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Cooperative molecular dynamics and strong/fragile behavior of polymers

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Abstract

The temperature dependence of the average relaxation time in the glass transition region is discussed. The relations for the number of the basic molecular kinetic units and the number of configurations in the cooperative rearranging region are described. The basic molecular kinetic units in the polymers are identified as fragments of the monomeric segments, called beads by Wunderlich. A model of the cooperative unit with the internal rearrangement is supported by the experimental results. Proportionality between the glass transition temperature and the activation energy of the cooperative unit is observed. A correlation is found between the fragility in the relaxation behavior of the supecooled liquids and the temperature dependence of the size of the cooperative region. The strength parameter is related to the strength of resistivity of a basic molecular kinetic unit against its involving in the cooperative rearrangement.

1. Introduction

The temperature dependence of the average relaxation time in the supercooled liquids obeys the Vogel–Tamann–Fultcher (VTF) equation

$$\tau(T) = A\exp(B/(T - T_\infty)) \quad (1)$$

where A, B and t_∞ are empirical constants [1]. This equation is applied to a variety of substances, which may be differentiated as amorphous polymers, networks including oxides, alcohols, simple and complex molecular liquids, molten salts and orientational disorded crystalline materials [2].

In comparing $\tau(T)$ of supercooled liquids, including polymers, the T_g-normalized Arrhenius plot has been found useful [3–10]. On this plot the degree of departure of $\tau(T)$ from the Arrhenius behavior is characterized by the terms fragility and strength introduced by Angell and corresponding empirical parameters [2–5].

One of the most successful molecular theories of $\tau(T)$ was suggested by Adam and Gibbs [11]. They explain $\tau(T)$ in terms of the cooperatively rearranging regions. In the case of polymers the number of "monomeric segments" which are rearranging cooperatively has been defined as the size of the region. The basic molecular kinetic units in the cooperative region according to Adam and Gibbs surmount essentially simultaneously the individual barriers restricting their rearrangement. The existence of Adam and Gibbs' cooperatively rearranging regions or some other sort of heterogeneity has been proposed by many authors [12–23].

An alternative model of the cooperative rearranging region (CRR) in which basic molecular kinetic units overcome the individual barriers in the cooperative rearrangement in series rather than simultaneously was found to be also in agreement with the Adam–Gibbs conceptions [24, 25]. This model was examined in alcohols and seems to be proved as the measured number of configurations was found to be approximately equal to the number of basic kinetic units in the CRR [25]. An accompanying subspectra of the cooperative molecular dynamics which is predicted by the model also seems to be observed experimentally [25].

The aim of this paper is to discuss the cooperative molecular dynamics in polymers. Using the rules for the "universal" change of the heat capacity and the configuration entropy per mole of beads at T_g [26–28],

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the basic molecular kinetic units in the cooperative motion are identified. The internal rearrangement within the CRR is also studied. The fragility in the behavior of the supercooled liquids is discussed from the point of view of the cooperative molecular dynamics.

2. Theory

2.1. The size of the cooperative rearranging region and the nature of the basic molecular kinetic units in polymers

Some polymers and a variety of substances in the temperature range below the melting point can be observed in supercooled liquid state or in the crystalline phase. It is well known that plastic deformation in crystals is observed only in the presence of vacancies and dislocations [29]. As plastic deformation is liquid-like behavior it is reasonable to assume that the presence of vacancies is a necessary condition for the dynamics in the liquids. Hence we accepted the Hirai–Eyring quasi lattice (or hole) model of liquids [30, 31]. As a hole permits rearrangement of several basic molecular kinetic units the process is cooperative, and we assume the Adam–Gibbs activation energy per cooperative rearranging region zu, but regard u and z as average

$$u = (u_1 + u_2 + \dots u_z)/z \tag{2}$$

where u_i are the barriers hindering the cooperative rearrangement of the basic units and z is their number in an act of rearrangement. The normal modes of vibrations is expected to correlate the cooperative rearrangement, but every basic kinetic unit seems to overcome its own barrier and the transition rate j for forming of a CRR with the size z is given by

$$j = C\mathrm{e}^{-u_1/kT}\mathrm{e}^{-u_2/KT}\dots\mathrm{e}^{-u_z/kT} \tag{3}$$

where C depends on the probability for hole formation and the normal modes of vibrations. The temperature dependence of C may be neglected in comparing the exponential terms [11, 24].

Using Eq. (2), Eq. (3) is reduced to the Adam–Gibbs type equation

$$j = C\exp[-(zu/kT)] \tag{4}$$

The relaxation time $\tau = 1/j$ [11] and

$$\tau = A\exp(zU/RT) \tag{5}$$

where R is the gas constant and U is per mole basic molecular kinetic units. In comparing Eqs. (1) and (5) we obtain

$$z = \frac{T}{T - T_\infty} \tag{6}$$

and

$$U = RB \tag{7}$$

Eq. (6) gives the number of the basic molecular kinetic units in the cooperative rearranging region. This equation was also obtained by Miller [32, 33], but with the interpretation that the basic kinetic units in polymers are monomeric segments. In the author's interpretation the basic molecular kinetic units in the cooperative rearrangement of the supercooled liquids are introduced by Wunderlich beads [26]. In general we regard beads as occupied lattice sites in the quasi lattice model of liquids [24]. The equations for the equilibrium properties of liquids with the beads as basic molecular units have been obtained [24] and the relation of the hole parameters to the cooperative molecular dynamics will be discussed elsewhere. In the carbon backbone polymers the majority of the beads consist of a mean chain atom with the side chain groups attached to it [26–28]. As the right interpretation of Eq. (6) is the key problem for the cooperative molecular dynamics, it will be useful to estimate the number of the basic kinetic units in the CRR. This is possible using Wunderlich's rule for the change of$\Delta c_\mathrm{p} = c_\mathrm{pl} - c_\mathrm{pc}$, where c_pl and c_pc are correspondingly heat capacity of the liquid and the crystal. Investigating 41 supercooled liquids Wunderlich found the average value of $\Delta c_\mathrm{p}(T_\mathrm{g}) = 11.3$ J/kmol beads, which he defined as "rule of constant $\Delta c_\mathrm{p}(T_\mathrm{g})$" [26]. The analogous rule for the configuration entropy was defined by Chang et al. [27, 28].

The $\Delta c_\mathrm{p}(T)$ for polymers and a variety of supercooled liquids is given by

$$\Delta c_\mathrm{p}(T) = a - bT, \tag{8}$$

where a and b are constants [35, 36]. The configuration entropy

$$\begin{aligned}\Delta S &= \int_{T_\infty}^{T} \Delta c_\mathrm{p}(T)\mathrm{d}\ln T \\ &= a\ln\frac{T}{T_\infty} - b(T - T_\infty) \approx a\frac{T - T_\infty}{T} - b(T \\ &\quad - T_\infty)\end{aligned} \tag{9}$$

and using Eqs. (6) and (9) we obtain

$$z(T) = \frac{\Delta c_\mathrm{p}(T)}{\Delta S(T)} \tag{10}$$

Using Wunderlich's value of $\Delta c_\mathrm{p}(T_\mathrm{g})$ and Chang et al. "universal" value of $\Delta S(T_\mathrm{g}) = 2.9$ J/kmol beads from

Eq. (10) we obtain the "universal" size of CRR at T_g to be 3.9 beads.

From Eq. (5) it follows that the distribution in relaxation times or relaxation spectrum which is always observed in glass-forming substances may arise from the distribution of z, U and A.

Adam and Gibbs discussed distribution of the sizes of the CRRs but assume that relaxation properties are governed by a critical lower limit size z^* and neglected the influence of the largest CRRs on the observed relaxation time. In this approximation the Adam–Gibbs molecular theory appears equivalent to Debeye's phenomenological theory with single relaxation time or with linear exponential decay function [18].

The majority of experimental results for the temperature dependence of the relaxation times are obtained from the frequency measurements from the equation $\tau = 1/2\pi\nu_m$ where ν_m is the frequency of the maximum of loss factors. τ obtained in this way, in the spectra case is usually called average relaxation time, but as a matter of fact it is the most probable, as the maximum of loss factors coincides with the maximum of the distribution function of the relaxation times [41–46]. Hence the VTF parameters, and in the majority of the cases WLF parameters are obtained from the most probable relaxation time. Recently the Kohlrausch–Williams–Watts decay function is often used for fitting of the experimental results, especially in light and neutron scattering experiments [47]. In this case Boese and Kramer calculated the average relaxation time [40], but the difference between the most probable and the average relaxation time is negligible [39, 40]. When WLF parameters are obtained on the basis of the time–temperature superposition principle by constructing the master curve, one and the same temperature dependence for the whole spectrum is assumed [41, 46].

From Eq. (5) it follows that the smallest size of the CRRs z^* will form the shortest relaxation time of the spectrum which is discussed in few cases only [48, 49]. As Adam–Gibbs use single relaxation time approximation to obtain WLF equation, some of their results are for the average relaxation time and not for the shortest relaxation time of the spectrum. Having in mind the previous facts and that the Eqs. (6) and (7) are obtained from the VTF equation they represent average CRR and average activation energy. Hence when Eq. (5) is used with average z and U it would be interpreted as average relaxation time, but in general with the corresponding A, z and U it would represent each individual time of the spectrum.

2.2. The internal rearrangement within the cooperative rearranging region and the number of configurations in the cooperative unit; Accompanying subspectrum of the cooperative molecular dynamics

As was discussed, Adam and Gibbs accepted z in Eq. (5) as the critical lower limit size of the CRR that yields nonzero transition probabilities with two configurations $w = 2$, one before rearrangement and the second during transition. This model of the cooperative rearranging region needs the basic kinetic units to overcome simultaneously their potential barriers and describe rearrangement of the cooperative unit in accordance its environment. On the other hand Eq. (3) implies that beads should be rearranged during the time of relaxation and that a second kind (or level) of rearrangement within the cooperative unit will exist in addition to the rearrangement of the cooperative unit in the accordance with its environment. It has to be examined which of these two models of the CRR will occur. Eq. (6) makes it possible for all physical parameters of this smallest thermodynamical system to be evaluated, including the number of configurations, and in this way to deduce the character of the rearrangement within the CRR. The z may be characterized by the configuration entropy s, given by

$$s = k \ln w \tag{11}$$

where w is the average number of configurations available to the cooperative unit. As the configuration entropy per mole of beads ΔS_b can be measured [27, 28] we obtain

$$s(T) = \frac{\Delta S_b(T)}{N_a} z(T) \tag{12}$$

From Eqs. (11) and (12) we obtain

$$w = \exp \frac{\Delta S_b(T) z(T)}{R} \tag{13}$$

Using Eq. (6) or (10) in Eq. (13) w within the CRR with the average size may be estimated. Applying universal values of $\Delta S_b(T_g)$ and $z(T_g)$ we get the universal value of $w(T_g) = 3.9$. Hence the average number of configurations in the CRR at T_g is approximately equal to the number of the beads in the same region. This result is expected as the minimal number of configurations per every CRR with internal rearrangement is $w = z + 1$, one before rearrangement and one per every rearranging bead and the ratio $w/z = (z + 1)/z$ will be close to unity. Results obtained support internal rearrangement within the CRR. On the other hand, this kind of rearrangement needs time for the displacement of every single bead or a spectrum of very short times in comparison to relaxation times will always be tied with the cooperative dynamics [25]. This accompanying subspectrum of the α relaxation times

which was called the configuration spectrum would be an inherent property of the cooperative molecular dynamics. As the beads during rearrangement overcome the potential barriers U this will be the basis for the prediction of the configuration spectrum.

From Eq. (11) with $w = 3.9$ the universal value for the configuration entropy per average CRR can be estimated as 1.88×10^{-23} J/K. Such approximate constancy of s was assumed by Adam and Gibbs only for the smallest CRR with a value $s = 9.57\times10^{-24}$ J/K CRR.

We draw attention to the fact that Adam and Gibbs use $w = 2$ as "first approximation" and that model of cooperative units with internal rearrangement is compatible with their conception for the cooperative motion.

2.3. Fragility from the point of view of cooperative dynamics

The temperature dependence of the molecular mobility is studied by the viscosityη, the average relaxation time or very often in polymers by the shift factor $a(T) = \eta(T/\eta(T_g)$ or $\tau(T)/\tau(T_g)$ given by the WLF (Wiliams–Landel–Ferry) equation

$$\log a(T) = -\frac{C_1(T - T_g)}{C_2 + T - T_g} \tag{14}$$

where C_1 and C_2 are empirical constants.

The degree of departure of $a(T)$ from the Arrhenius behavior is measured by the steepness (or fragility) index

$$m = \frac{d\log a(T)}{d(T_g/T)} \tag{15}$$

or by the strength parameter [2–4]

$$D = B/T_\infty \tag{16}$$

The apparent activation energy

$$U_{app} = R\frac{\mathrm{d}\ln a(T)}{\mathrm{d}(1/T)} \tag{17}$$

is related to the steepness index by the equation

$$U_{app}(T) = 2,3RT_g m(T) \tag{18}$$

The steepness index is usually used at T_g and from Eqs. (14) and (15) we obtain

$$m(T_g) = T_g C_1/C_2 \tag{19}$$

The U_{app} and m are closely related to the average size of the cooperative units. From Eqs. (6), (14) and (17) we obtain

$$U_{app} = Uz^2(T) \tag{20}$$

The obtained result in this way is in agreement with the temperature independence of U [11] and with the statement that U_{app} is a measure for the cooperative motion [37]. From Eqs. (6) and (19) we obtain

$$m(T_g) = C_1 z(T_g) \tag{21}$$

For the characterization of the rate of decrease of the cooperative unit with the increase of temperature it is useful to introduce a temperature index of decooperativity

$$\delta = \frac{\mathrm{d}z}{\mathrm{d}(1/T)} = T_\infty z^2(T) \tag{22}$$

From Eqs. (20) and (22) it follows that U_{app} may be presented as

$$U_{app} = \frac{U}{T_\infty}\frac{\mathrm{d}z}{\mathrm{d}(1/T)} \tag{23}$$

Hence the U_{app} reflects the rate of decrease of the size of the cooperative units. On the basis of Eqs. (20) and (23) it may be understood why measured values of U_{app} around T_g are higher than the dissociation energies of the molecules [37, 41].

From Eq. (5) for the shift factor we obtain

$$\log\frac{\tau(T)}{\tau(T_g)} = \frac{Uz(T_g)}{2.3RT_g}\left(\frac{z(T)/z(T_g)}{T/T_g} - 1\right) \tag{24}$$

and as $Uz(T_g)/RT_g$ is approximately constant, to the same degree as fractional free volume $f(T_g) = 0.025$ [41], the T_g-scaled Arrhenius plot in fact reproduces the temperature dependence of $z(T)/z(T_g)$. The last conclusion does not depend on specific relations for z, but if z is evaluated from Eq. (6) and similarity in the log $a(T) - T_g/T$ with $z(T)/z(T_g) - T_g/T$ plots are observed, this should be an additional support for the correctness of Eq. (6).

3. Experimental verification of the theory

3.1. The size of the cooperative rearranging region and the nature of the basic molecular kinetic units in the glass forming liquids

3.1.1. The size of the cooperative rearranging region in the isomeric n-paraffin hydrocarbons. Dependence of the size of the cooperative unit on the degree of polymerisation

Before discussing z in polymers, the results for the supercooled liquids which may be regarded as polymers with very low molecular weight shall be considered. The experimental results for T_g, T_∞ and the configuration entropy of three isomeric n-Paraffins are listed in the Table 1.

The beads in this case are the groups -CH_3, -CH_2- and -$CHCH_3$ and the number of beads coincides with

Table 1
Size of the CRR in the isomeric *n*-paraffin hydrocarbons

Substances	T_g (K)	T_∞ (K)	$z(T_g)$	n	$\frac{z(T_g)}{n}$	$\Delta S(T_g)$ (J/kmol bead)	$w(T_g)$	$\frac{w(T_g)}{z(T_g)}$	Reference
2-Methylbutane $CH_2CHCH_3CH_2CH_3$	65	50	4.3	4	1.1	3.52	6.2	1.44	38
2-Methylpentane $CH_3CHCH_3(CH_2)_2CH_3$	78	57	3.7	5	0.74	3.98	5.9	1.59	28
4-Methylnonane $CH_3(CH_2)_2CHCH_3(CH_2)_4CH_3$	116	89	4.3	9	0.48	4.52	10.4	2.42	28

the number of C-atoms in the chain backbone. The side chain -CH_3 groups are not counted as a beads [26, 28]. Comparing the results in the table it is easy to be realize that beads are basic kinetic units. Indeed 2-Methylpentane has only one -CH_2- group more than the 2-methylbutane and, as in this case this structural unit is in the same time kinetic unit, we realize that beads are basic kinetic units. In a variety of substances, such as for example Se, *n*-alcanes, *n*-alcohols and many polymers with small side chain groups where structural units forms a linear chain (or molecule), the structural units coinside with the basic kinetic units, i.e. the beads [26-28]. In general, though, beads should not be identified with the structural units [26-28]. The $z(T_g)$ is estimated from Eq. (6) and the average size of the CRR is compared with the size of the molecule with the relation $z(T_g)/n$, where n is the number of beads in the molecule. It may be seen from the table that $z(T_g)$ in 2-methylbutane practically coinsides with the size of the molecule, but in 4-methylnonane $z(T_g)$ it is nearly half of the molecule. It is clear from this discussion that z in polymers can reasonably be compared with the monomeric (repeated) units. It is interesting that in isomeric *n*-paraffin the value of the average $z(T_g)$ is close to the predicted "universal" values and that $w(T_g) \geq z(T_g)$.

It may be seen from the table that in the listed isomeric *n*-paraffins sizes of the CRRs are nearly the same and the question arises to which degree z depends of the size of the molecules or in the polymers to the degree of polymerization. In *n*-alcanes z is fixed at *n*-pentadecane and for higher homologous members it practically does not change with the increasing number of -CH_2- beads [24]. Hence as *n*-alcanes appear as oligomers of polyethilene in this polymer z is expected to be independent of the degree of polymerization P above $P = 7$–8. The same relative independence of z from the degree of polymerization is observed for the polymers in Fig. 1. The results for PMMA and PVC are from Saito [52] and for PI from Adechi and Kotaka [39] and Boese and Kramer [40]. The first point for PI is for $P = 14$ and below the entanglement point for this polymer, and all the other results in Fig. 1 are above entanglement points of the corresponding polymers. In comparing glass transition temperatures with $z(T_g)$, from the degree of polymerization in Fig. 1, it may be realized that $z(T_g)$ are far more independent of P than glass transition temperatures.

3.1.2. The size of the cooperative rearranging region and the basic kinetic units in the saturated carbon polymers

The parameters characterizing the temperature dependence of τ for the α relaxation in the saturated carbon backbone polymers are listed in Table 2.

The conventional measured dilatometric or calorimetric T_g and corresponding average $\tau(T_g)$ when they are measured are given at the first position in the table. When examining the fragility of the supercooled

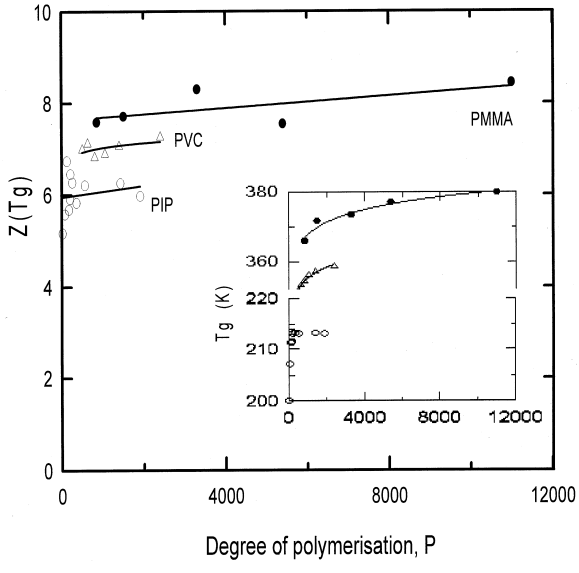

Fig. 1. The size of the cooperatively rearranging regions in polyisoprene (PI), polyvinyl chloride (PVC) and polymethyle methacrilate (PMMA) as a function of the degree of polymerization. In the inset, glass transition temperatures as a function of degree of polymerization for the same polymers are given.

Table 2
The α relaxation parameters of the saturated carbon backbone polymers

Polymers[a]	T_g (K)	C_1	C_2	log $\tau(T_g)$ (s)	U (kJ/mol bead)	$z(T_g)$	n	Reference
PIB	205	16.1	107.0		32.96	1.92	2	1, 41
PE	231	14.8	73.2		20.74	3.16	2	50
PP	253	18.0	47.6	3	16.40		2	51
	256	17.0	50.4	2		5.08		
PMA	276	16.8	53.6		17.23	5.15	2	41
PVClA	296	17.6	51.0		17.13	5.80	4	41
PVA	304	17.4	43.4	4.4	14.48		4	52
	317	15.0	50.3	2		6.30		
PVC	356	16.7	51.8	0.8	16.60		2	52
	353	17.9	48.3	2		7.29		
PMMA	373	16.1	45.0	2	13.87	8.30	3–4	52

liquids T_g is usually defined as temperature at which $\tau = 100$ s [2]. Hence for polymers where average τ at conventional T_g are known, the transition to the $T_g(\tau = 100)$ was done and they are listed at the second position in Table 2. As may be seen from the table, both glass transition temperatures coincide only for PMMA. In the following T_g at which $\tau = 100$ s and the corresponding WLF parameters are used for the polymers in Table 2. It should be mentioned that the $U = 2.3RC_1C_2$ and $T_\infty = T_g - C_2$ are independent from the reference temperature in the WLF equation. The number of the beads n in the monomeric units is taken from Wunderlich and Jones [34], and Chang and al. [28]. As may be seen from the table, the size of the cooperative unit of the listed polymers increases with the increase of T_g. As U slightly changes with T_g, the activation energy per cooperative unit appears proportional to T_g (Fig. 2).

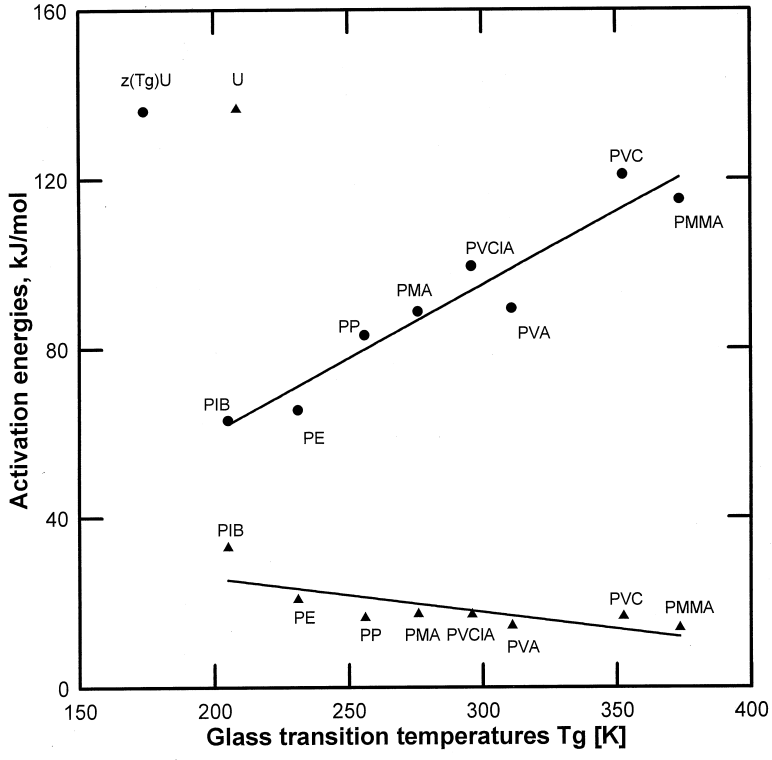

Fig. 2. The activation energies of the cooperative rearranging regions and of a basic molecular kinetic unit as function of the glass transition temperatures in the saturated carbon backbone polymers.

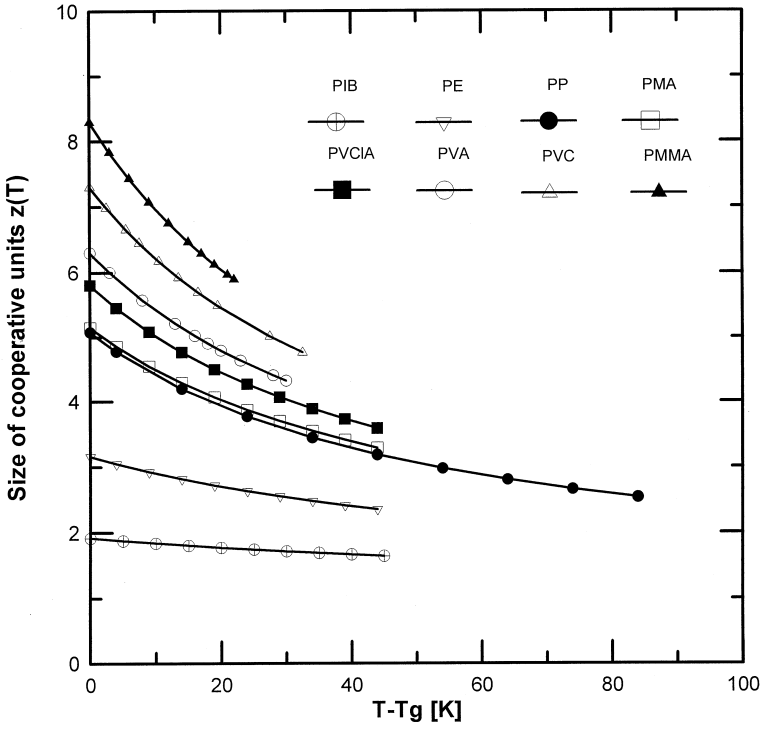

Fig. 3. Temperature dependence of the size of cooperatively rearranging regions in the saturated carbon backbone polymers.

Fig. 3 shows the temperature dependence on the average size of the cooperative units in the experimentally investigated ranges. It may be seen from Fig. 3 that the steepness of the curves increases with the increase of the size of the CRRs. This property is related to the fragility, as will be discussed later.

From Table 2 it may be seen that the values of average $z(T_g)$ are around the universal value of 3.9 beads, which may be regarded as supporting the statement that beads are basic kinetic units in the cooperative molecular motion.

3.2. The internal rearrangement within the cooperative unit

3.2.1. The number of configurations within the cooperative unit

The configuration entropy at T_g is accepted as equal to the difference between the entropy of glass and crystal at $T = 0$ K [11, 27, 28, 53]. Hence $\Delta S(T_g) = S_g^0$ may be measured for the semicrystalline polymers. The saturated polymers for which the experimental results for S_g^0 and T_∞ are available are listed in Table 2. The number of configurations in the cooperative units at T_g is estimated by Eq. (13).

The obtained result $w(T_g)/z(T_g) > 1$ in the table indicates the internal rearrangement within the cooperative unit.

3.3. The accompanying subspectra of the cooperative molecular dynamics

As it was discussed in Section 1.2 the result $w(T_g) \geq z(T_g)$ presupposes that cooperative rearrangement is connected to an accompanying subspectrum due to the individual overcoming of the potential barrier U by the basic molecular species.

By neutron and light scattering study of the supercooled liquids including polymers in the THz range around T_g, a relaxation process called beta fast β_f was observed recently [54–57]. The temperature dependence of the β_f process is weak, but nevertheless the activation energies for the polymers listed in Table 4 are estimated [56].

As may be seen from the table the measured U_e and the predicted U_p are in reasonable agreement. This result is additional evidence for the existence of the internal rearrangement inside the CRR, compatible with the previous section. The other interpretations of theβ_f process are discussed by Zorn et al. [56].

It is interesting to mention that if Arrhenius' law is accepted for the configurational times with the same vibrational time A as for the cooperative units, reasonable values for the configurational times are obtained [25]. Common average vibrational time per cooperative unit and per bead implies that the normal mode of vibrations correlates at least to some degree

Table 3
The number of configurations within the cooperative units of semicrystalline polymers.

Polymers[a]	T_g (K)	T_∞ (K)	n	S_g^0 (J/K mol beads)	$w(T_g)$	$w(T_g)/z(T_g)$	Reference
PDS	151	81	2	4.45	3.3	1.5	41, 53
PPO	198	174	3	2.66	14.0	1.7	41, 53
PEO	216	180	3	3.70	14.4	2.4	33, 53
PE	237	158	2	3.80	3.9	1.3	42, 53
PP_i	260	206	2	3.29	6.5	1.4	28, 53

[a] Polydimethyl siloxane (PDMS), Polypropylene oxide (PPO), Polyethylene oxide (PEO) and isotactic PP_i.

the rearrangement of the basic kinetic units in the cooperative molecular dynamics.

3.3.1. The internal rearranging cooperative units in the glass transition process

The most widely accepted definition of the glass transition temperature is the temperature where during cooling the structure relaxation time of the liquid becames equal to a definite "time scale" t_e and below this temperature the liquid is "frozen" in glass. As was mentioned in Section 2.1.2 recently, many authors accepted $t_e = \tau(T_g) = 100$ s. As in the real liquid spectrum of the relaxation times exists at T_g average relaxation time (for convenience in this section we shall mark it with τ_v) $\tau_v = t_e$, i.e. the microheterogeneous ranges with τ_v will be frozen in glass. At this temperature the shorter relaxation times τ_s than the average $\tau_s < \tau_v$ are still in the liquid phase as for this part of the spectra $\tau_s < t_e$. At the same temperature the longer relaxation times τ_l than average ($\tau_l > \tau_v$) are already "frozen in" and part of the sample is already transformed in glass. In such a way in the case of the spectrum during cooling, hierarchy in the freezing process exist. The longest relaxation times will be "frozen in" at a temperature $T_l > T_g$. Hence in accordance of above definition of T_g, roughly half of the sample is in liquid and half in the glassy state. Now there is a temperature $T_f < T_g$ where at the same fixed "time scale" during cooling the shortest relaxation times will became longer than t_e and the whole spectrum will be "frozen" or the whole sample will be transformed into glass. T_f is experimentally observable and for example may be chosen as temperature at the low temperature end of the α-relaxation peak of loss factors measured at a fixed frequency as a function of temperature. The frequency $\nu = 1.6\times10^{-3}$ Hz is equivalent to $t_e = 100$ s. T_f, where full transition of the liquid in the glass is observed also may be regarded as a sort of glass transition temperature. If the glass transition temperature is defined as temperature above which equilibrium liquid is observed, correspondingly T_l should be this point. Hence it is interesting to consider the relation between T_g, T_f and T_∞ using the Adams–Gibbs model and model with internal rearranging of CRRs with distribution of their sizes.

The experimental results in the previous two sections supported the internal rearrangement within the cooperative unit and it follows that it will behave as a liquid unit. Hence the liquid properties during the heating of glass will be introduced by cooperatively rearranging regions. On the contrary when a liquid is cooled down, at a temperature T_l the largest cooperative units with the highest $z\cdot U$ and A, which produce the largest τ in the spectrum as it follows from Eq. (5), will be "frozen" and will be transformed to glass domains. Hence under T_l the liquid will be a mixture of the cooperatively rearranging regions (liquid units) and glass domains. At T_g a rough equilibrium between size and concentration of the liquid units and glass domains will be established. In the glass domains no more configurational rearrangement will occur with the same meaning as T_g is defined, i.e. configurational motion will be "frozen in" at a chosen "time scale". Below T_g the size and concentration of glass domains will increase and only cooperative units with smaller than average $z\cdot U$ and A will be preserved as liquid

Table 4
Comparison of measured and predicted activation energies for the configuration spectrum.

Polymers	U_e (kcal/mol)	C_1	C_2	T_g (K)	U_p (kcal/mol beads)	Reference
PB[a]	2	13.4	50.5	172	3	41, 56
PI	2	12.5	34.3	213	2	40, 56
PVC	4.5	16.8	52.0	354	4	52, 56

[a] Polybutadiene (PB), Polyisoprene (PI).

units. At a temperature T_f the last and the smallest, i.e. with the smallest $z \cdot U$ and A cooperative units will be "frozen" and liquid will be fully transformed into glass.

A convenient method for estimation of the distribution of relaxation times on the temperature axis is the method of thermally-stimulated depolarisation currents (TDC) [49, 58–62] The TDS method is based on the temperature dependence of the relaxation times. At given temperature during the polarisation time t_p, under the influence of the field dipoles having relaxation times $\tau < t_p$ are oriented. Then the sample is cooled to a temperature at which the relaxation times are of the order of several hours or longer. Correspondingly, when the field is switched off after cooling, the dipoles remain frozen and oriented. On warming, the sample, the relaxation times decrease, the dipoles are disoriented and TDC is recorded. It is evident that by choosing the temperature and time of polarization and temperature at which the field is switched off, different relaxation processes or polarization due to only to a part of spectrum of a given relaxation process can be observed. Some authors assume that with good approximation with multistage TDC, polarization from nearly individual relaxation time from the spectra may be investigated [61, 62]. TDS method appears to be equivalent of the frequency measurements in the range of 10^{-2}–10^{-3} Hz just in the range of "time scale" usually used for measuring T_g. Glass transition temperature measured by this method corresponds to the temperature of the maximum of the TDC from an α-relaxation process [58]. An estimation of T_l, T_g and T_f by TDC in PMMA gives $T_l = 130°C$, $T_g = 110°C$ and $T_f = 45°C$ [49, 59, 60]. The T_f, Tg and T_l are taken correspondingly as points of the onset, maximum and end of the TDC from a dipole α-relaxation process. Hence T_f is lower than $T_\infty = 55°C$ (estimated from results of Saito from Table 2) and this is not surprising as T_∞ is obtained by extrapolation of average relaxation time which correspond to CRRs with average size. As a matter of fact T_f and T_l are a measure of the width of the distribution of relaxation times [49, 58, 60] and correspondingly of the size of the cooperative units. T_f corresponds to the shortest relaxation times and to the smallest CRRs and in this way may be regarded as related to Adams–Gibbs z^*. Naturally, these three points in a given sample, as is well known for T_g, will depend on the cooling or the heating rates, respectively. It is interesting that T_l could be related to dynamical glass transition temperature T_c of the MCT as far as T_c is the point where "there is cross over from activated glass like transport in the strongly supercooled region $T < T_c$ to the liquid-like transport in the moderately supercooled region $T > T_c$" [63, 64].

The above scenario is for a real glass transition process with a real example for PMMA. The VTF and WLF equations are applicable at temperatures above T_g [41, 46]. Near to T_g the parameters in these equations became dependent on the cooling rate and thermal history of the sample. [65]. Such behavior is expectable as in the polymers wide distribution of the relaxation times is observed [41, 42, 45, 46]. Independently of these facts usually above T_g supercooled liquids are assumed to be in the equilibrium. Below T_g liquid is not in equilibrium, but Eqs. (1) and (9) may be extrapolated below T_g and this is naturally only one idealization, the liquid is called an "ideal supercooled liquid" [38]. From Eqs. (1) and (9) it follows that at T_∞ the average relaxation time will diverge and configurational entropy will vanish, i. e. configurational rearrangements will be "frozen in" in principle. This is the reason that VTF temperature T_∞ is sometimes called the "ideal glass transition temperature". Such extrapolation also may be applied for Eq. (6) from which it follows that at T_∞ average in size CRRs will became infinitely large and from Eq. (5) we obtain that τ just as in the case of the VTF equation will diverge. Extrapolation of Eq. (6) below T_g is also idealization and infinitely large z is also idealization; in the real liquids CRR with average size became the largest as a function of temperature at T_g.

3.4. The cooperative molecular dynamics and fragile/strong patterns

The T_g-scaled Arrhenius plots of segmental relaxation times for the polymers listed in Table 2 are shown in Fig. 4. The temperature dependence of $\tau(T)$ for PIB is close to the Arrhenius' behavior and this polymer is classified as strong while PVC and PMMA are observed at the fragile end. As may be seen from Fig. 4 the departure from Arrhenius behavior, fragility, for the investigated carbon backbone polymers increases with the increase of theT_g.

In Fig.5 the T_g-normalized Arrhenius plots for $z(T)/z(T_g)$ are given. In comparing Figs. 4 and 5 a coincidence in the behavior is observed, which was predicted by Eq. (24). Hence the fragility reproduces the temperature dependence of the size of the cooperative unit.

Interesting results are observed when we compare the cooperative molecular dynamics of polymers to the dynamics of other supercooled liquids. The parameters of the cooperative molecular dynamics in inorganic supercooled liquids are given in the Table 5.

The first two liquids are ionic and the others represent networks. From Fig. 6 it can be seen that proportionality between activation energy per CRR and T_g is observed in the same manner as with the polymers. The same behavior is observed in alcohols [25]

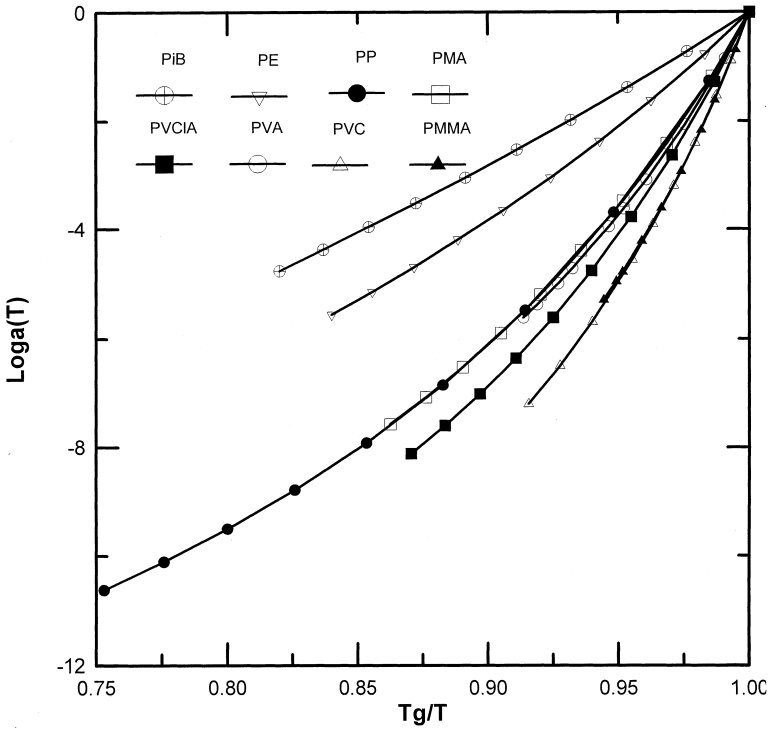

Fig. 4. T_g-scaled Arrhenius plots for the saturated carbon backbone polymers. The points are obtained by the WLF equation.

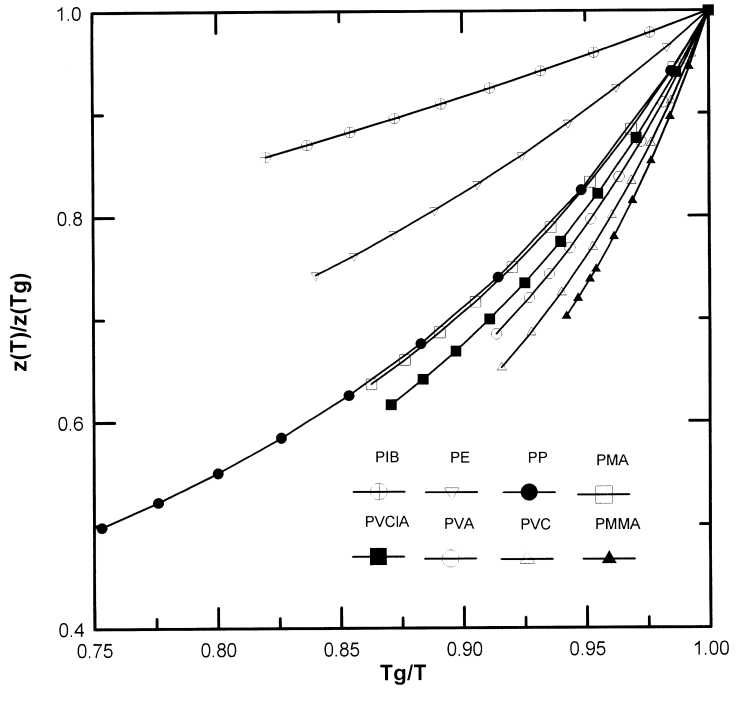

Fig. 5. T_g-normalized size of the cooperative units as function of the T_g-scaled temperatures for the saturated carbon backbone polymers.

Table 5
The parameters of the cooperative molecular dynamics in inorganic supercooled liquids

Substance	T_g (K)	C_1	C_2	U (kJ/mol beads)	$z(T_g)$	Reference
$Ca_{0.4}K_{0.6}(NO_3)_{1.4}$	333	15.8	33	9.97	10	66
$ZnCl_2$	375	17.2	115	37.97	3.26	67
B_2O_3	526	15.2	263	76.53	2	66
SiO_2	1373	13.4	1120	287.30	1.23	68

and this seems to be a common characteristics of all glass-forming substances.

An interesting difference between saturated carbon back polymers and other supercooled liquids is observed in comparing U and T_g. Indeed while in the polymers U decreases with the increase of T_g, Fig. 2, in the other glass-formers (Fig. 6) the opposite phenomenon is observed. The fact that different combinations of z with U is observed suggests a possible explanation for the thermoreological simple behavior observed in polymers [41]. The thermoreological simple behavior or time–temperature superposition principle requires all relaxation times in the α relaxation spectrum to possess one and the same activation energy [41, 46]. As random distribution of the potential barriers in the topological disordered structure of polymers is observed [69], this phenomenon is not explained from the molecular point of view. If it is accepted that in one and the same polymer large z is combined with small U and vice versa in such a way that the products zU are equal, then the spectrum will obey the time-temperature superposition principle. On the other hand it is obvious from Fig. 3 that the temperature range of validity of this principle will increase with the strength of the polymers and in general not only polymers but strong liquids are expected to obey this principle. It is interesting to note that in the great majority of supercooled liquids a correlation between the fragility index and the stretching parameter β in the Kohlraush–Williams–Watts response function is found [2] or in terms of the distribution of relaxation times in fragile liquids a wide distribution is observed. From the point of view of the size of the CRR this phenomenon seems to be a reasonable consequence, as

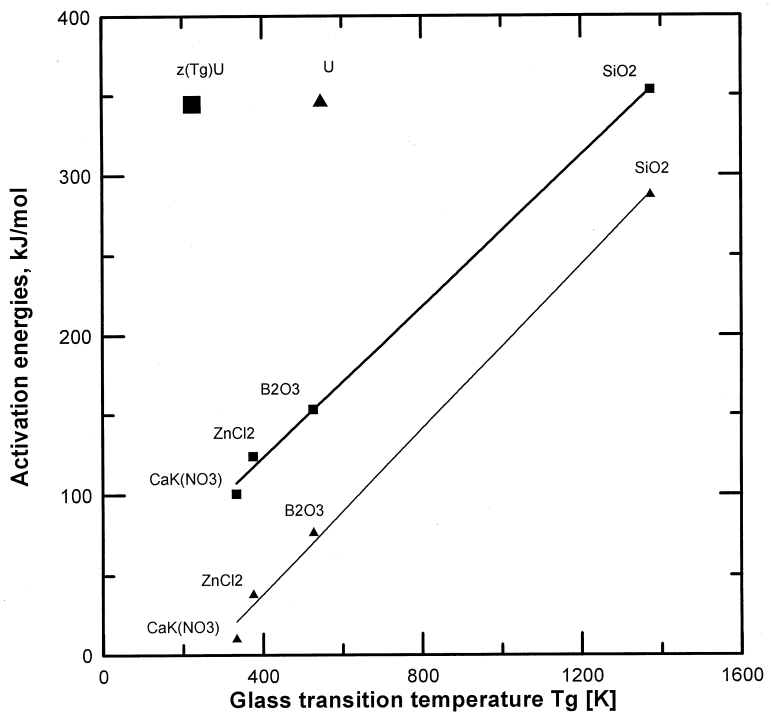

Fig. 6. The activation energies of the cooperative rearranging regions and of a basic molecular kinetic unit as function of glass transition temperatures in the inorganic supercooled liquids.

a large average z in fragile liquids gives a possibility for wide distribution in U and z and correspondingly in τ.

In Fig. 7 the fragility index is plotted as function of the size of the cooperative units for supercooled liquids from Tables 2 and 5. As it may be seen, a linear dependence is observed in agreement with Eq. (21) as C_1 in the investigated liquids varies in a narrow range (Tables 2 and 5). Earlier both constants C_1 and C_2 were considered universal if T_g is chosen as reference temperature [41]. Indeed the values of C_1 in Tables 2 and 5 are close, but C_2 varies in a wide range. In the saturated carbon backbone polymers C_2 decreases with the increase of T_g, while in the inorganic glass-former just the opposite behavior is observed.

From the quantity characterizing the cooperative molecular dynamics z and U the steepness index is directly related to the size of the CRR. On the other hand the strength parameter D is closely related to the U. Polymers and also inorganic glass-formers with higher U exhibit a stronger behavior (Tables 2 and 5). Indeed $D = B/T_\infty = U/RT_\infty$ or the strength parameter reflects the strength of resistivity of a basic molecular species against its involvement by thermal energy, at ideal glass transition temperature RT_∞ in the cooperative rearrangement. In Fig. 8 the energetic ratio at T_g per basic species U/RT_g and per CRR $z(T_g)U/RT_g$ as function of D are shown. It may be seen from the figure that the energetic ratio per the CRR is practically the same for all supercooled liquids, while U/RT_g increases with the strength of the liquids. From the figure it is also obvious that the configuration spectrum will be better resolved from the relaxation spectrum in the fragile substances than in the strong ones.

4. Summary and conclusion

The equations for measuring the number of the basic molecular kinetic units in the process of the cooperative rearrangement are described. The basic molecular kinetic units are identified as fragments of the monomeric units called beads by Wunderlich. The identification of the basic kinetic units in the cooperative rearranging region makes it possible the number of configurations in this region to be measured. The rearrangement of the cooperative unit in accordance to its environment causes the α-relaxation spectrum of polymers. During the rearrangement of the cooperative rearranging region in accordance to its environment internal rearrangement of the basic molecular kinetic units within the cooperative regions exist. This internal rearrangement is assumed to cause an accompanying subspectrum of the α-relaxation times, called configur-

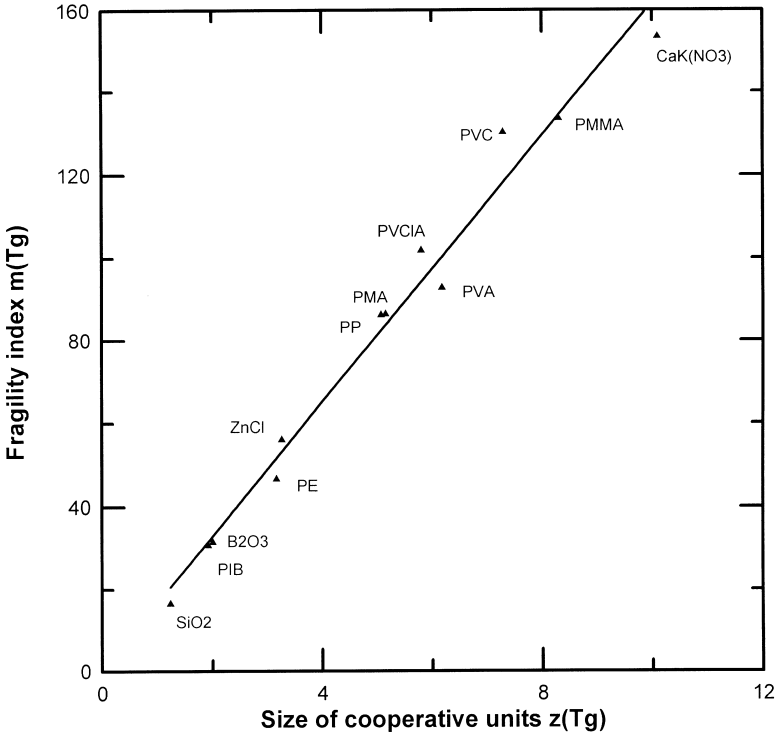

Fig. 7. The fragility index as function of the size of the cooperative units for polymers and inorganic supercooled liquids.

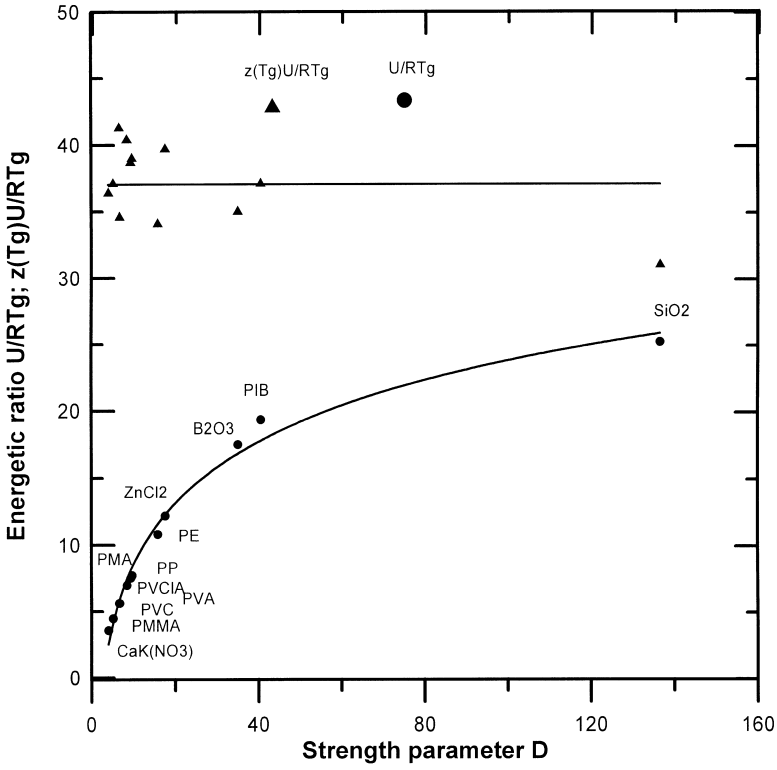

Fig. 8. The energetic ratio at T_g of the cooperative rearranging regions and of a basic molecular kinetic unit as function of the strength parameter for the substances marked on the curves.

ation spectrum. The activation energy of the configuration spectrum may be predicted from the VTF equation. The popular T_g-normalized Arrhenius plot for the illustration degree of departure from Arrhenius behavior was obtained to reproduce the temperature dependence of the size of the CRR. The steepness or fragility index has been obtained to be proportional to the size of the CRR.

In discussing the experimental results it was observed that in all supercooled liquids T_g is proportional to the activation energy of the CRRs. The measured number of configurations in the cooperative unit of the polymers is equal or higher than the number of beads in these units. This result is regarded as supporting the model of cooperative unit with internal dynamics. Reasonable coincidence of the predicted and observed activation energies of the configuration spectra may be regarded also as evidence for this kind of dynamics. A scenario of the glass transition process on the basis of the cooperative units with the internal rearrangement is suggested.

The activation energy of the basic kinetic units in the polymers decreases with the increase of T_g, while the opposite phenomenon in the inorganic supercooled liquids is observed. The combination of z with U in polymers is supposed to cause the thermoreological simple behavior of these substances. From the point of view of the cooperative molecular dynamics the strength parameter reflects the effectiveness of thermal energy RT to excite a basic molecular kinetic unit in the cooperative rearrangement. In the fragile liquids this effectiveness is higher in comparison to the strong ones.

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References

[1] Berry JC, Fox TG. Adv Polym Sci 1968;5:21.
[2] Bohmer R, Ngai KL, Angell CA, Plazek DJ. J Chem Phys 1993;99:4201.
[3] Angell CA In: Ngai K, Wright GB, editors. Relaxation in complex systems. Springfield, VA: National Technical

Information Service, US Department of Commerce, 1985. p. 1.
[4] Angell CA. J Non-Cryst Solids 1991;13:131–3.
[5] Angell CA. Science 1995;267:1924.
[6] Plazek DJ, Ngai KL. Macromolecules 1991;24:1221.
[7] Roland CM, Ngai K L. Macromolecules 1991;24:5351.
[8] Ngai KL, Roland CM. Macromolecules 1993;26:6894.
[9] Roland CM, Ngai KL. Macromolecules 1996;29:5747.
[10] Brunacci A, Cowie JMC, Ferguson R, Gomez Ribelles JL, Vidaurre Garayo A. Macromolecules 1996;29:7976.
[11] Adam G, Gibbs JH. J Chem Phys 1965;43:139.
[] Tweer H, Simmous IH, Macedo PB. J Chem Phys 1971;54:1952.
[13] Cohen MH, Grest GS. Phys Rev B 1979;20:1077.
[14] Donth E. J Non-Cryst Solids 1982;53:325.
[15] Hodge IM. Macromolecules 1987;20:2897.
[16] Jacobson P, Borgesson L, Torell LM. J Non-Cryst Solids 1991;131(133):104.
[17] Donth E. J Non-Cryst Solids 1991;131(133):204.
[18] Ngai KL, Rendell RW, Plazek DJ. J Chem Phys 1991;84:3018.
[19] Ngai KL. J Non-Cryst Solids 1991;131(133):80.
[20] Matsuoka S, Quan X. J Non-Cryst Solids 1991;131(133):293.
[21] Chamberlin RV, Bohmer R, Sanchez E, Angell CA. Phys Rev B 1992;46:5758.
[22] Stillinger F, Hodydan JA. Phys Rev E 1994;50:2064.
[23] Odagaki T. Phys Rev Lett 1995;75:3701.
[24] Solunov ChrA. Balkan Phys Lett 1995;3:26.
[25] Solunov ChrA. Bulg J Phys 1997;24:32.
[26] Wunderlich B. J Chem Phys 1960;64:1052.
[27] Bestul AB, Chang SS. J Chem Phys 1964;40:3731.
[28] Chang SS, Bestul AB, Horman JA. Proceedings of the 7th International Congress on Glass, vol. 26. New York: Gordon and Breach, 1965. p. 1.
[29] Kittel Ch. Introduction to solid state physics. New York: Wiley, 1977.
[30] Hirai N, Eyring H. J Appl Phys 1958;29:810.
[31] Hirai N, Eyring H. J Polym Sci 1959;37:51.
[32] Miller AA. J Chem Phys 1968;49:1393.
[33] Miller AA. Macromolecules 1978;11:859.
[34] Wunderlich B, Jones LD. J Macromol Sci Phys 1969;B3:67.
[35] Krevelen DW. Properties of polymers, correlation with chemical structure. Amsterdam: Elsevier, 1972.
[36] Mathod VA. Polymer 1984;25:579.
[37] Wiliams G. In: Davies M, editor. Dielectric and related molecular processe, vol. 2. London: Chemical Society, 1975. p. 151.
[38] Sugisaki M, Adochi K, Suga H, Seki S. Bull Chem Soc Jpn 1968;41:593.
[39] Adachi K, Kotaka T. Macromolecules 1985;18:466.
[40] Boese D, Kramer F. Macromolecules 1990;23:829.
[41] Ferry JD. Viscoelastic properties of polymers. New York: Wiley, 1980.
[42] Fuoss RM, Kirkwood JB. J Amer Chem Soc 1941;63:385.
[43] Nowick AS, Berry BS. IBM J Res Dev 1961;5:297.
[44] Cole RH, Cole KS. J Chem Phys 1941;96:245.
[45] Harviliak S, Negami S. J Polym Sci Polym Symp 1966;14:89.
[46] McCrum NG, Read BD, Williams G. Anelastic and dielectric effects in polymer solids. New York: Wiley, 1987.
[47] Williams GW. J Non-Cryst Solids 1991;131(133):1.
[48] Higasi K, Bergmann K, Smyth PC. J Phys Chem 1961;64:880.
[49] Solunov ChA, Ponevsky ChS. J Polym Sci Polym Phys Ed 1977;15:969.
[50] Davies GT, Eby RK. J Appl Phys 1973;44:4274.
[51] Schaefer D, Spiess KW, Suter HW, Fleming WW. Macromolecules 1990;23:3431.
[52] Saito S. Kolloid Z Z Polymers 1963;189:116.
[53] Rabynovich IB, Lebedev BV. Visokomol Soed 1979;21:2025.
[54] Frick B, Richter D. Phys Rev B 1993;47:14759.
[55] Colmenero J, Arbe A, Alyeria A. Phys Rev Lett 1993;71:2603.
[56] Zorn R, Arbe A, Colmenero J, Frick B, Lietter D, Buchenau U. Phys Rev E 1959;781:52.
[57] Wuttke J, Petry W, Coddens G, Fujara F. Phys Rev E 1995;52:4026.
[58] van Turnhout J. Thermally stimulated discharge of polymer electrets. Amsterdam: Elsevier, 1985.
[59] Solunov Chr, Hedvig P. Processing of the Third Tihany Symposium on Radiation Chemistry. Budapest: Hungerian Academy of Sciences, 1971. p. 899.
[60] Solunov ChrAl, Vassilev TA. J Polym Sci Polym Phys Ed 1974;12:1973.
[61] Lacabanne C, Chatain D. J Polym Sci Polym Phys Ed 1973;11:2315.
[62] Gobrcht H, Hofmann D. J Phys Chem Solids 1996;24:509.
[63] Gotze W. In: Hansen JP, Levesque D, Ziun Jastin J, editors. Liquids, Freezing and the Glass Transition. Amsterdam: North-Holland, 1991. p. 287.
[64] Gotze W. Ferroelectric 1992;128:307.
[65] Schwarzel FR, Zahradnik F. Rheol Acta 1980;19:586.
[66] Grimsditch M, Torell LM. In: Richter D, et al., editors. Springer Proceedings in Physics, Dynamics of Disordered Materials, vol. 37. Berlin: Springer, 1989. p. 196.
[67] Eastel AJ, Angell CA. J Chem Phys 1972;56:4231.
[68] Bruckner R. J Non-Cryst Solids 1970;5:123.
[69] Solunov ChrA, Ponevsky Chr. J Polymer Sci Polym Phys Ed 1976;14:1801.