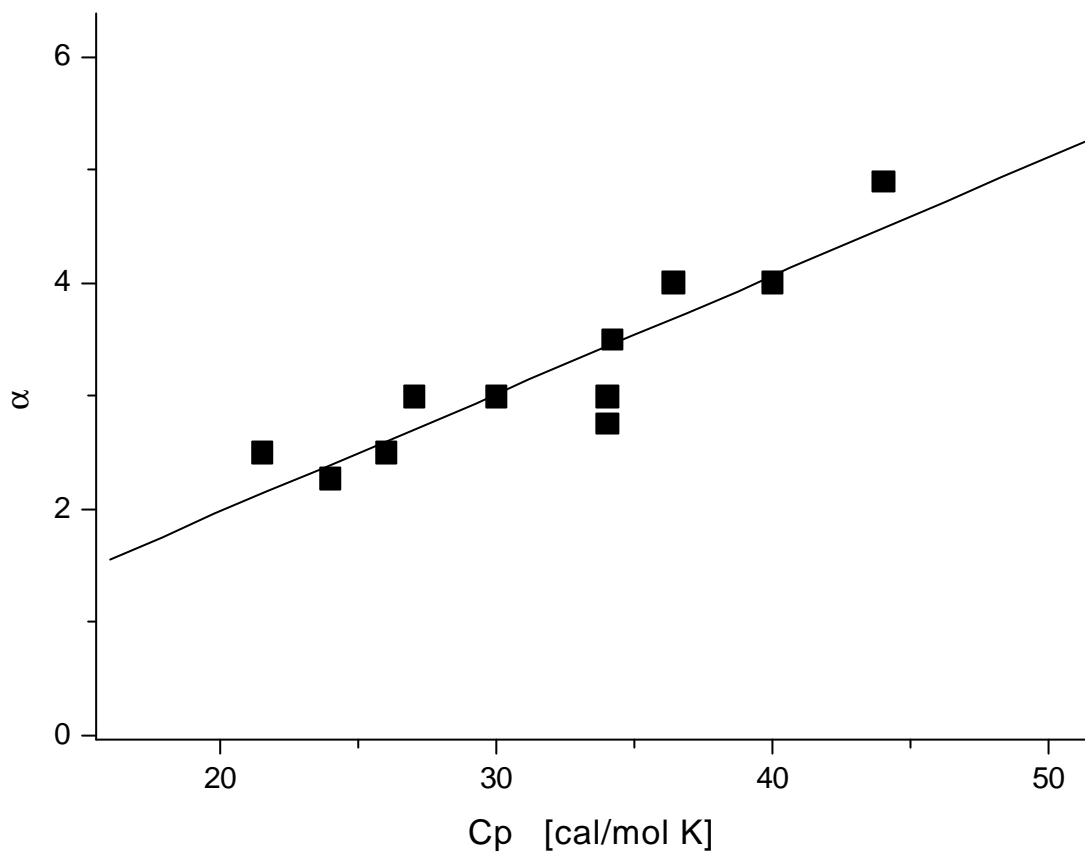


Fig.2 Dependence of parameter α on average heat capacity. The solid line has a slope 0.1

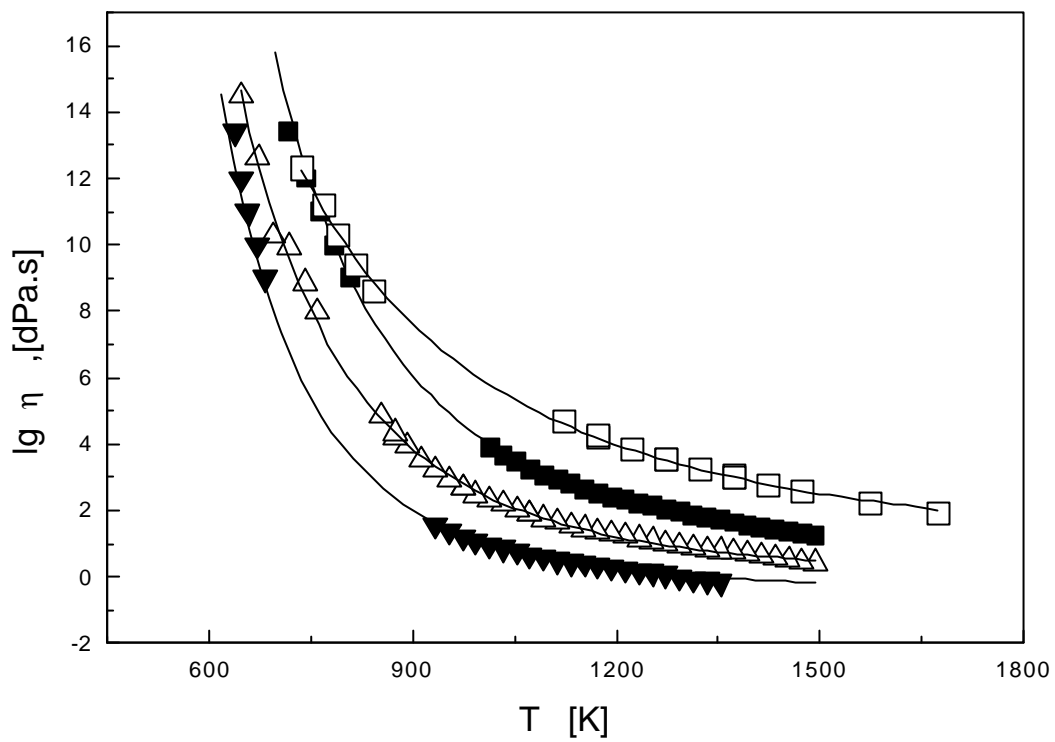


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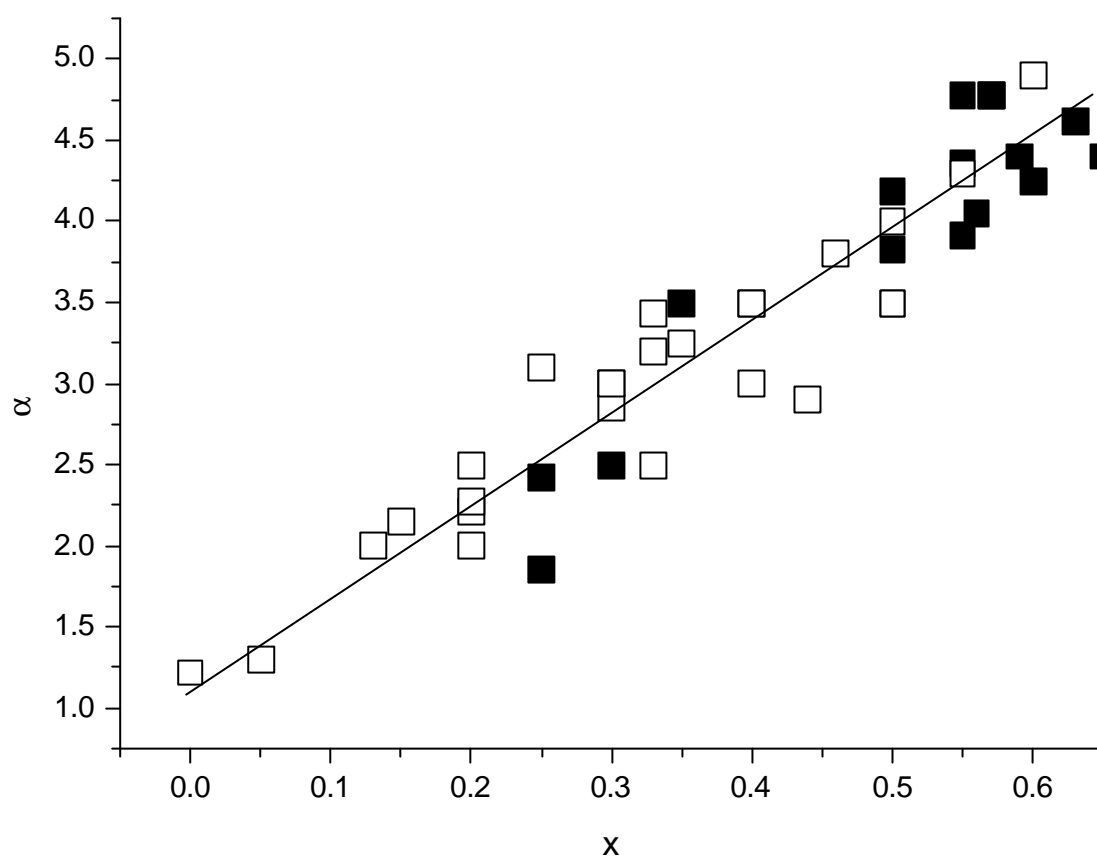


Fig.4 Composition x , dependence of parameter α . \square - two-component silicates; \blacksquare - three component silicates. Solid line has a slope equal to 6.

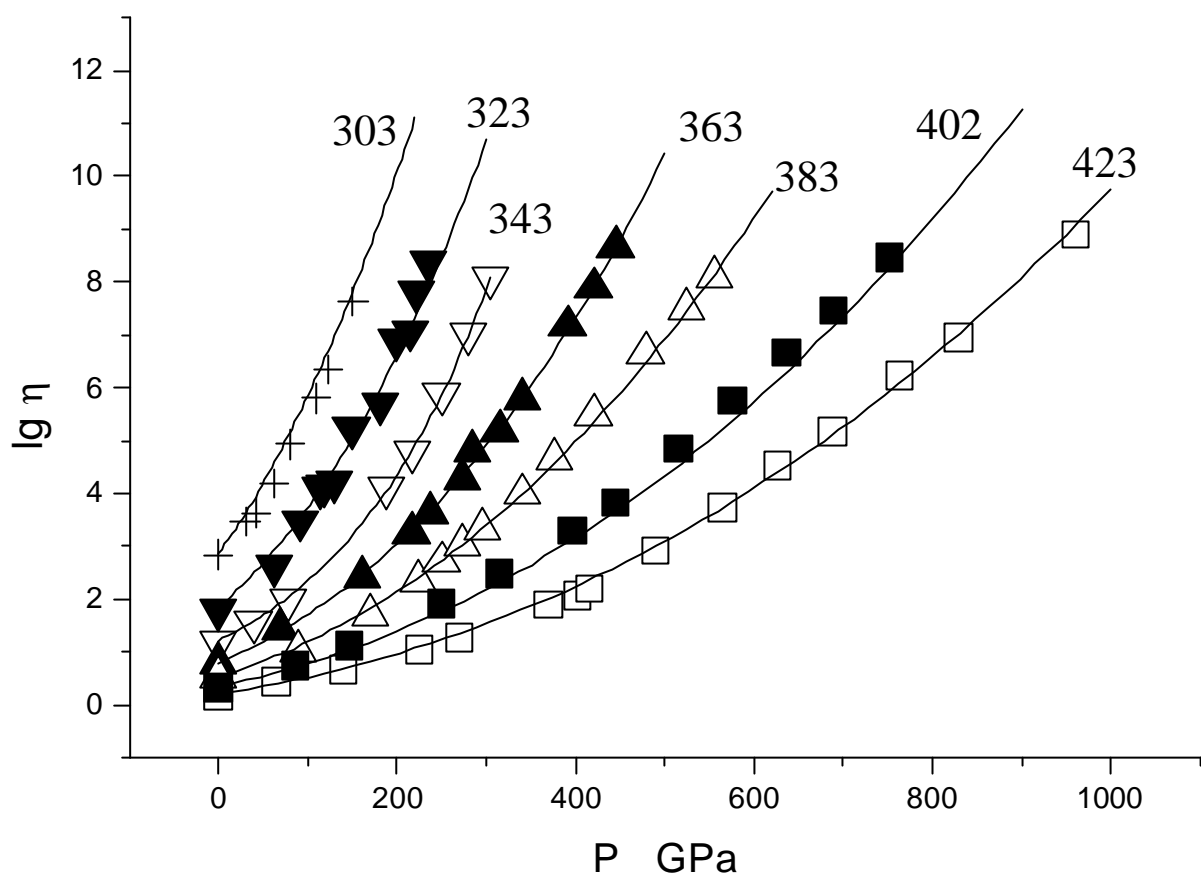


Fig.5 Pressure dependence of viscosity of OTP (orto therpenyl) at temperatures given as parameter at each curve. Solid lines are according to Eq.(41).

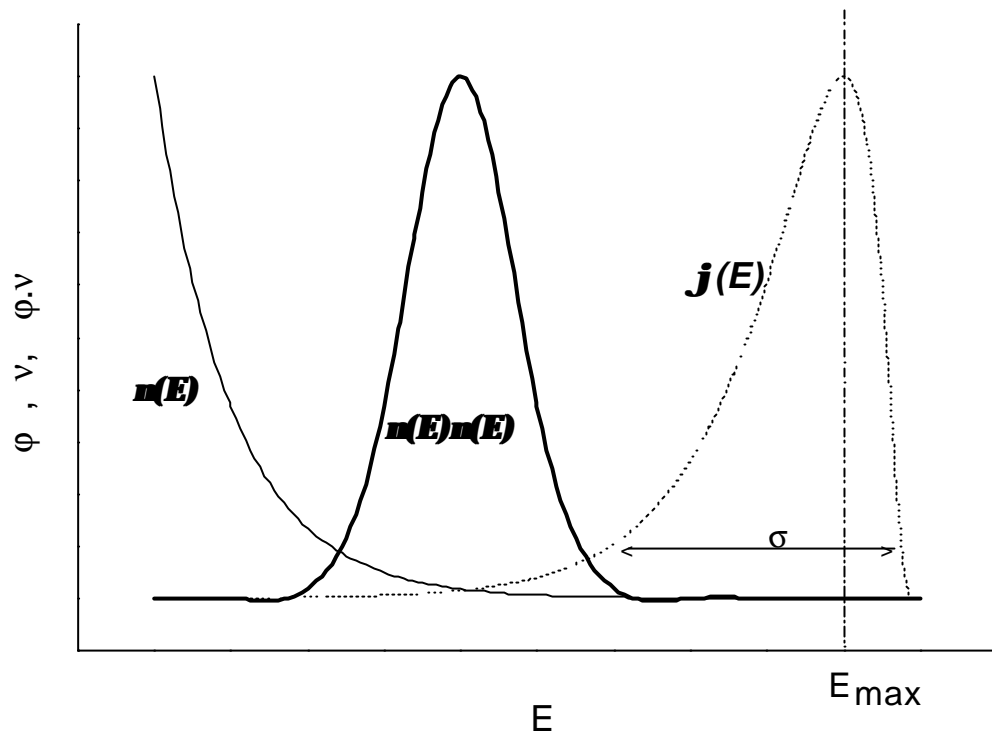


Fig. 6 The thin solid line represents the dependence of the jump frequency $n(E)$ on the activation energy (according to Eq.(14)). The dotted line is a schematic representation of the continuous distribution function $j(E)$. The product $n(E) \cdot j(E)$ is presented by the thick solid line.