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The influence of disorder on shear viscosity of undercooled melts is described by the formula $\eta = \eta_0 \cdot \exp(\theta/T)^a$. It is shown that this expression reproduces the existing experimental data with a reasonable accuracy for a broad range of substances of various nature (silicates, borates, germanates, phosphates, Se, glucose, glycerin, $As_2 Se_3$, etc.). Angell and Sichina [Ann. NY Acad. Sci. **279**, 53 (1976)] distinguish between "strong" and "fragile" liquids on the basis of their heat capacity. The present model provides a physical ground for such classification. Also the isostructural viscosity of glasses is easily described. The present approach gives a natural explanation to the empirical rule of Bimen and Kauzmann.

I. INTRODUCTION

A number of models have been developed to describe the temperature dependence of the viscosity of undercooled melts. According to the free volume approach[1-5] the variation of viscosity with temperature T depends on the ratio of the occupied volume to the free volume. A similar result is obtained in the papers of Spaepen and Turnbull[6,7] where the structural relaxation of metallic glasses is investigated.

In general, the relaxation time τ is proportional to shear viscosity η

$$\tau = K \cdot \eta, \tag{1}$$

where K is the relaxation module (according to Ref. 8 $K \approx 4 \times 10^{-10}$ Pa^{-1}).

Gibbs *et al.*[9,10] consider the molecular motion as a cooperative process involving a simultaneous rearrangement of a large number of particles. For this reason both τ and η should depend on the configurational entropy, S_{conf}. According to Adam and Gibbs[10] the relaxation time is given by

$$\tau = \tau_0 \cdot \exp(A/TS_{conf}), \tag{2}$$

where τ_0 and A are constants. Gutzow[5] has shown that the free volume model also leads to an entropy dependence of τ. The configurational entropy is expressed through the excess heat capacity C_{conf} as

$$S_c(T) = \Delta S_m + \int_{T_m}^{T} \frac{C_{conf}}{T} dT, \tag{3}$$

where T_m is the melting point, while ΔS_m is the entropy of melting. For a constant C_{conf} Eq. (3) yields

$$S_{conf}(T) = \Delta S_m + C_{conf} \ln(T/T_m). \tag{3a}$$

Scherer[11] has shown that the free volume model[3] is not able to describe properly the isostructural viscosity[12,13] of oxide glasses. Although the Adam–Gibbs equation (2) represents well the viscosity of some glasses[11,14] it fails[15-18] for others.

It is well known that despite the differences in the mechanism of molecular transport all undercooled melts show a remarkable similarity in the temperature dependence of their shear viscosity. This is the reason why a generalized model was suggested in our previous paper[19] describing phenomenologically the kinetics of molecular motion in undercooled liquids and glasses.

II. DESCRIPTION OF THE MODEL

The most general representation of the transition rate ($\nu \equiv \tau^{-1}$) dependence on the temperature T and on the activation energy E is formulated in terms of the active complex theory as

$$\nu = \nu_0 \cdot \exp\left(-\frac{E}{RT}\right). \tag{4}$$

The disorder in the amorphous media inevitably leads to some probability distribution function, $P(E, \sigma)$, of the appearance of activation energy E. Here σ is the variance of the probability distribution function. This common understanding is confirmed by computer simulations showing the particle motion in undercooled melts to be a cooperative process with a broad distribution of barrier heights.[20-22]

The mean transition rate is defined as

$$\langle \nu \rangle = \int_0^{E_{max}} P(E, \sigma) \cdot \nu(E) \cdot dE. \tag{5}$$

Equation (4) can be solved for any specified choice of $P(E, \sigma)$. In the case of Poisson distribution $P(E, \sigma)$ is given by

$$P(E, \sigma) = \frac{\exp[(E - E_{max})/\sigma]}{\sigma \cdot \exp(-E_{max}/\sigma)}. \tag{6}$$

The solution of Eq. (5) together with Eqs. (4) and (6) yields

$$\langle \nu \rangle = \frac{\nu_0 \cdot \{1 - \exp[-(E_{max}/\sigma)((\sigma/RT) - 1)]\}}{(\sigma/RT - 1) \cdot [1 - \exp(-E_{max}/\sigma)]}$$
$$\times \exp(-E_{max}/\sigma). \tag{7}$$

For $RT \ll \sigma < E_{max}$, Eq. (7) is transformed to

$$\langle \nu \rangle = \nu_1 \cdot \exp\left(-\frac{E_{max}}{\sigma}\right), \tag{8}$$

in which the exponential term changes with temperature (respectively with σ) much steeper than the preexponential factor

$$\nu_1 = \frac{\nu_0 \cdot \{1 - \exp[-(E_{max}/\sigma)((\sigma/RT) - 1)]\}}{((\sigma/RT) - 1) \cdot [1 - \exp(-E_{max}/\sigma)]}$$
$$\cong \text{const}. \tag{9}$$

Note that the mean transition rate is expressed, usually,

in terms of a mean effective value $E_{eff}(T)$ of the activation energy as

$$\langle v \rangle = v_1 \cdot \exp(-E_{eff}(T)/RT). \quad (10)$$

The effective activation energy for molecular motion can be obtained when Eqs. (8) and (10) are compared

$$E_{eff}(T) = E_{max}(RT/\sigma). \quad (11)$$

III. INFLUENCE OF THE ENTROPY

In our previous paper[19] we demonstrated that the expression

$$\sigma = \sigma_m \cdot \exp\left(\frac{2 \cdot (S - S_m)}{ZR}\right) \quad (12)$$

describes the dependence of variance σ on entropy S with sufficient accuracy for every probability distribution function $P(E,\sigma)$ of practical interest. Here σ_m is the variance of the system at a reference state with an entropy S_m while Z is the degeneracy of the system, i.e., Z is the number of escape channels available to each particle. Clearly, Z depends on the coordination number of the structure and the symmetry of the molecules.

Equation (11) assumes that (i) a system of N particles has $NZ/2$ escape channels and (ii) the activation energy barrier for each channel is statistically independent.

It follows that for a constant heat capacity C_p the entropy S is given by

$$S = S_m + C_p \ln(T/T_m), \quad (13)$$

so that

$$\sigma = \sigma_m (T/T_m)^a, \quad (14)$$

where

$$a = \frac{2 \cdot C_p}{ZR} \quad (15)$$

and T_m is a reference temperature at which $\sigma = \sigma_m$. Since T_m could be any temperature with known σ_m it is convenient to choose for T_m the melting point.

Taking into account Eqs. (8) and (15) the temperature dependence of η is expressed as

$$\eta = \eta_0 \cdot \exp\left(\frac{\theta}{T}\right)^a, \quad (16)$$

where

$$\theta = \left(\frac{E_{max}}{\sigma_m}\right)^{1/a} T_m, \quad (17)$$

while the preexponential constant η_0 is the lowest possible value of the viscosity of the melt at extremely high temperatures. According to Ref. 12 $\eta_0 = 10^{-(1.5 \pm 1)}$ Pa s. Taking into account Eqs. (11) and (14) the effective activation energy for molecular motion becomes

$$E_{eff}(T) = RT \cdot \left(\frac{\theta}{T}\right)^a. \quad (18)$$

Clearly, θ is the temperature at which $E_{eff}(\theta) = R\theta$.

IV. 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 when the temperature is lowered further on. In this way the structure is fixed so that the state of the system becomes a nonequilibrium one. The set of intensive parameters (e.g., pressure, temperature, etc.) is not sufficient to describe it completely. For this reason Tool and Eichlin[23] 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 an equilibrium state. Glasses are typical representatives of this type of nonequilibrium systems. Their viscosity is still measurable[12] and is known[11-13] in the literature as "isostructural."

Basically, the entropy of undercooled melts splits into two parts: configuration entropy S_{conf} and vibration entropy S_{vibr}. Respectively, the heat capacity is $C_p = C_{conf} + C_{vibr}$.

Below the fictive temperature T_f, the configurational entropy S_{conf} is fixed (i.e., C_{conf} vanishes), so that S can be determined as

$$S = S_m + C_p \ln\left(\frac{T_f}{T_m}\right) + C_{vibr} \ln\left(\frac{T}{T_f}\right). \quad (19)$$

In this way the variance becomes

$$\sigma = \sigma_m \left(\frac{T_f}{T_m}\right)^a \cdot \left(\frac{T}{T_f}\right)^g, \quad (20)$$

where the power exponent g is

$$g = a \cdot \frac{C_{vibr}}{C_p}. \quad (21)$$

Taking into account Eqs. (8), (19), and (21) the temperature dependence of η below the glass transition region is expressed as

$$\eta = \eta_0 \cdot \exp\left[\left(\frac{\theta}{T_f}\right)^a \cdot \left(\frac{T_f}{T}\right)^g\right]. \quad (22)$$

It will be shown below that Eq. (22) gives an easy experimental way for determination of the exponent g.

V. COMPARISON WITH EXPERIMENT

Equation (16) contains three parameters. We have already discussed the physical meaning of θ, η_0, and a. In addition to the better fitting the existing experimental data an advantage of Eq. (16) as compared to the other three parameter equations is that there is no need of a mathematical fitting procedure in order to determine the values θ, a, and η_0. An easy way to obtain their values from the experimental data is proposed here. Figure 1 shows semilogarithmic plot of shear viscosity η of LiPO$_3$ glassforming melt. The experimental points are from[29] while the solid line is drawn according to Eq. (16). At a given temperature T the slope $L(T)$ of the log η against $1/T$ curve is

$$L(T) = \frac{a}{2,3} \cdot \left(\frac{\theta}{T}\right)^{a-1} \theta. \quad (23)$$

It is readily seen that the exponent a can be obtained when comparing the slopes for two temperatures.

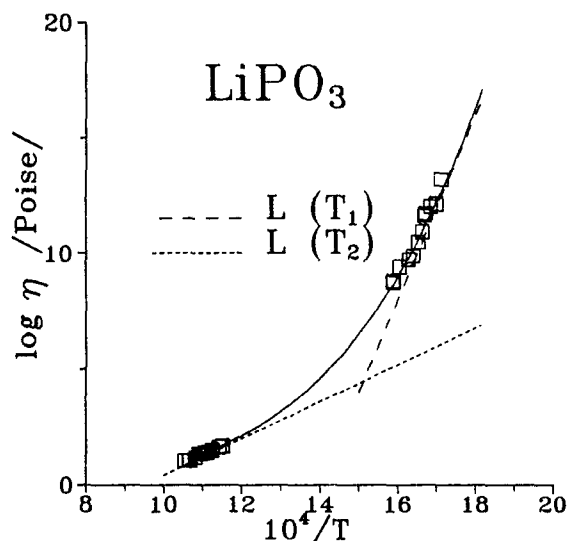$$a = 1 + \frac{\ln[L(T_1)/L(T_2)]}{\ln[T_2/T_1]}. \quad (24)$$

FIG. 1. A semilogarithmic plot of shear viscosity η of $LiPO_3$ glassforming melt. The experimental points are from Ref. 29. The solid line is according to Eq. (16); the corresponding values of parameters $\log \eta_0$, θ, and a are listed in Table I.

TABLE I. Table of coefficients of equation $\eta = \eta_0 \cdot \exp(\theta/T)^a$, where η is in poise.

#	Substance	$a \pm 0.25$	θK	$\lg \eta_0$
1.	$3Li_2O \cdot 7SiO_2$	3	2 200	0.53
2.	$2Na_2O \cdot 8SiO_2$	2.25	3 400	-0.06
3.	$3Na_2O \cdot 7SiO_2$	3	2 200	0.9
4.	$3.3Na_2O \cdot 6.7SiO_2$	2.25	3 100	1.5
5.	$4Na_2O \cdot 6SiO_2$	2.5	2 700	-0.15
6.	$2K_2O \cdot 8SiO_2$	2.5	2 900	0.84
7.	$3PbO \cdot 7SiO_2$	3	2 300	0.66
8.	$4PbO \cdot 6SiO_2$	3.5	1 900	0.2
9.	$5PbO \cdot 5SiO_2$	4	1 550	-0.04
10.	$6PbO \cdot 4SiO_2$	4.75	1 300	-0.49
11.	B_2O_3	3.25	1 430	1.35
12.	$13,5Na_2O \cdot B_2O_3$	3.5	1 700	0.09
13.	$33,3Na_2O \cdot B_2O_3$	5.75	1 350	-0.26
14.	$97,8B_2O_3 2,17SiO_2$	3.25	1 450	1.38
15.	$94B_2O_3 5,95SiO_{22}$	3	1 600	1.29
16.	$89,3B_2O_3 10,7SiO_2$	3	1 600	1.45
17.	$51,6B_2O_3 48,4SiO_2$	1.5	5 600	0.6
18.	$44,6B_2O_3 55,4SiO_2$	1	21 302	-0.02
19.	$6Li_{22}O \cdot 94B_2O_3$	4.25	1 350	0.36
20.	$13,9Li_2O86,1B_2O_3$	4.75	1 400	-0.19
21.	$33.5Li_2O \cdot 67B_2O_3$	4.25	1 700	-1.72
22.	$19.5K_2O \cdot 80.5B_2O_3$	4	1 600	-0.16
23.	$24.4K_2O \cdot 26.5B_2O_3$	4	1 600	0.007
24.	$18BaO \cdot 82B_2O_3$	4	1 900	-0.97
25.	$23,9BaO \cdot 76B_2O_3$	4.5	1 800	-0.9
26.	GeO_2	1.4	10 000	-1.34
27.	$5Na_2O \cdot 95GeO_2$	3.25	2 000	0.11
28.	$10Na_2O \cdot 90GeO_2$	4.5	1 600	-0.13
29.	$29,6Na_2O \cdot 70GeO_2$	6.5	1 200	0.43
30.	$20PbO \cdot 80GeO_2$	4.25	1 600	0.33
31.	$30PbO \cdot 70GeO_2$	6.25	1 200	0.66
32.	$40PbO \cdot 60GeO_2$	5.5	1 250	0.25
33.	$50PbO \cdot 50GeO_2$	5.25	1 200	0.33
34.	$500Na_2O \cdot 50P_2O_5$	8	835	0.43
35.	$50Li_2O \cdot 50P_2O_5$	5	1 150	-0.03
36.	Se	4	701	-0.69
37.	As_2Se_3	3.25	1 300	0.97
38.	Glycerin	4	450	-1.19
39.	Glucose	6.25	515	-0.99

As soon as the value of the parameter a is known the determination of θ and η_0 through Eqs. (23) and (16) is trivial.

In terms of Eq. (16) we described successfully the temperature dependence of viscosity of 39 substances of various nature: typical glassformers,[25] organic substances (glucose and glycerin[26]), transition metals (Se[27]), phosphates ($NaPO_3$[28] and $LiPO_3$[29]) and a representative of chalcogenide glassforming substances (As_2Se_3[30]). The numerical values of $\log \eta_0$, a, and θ are given in Table I. The theoretical curves are always in excellent agreement with the experimental data as illustrated for $LiPO_3$ in Fig. 1, for As_2Se_3 in Fig. 2, and for glassforming melts of the system $\alpha PbO \cdot (100 - \alpha)SiO_2$ in Fig. 3.

Angell[31] distinguishes between "strong" and "fragile" liquids. "Strong" are liquids that have low values of C_{conf} and tend to obey the Arrhenius behavior while "fragile" liquids have high values of C_{conf} and show strong curvature in the $\log \eta(T)$ dependence. This observation finds a natural explanation in terms of Eq. (16) since the value of the exponent a depends strongly on the heat capacity of the system.

Figure 4 shows a semilogarithmic plot of isostructural (dashed line) and equilibrium (solid line) viscosity η of pyrex glass as reported in Ref. 24. At the intersection point (temperature $T_g = T_f$) the slope L_g of the curve of isostructural viscosity is about one-half as great as the slope $L(T_g)$ of the equilibrium curve. In analogy with Eq. (23) $L_g(T)$ is given by

$$L_g(T) = \frac{g}{2,3} \cdot \left(\frac{\theta}{T_f}\right)^a \left(\frac{T_f}{T}\right)^{g-1} T_f, \qquad (25)$$

so that for $T_f = T$ Eq. (24) yields

$$L_g(T_f = T) = \frac{g}{2,3} \cdot \left(\frac{\theta}{T_f}\right)^a T_f. \qquad (26)$$

It follows from Eqs. (22) and (24a) that

$$\frac{L_g(T_f = T)}{L(T)} = \frac{g}{a}. \qquad (27)$$

In this way the investigation of the ratio of the mentioned two slopes is an easy experimental method to determine exponent g.

VI. INTERPRETATION OF THE BIMEN–KAUZMANN RULE

Although the glass transition temperature T_g changes with cooling and heating rates, it varies in a limited range. This was the reason why Bimen and Kauzmann formulated their famous empirical rule according to which, for the typically used heating rates, T_g is related to the melting point in the following way:

$$T_g \cong \tfrac{2}{3} T_m. \qquad (28)$$

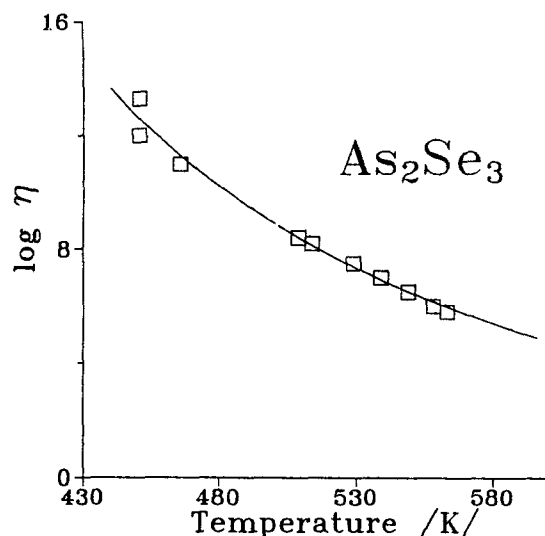By the time this rule was first formulated, only typical

FIG. 2. A semilogarithmic plot of shear viscosity η of As_2Se_3 glassforming melt. The experimental points are from Ref. 30. The solid line is according to Eq. (16); the corresponding values of parameters log η_0, θ, and a are listed in Table I.

FIG. 4. A semilogarithmic plot of isostructural (dashed line) and equilibrium (solid line) viscosity η of Pyrex glass as reported in Ref. 25.

glassformers were investigated. As soon as some new techniques for ultrahigh cooling rates were developed a number of substances were obtained in a glassy state with $T_g \ll 2/3 T_m$. Nowadays the Bimen–Kauzmann rule can be regarded as treating the upper limit of the glass transition temperature

$$T_g \leqslant 0.7 T_m. \tag{28a}$$

The following discussion is to explain the physical background of this empirical rule.

For normal heating rates T_g is the temperature at which the viscosity is $\eta(T_g) \cong 10^{12.5}$ Pa s (this is often known as
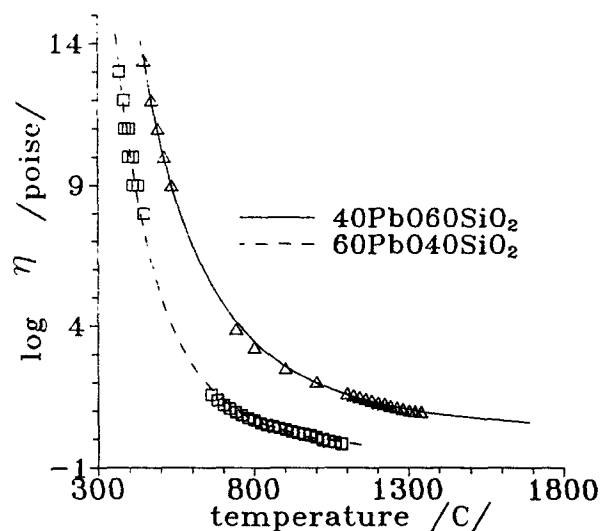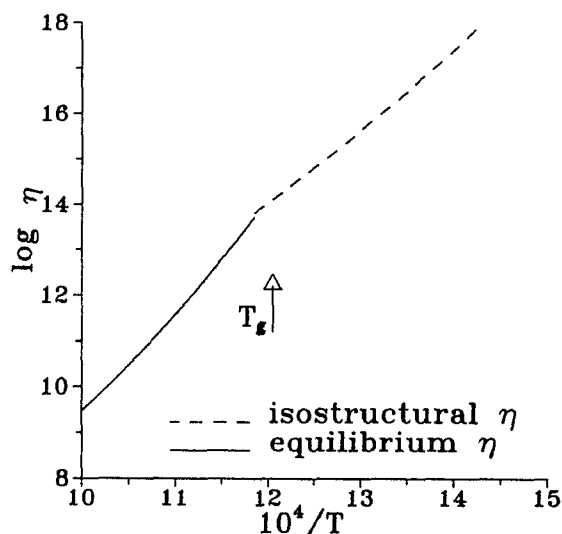

FIG. 3. A semilogarithmic plot of shear viscosity η of αPbO $\cdot (100 - \alpha)SiO_2$. The experimental points are from Ref. 25. The solid and dashed lines are according to Eq. (16); the corresponding values of parameters log η_0, θ, and a are listed in Table I.

$10^{13.5}$ poise rule). When $\eta(T_g)$ is expressed through Eq. (16) for T_g is obtained

$$T_g = \theta \cdot \left\{ \ln \frac{10^{12.5}}{\eta_0} \right\}^{-1/a}. \tag{29}$$

Taking into account Eq. (18), θ can be expressed through the effective activation energy for molecular motion at the glass transition temperature $E_{\text{eff}}(T_g)$ as

$$\theta = \left(\frac{E_{\text{eff}}(T_g)}{RT_g} \right)^{1/a} T_g. \tag{30}$$

From Eqs. (28a)–(30) it follows that

$$\frac{E_{\text{eff}}(T_g)}{RT_m} \frac{T_m}{T_g} \leqslant \ln \frac{10^{12.5}}{\eta_0}. \tag{31a}$$

As we have already mentioned, $\eta_0 \cong 10^{-1}$ (see for instance Table I). So, when Eq. (28a) is accounted for it renders that

$$\frac{E_{\text{eff}}(T_g)}{RT_m} \leqslant 23. \tag{31}$$

Practically, the last expression is equivalent to the Truton's rule for the evaporation energy E_{ev}. In this way the Bimen and Kauzmann rule can be reformulated to state that the effective activation energy for molecular motion never exceeds the evaporation energy $E_{\text{eff}} < E_{\text{ev}}$.

VII. CONCLUDING REMARKS

One of the primary assumptions of the present paper is that the probability distribution function, $P(E,\sigma)$, of the appearance of activation energy E is a Poissonian one [see Eq. (6)]. A distribution of Gauss was also discussed in Ref. 19. The problem is still soluble but the final formulas are somewhat more complicated. However, it should be noted that in this case the numerical results are quite close to these obtained when the Poisson distribution is applied.

Some additional deviation of the explicit $P(E,\sigma)$ form could appear when nonequilibrium systems are investigated. Although, this effect could play an important role for the relaxation phenomena in glasses, and especially for the "memory effect," our opinion is that the absolute σ value and its variation with temperature is much more important for the shear viscosity value than possible minor changes of the explicit form of the $P(E,\sigma)$ formula.

ACKNOWLEDGMENT

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