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06

Processes occurring during the transition from strong to fragile relaxation in glass-forming substances

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Processes occurring in the vicinity of the crossover point in glass-forming substances on the example of epoxy resin are considered. The crossover point is considered as the strong-to-fragile transition in glassformers. The transition is accompanied by the association of free molecules into clusters with decreasing temperature. It is shown that the frequency (temperature) spectra of the substance exhibiting the transition can be represented as the sum of the spectra corresponding to the motion of free molecules and clusters. In the transition region the nature of internal friction changes. It is shown that strong relaxation is due to the movement of free molecules and molecule-molecule interaction; cluster relaxation is caused by inter-cluster interaction. Three different types of interaction are observed simultaneously in the transition region: cluster-cluster, molecule-molecule, and molecule-cluster. It is shown that the secondary relaxation of the β-type is caused by free molecules motion and molecule-cluster interaction. The presence of clusters is a necessary condition for the emergence of secondary relaxation.

Keywords: Glass forming substances, fragility, viscosity, relaxation.

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Introduction

Viscous fluid and glass dynamics is of great interest to researchers. Properties of these substances have been extensively studied using various experimental methods and models [1–3]. Dynamic behavior of glass-forming substances (GFS) is examined by the dielectric spectroscopy that is widely used to provide information concerning dynamic processes of glassformers [2,3]. Dielectric loss frequency spectra of GFS usually demonstrate two relaxation processes: α and β. Primary α-relaxation demonstrates a dominant loss peaks at low frequencies; secondary relaxation shows pronounced high-frequency β-peaks. Presently it is considered that the α-relaxation corresponds to a slow overall structural rearrangement of a system; the β-relaxation is associated with fast local dynamics. It is known that the β-relaxation is molecular in nature and is caused by intermolecular interaction [1–3]. Both types of relaxation are universal properties of amorphous materials.

Width and position of the α-peak strongly depend on temperature and pressure. Relaxation time or primary relaxation time constant τ_α ($\tau_\alpha = 1/2\pi f_m$, here f_m is the position of loss peak maximum) increases by many orders of magnitude when the substance is cooled down from the liquid to glassy state. Twofold change in temperature induces a frequency shift of the loss peak maximum by ~ 14 decades [1–3]. The relaxation time is proportional to a liquid viscosity [1].

To date, many various physical models describing the GFS properties have been accumulated (see, for example, work [4]). Unfortunately, the existing models cannot explain a number of critical properties. The simplest model of the temperature dependence is an activated behavior, where the viscosity (η) and relaxation time are functions of some temperature-independent activation energy ΔE, measured in units of temperature. This model leads to the Arrhenius temperature dependence [5]:

$$\eta = \eta_0 \exp\left(\frac{\Delta E}{T}\right) \quad \tau_\alpha = \tau_0 \exp\left(\frac{\Delta E}{T}\right), \tag{1}$$

where η_0 and τ_0 are viscosity and time constant high-temperature limits. Despite the wide aplicability of law (1), substances accurately described by this equation occur quite rarely. Temperature dependence is usually stronger than a simple exponent (1).

The concept of „fragility" [1–3] has been introduced to describe the non-Arrhenius non-exponential relaxation temperature dependence of η and τ. Fragility is a measure of how much this temperature dependence deviates from the Arrhenius law, which is referred to as a „strong" one. Consecutively, materials, which obey the Arrhenius law, are called strong materials, and non-Arrhenius materials are called fragile. Note that description of glasses also uses terms „long" and „short" glasses [6,7], which are equivalent to terms „strong" and „fragile".

Temperature dependence η and τ is usually illustrated by the Angell plot [1,3], where the logarithm η (or τ) is shown as function of the T_g-scaled inverse temperature, (T_g/T), (schematic diagram is shown in Fig. 1). Here, T_g is the glass transition temperature. The Arrhenius law in such coordinates is a straight line with slope ΔE,

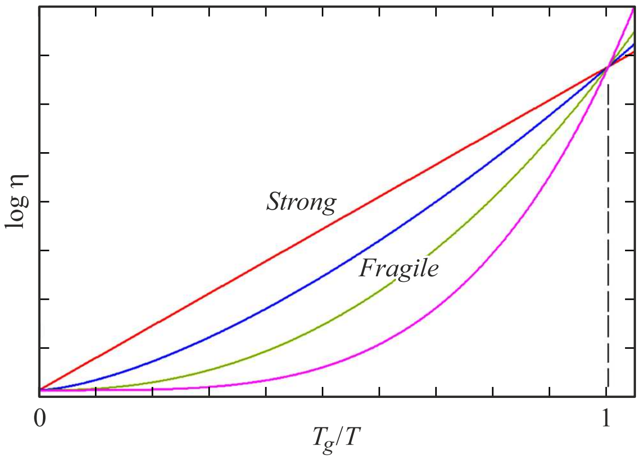

Figure 1. Typical dependences of viscosity logarithm on reciprocal temperature normalized to the glass transition temperature (Angell plots). Straight line corresponds to the Arrhenius law, concave lines correspond to the fragile relaxation.

and the fragile behavior corresponds to a concave curve. Different substances are characterized by varying degrees of concavity.

The Adam–Gibbs model of cooperative relaxation [8] is successfully used to describe the temperature dynamics of GFS. The model is based on the concept of cooperatively rearranging regions. This concept leads to correlation between fragility and cooperativity: fragile systems are considered to have higher cooperativity. As the liquid cools down, the region size gradually increases, leading to a decrease in the system configuration entropy [8,9], which in turn leads to an increase in viscosity. Though the main principles of the model have repeatedly subjected to significant criticism, the model is still widely used. Cluster models are closely related to the AG model [10–13]. Clusters or other associations of molecules are often used as a hypothesis for explaining the observed phenomena where not only a stable molecular conglomerate, but also a local increase in density can be regarded as a cluster. Size distribution of clusters in supercooled liquids and glasses was observed in [14] using the confocal microscopy. Heterogeneity provided by clusters has been also observed by Ediger [15]. Some authors [16] believe that it is clustering that inhibits glass crystallization.

Another possible approach to describing temperature properties is the use of analytical functions. There is currently a number of functions describing the temperature behavior of η and τ; the Vogel–Fulcher–Tamman function being the most commonly used [17]. This function is widely used for data interpolation, but rarely gives adequate approximation across the entire range of temperatures. There are more accurate functions, for example, MYEGA [18] and exponential function [19,20]. The exponential function has the form as [19]:

$$\tau(T) = \tau_0 \cdot \exp \frac{\Delta E}{T^n}. \tag{2}$$

Here, n is the fragility index, at $n > 1$ the function describes fragile behavior, $n = 1$ corresponds to the Arrhenius law. The practical modeling shows, that function (2) is easy-to-use and can describe experimental spectra in a wide temperature range with high accuracy [20]. Function (2) is used in this work for simulating temperature dependences of GFS.

There are currently two known types of liquid–liquid transition in GFS: transition from fragile to strong relaxation with temperature decrease and reverse transition from strong to fragile relaxation. Transition from fragile to strong relaxation was first detected in supercooled water in work [21], heat capacity anomaly was detected at transition point [22]. Unfortunately, transitions from strong to fragile relaxation are poorly understood. Such transition has been found in α-picoline by authors of work [23]. The authors have shown that at a certain temperature transition from single-particle to cooperative dynamics occurs as the temperature decreases.

Crossover phenomenon is observed for many glass-forming systems of different composition [24,25]. Crossover is defined as an imaginary point where strong ($\alpha\beta$), fragile (α) and secondary (β) relaxation curves are intersected on the Angell plot. There is currently no consensus on the nature of crossover. Some authors believe that this is just an intersection of curves, for example, work [26]. Or crossover is interpreted as a great increase in the degree of intermolecular cooperation [27]. But it is commonly recognized that dynamic characteristics and other substance properties vary at the crossover temperature T_C ($T_C > T_g$). Note that the above-mentioned crossover and the crossover effect observed during glass annealing [6], — these are various phenomena having the same name.

This paper describes dynamic processes flowing in glass-forming substances in the crossover region. The consideration provides better understanding of relaxation processes and phenomena occurring above the glass transition point.

1. Transition from strong to fragile relaxation

Temperature behavior of glass-forming substances is explained using the main principles of the Adam–Gibbs model: strong relaxation is induced by molecules motion, fragile relaxation is cooperative. We also believe that the cooperative relaxation is caused by the motion of stable molecular associations or clusters.

Let us consider the Angell plot for a substance with well-defined crossover point. A considerable array of experimental data accumulated by now makes it possible to easily find the measurements demonstrating this phenomenon. From a range of available practical spectra (for example, works [28–33], etc.), we have chosen dielectric spectra of epoxy resin (dependence of dielectric loss on frequency and temperature) [28,29]. Epoxy resin in this case is a convenient material demonstrating a clearly pronounced crossover. Frequency spectra of epoxy resin DGEBA were chosen from several similar dependences [28,29].

Angell plots corresponding to frequency spectra of DGEBA are shown in Fig. 2. Fragile relaxation is approximated by exponential function (2) (dashed line). Method of data acquisition for the Angell plots from the frequency-temperature spectra is described in [19], simulation of practical dependences is described in [20].

Fig. 2 shows that DGEBA demonstrates the typical Angell plot with T_C, at which the relaxation behavior varies. Measurement were performed in the temperature range from 256 K to 353 K. Conditional glass transition point ($\tau = 100\,\mathrm{s}$) for DGEBA $T_g \approx 255\,\mathrm{K}$, intersection of strong and fragile curves, or crossover point $T_C \approx 310\,\mathrm{K}$, these values were obtained by extrapolation. At temperatures above T_C, the time constant logarithm is linearly dependent on $1/T$, i.e. the process with constant activation energy is observed (Arrhenius law). Below T_C , the strong relaxation is divided into two different processes: primary α-relaxation (fragile) and secondary β-relaxation (strong), in the literature this phenomenon is called the $\alpha\beta$-splitting [2]. Fragile part of the curve (α-relaxation) obeys law (2) ($n = 9$), the β-relaxation obeys the Arrhenius law, ($n = 1$).

As it follows from Fig. 2, at T_C , transition from strong to fragile relaxation (S-F transition) takes place. As mentioned above, the strong relaxation ($\alpha\beta$) is caused by interaction of free molecules, while the α-relaxation is due to cooperative motion or cluster interaction. Hence, free molecules are associated into clusters at T_C. According to Surovtsev et al. [23], S-F transition is stepwise at T_C, but the review of practical spectra shows that transition takes place in some frequency (temperature) range in the neighborhood of T_C, or in the transition area.

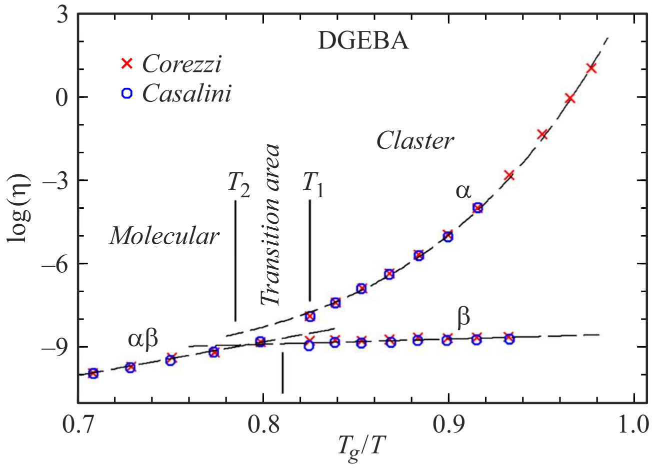

Figure 2. Dependence of relaxation time logarithm τ on relative reciprocal temperature for DGEBA epoxy resin. According to Corezzi [28] and Casalini [29]. For the $\alpha\beta$-relaxation $n = 1$, for the α-relaxation $n = 9$ (function (2)).

2. Analysis of the epoxy resin frequency spectrum

From the foregoing it follows that above T_C, dielectric loss is caused by free molecules motion, and below loss is induced by the cluster motion. Based on this, we assume that the GFS frequency spectra are the superposition of free molecule and cluster spectra.

To confirm this assumption, the frequency spectrum model (an averaged spectrum) was drown, various spectra of DGEBA [28,29], PPGE [28] Epon828 [30], etc., were taken as a pattern. Relaxation times for these substances were measured in the range of 250−350 K, the crossover temperature is within $T_C = (290 \pm 5)\,\mathrm{K}$. Fig. 3, *a* shows the typical spectra having the most specific features of spectra of the above-mentioned substances. Simulation has shown that the frequency spectrum (Fig. 3, *a*) can be quite accurately shown as a sum of cluster (Fig. 3, *b*) and molecular (Fig. 3, *c*) spectra. Havriliak–Negami (HN) function [34] was used to simulate practical spectra. Loss peaks *1–10* (Fig. 3, *a*) are a superposition of cluster (Fig. 3, *b*) and molecular (Fig. 3, *c*) peaks. Peaks *11–13*, which occur above the crossover temperature, are purely molecular peaks.

Fig. 3, *a* shows that the spectra can be divided into three areas corresponding to different types of relaxation: fragile relaxation area (α), transition area and strong relaxation area ($\alpha\beta$). Transition area boundaries are denoted as T_1 and T_2 (Fig. 3, *a*), but note that the transition area has no clear boundaries. The left-hand spectra (α) have wide asymmetric peaks of the primary relaxation (peaks *1–5*). Peaks width significantly depends on temperature; peaks shape is adequately described by the HN distribution. It can be easily seen that all α-peaks are the superposition of two peaks: α-peak itself and a wide symmetric low-amplitude β-peak placed in the transition area. The right-hand part of the figure (area $\alpha\beta$) shows relatively narrow $\alpha\beta$-peaks with faint asymmetry (peaks *11–13*). The shape of these peaks is also described by the HN function. At the same time, peaks *9*, *10* are not described by the HN distribution. Moreover, it follows from Fig. 3, *a* that in the neighborhood of T_C , there are irregular loss peaks (peaks *6–8*), which also do not obey the known analytical distributions. Peaks *6–10* can be described only as superposition of HN peaks. In addition, the transition area has wide low-amplitude secondary β-peaks, whose positions is weakly dependent on temperature. Consequently, the presence of irregular peaks and secondary peaks is the sign of a crossover.

Since the molecular process transforms into cluster in the transition area, then, accordingly, the substance structure and relaxation behavior vary. Obviously, cluster peaks

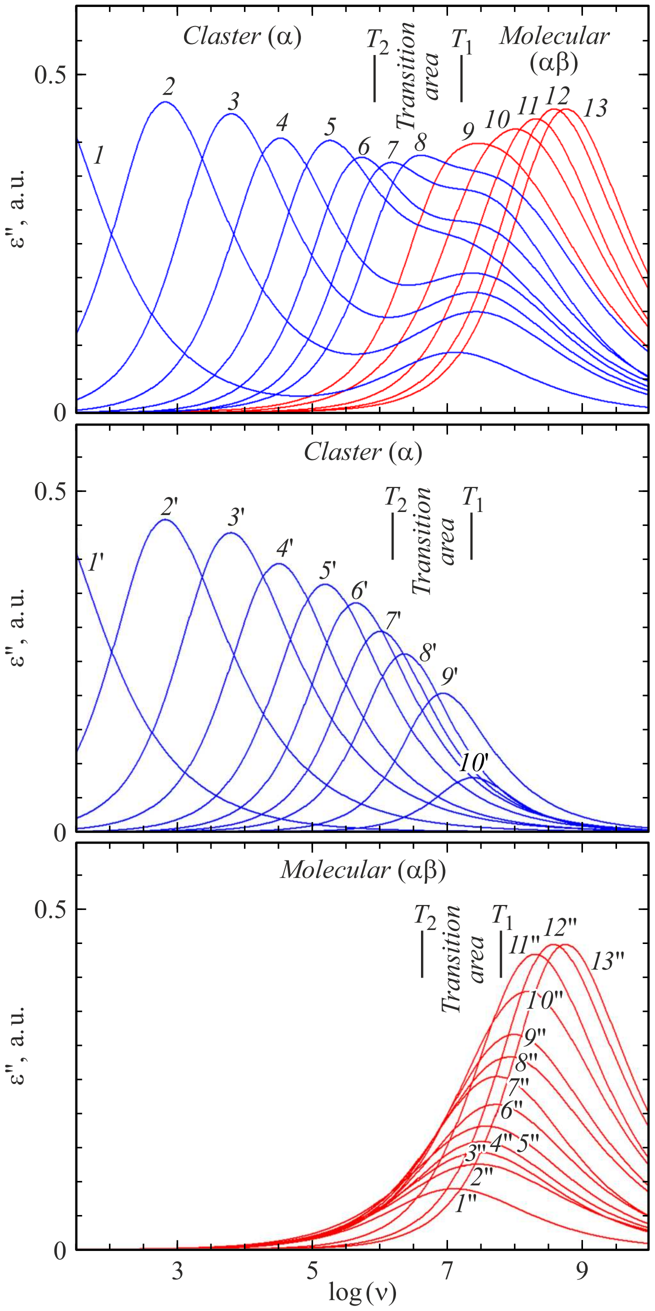

Figure 3. Simulation of dielectric loss frequency spectra of DGEBA, PPGE and Epon828 epoxy resins in the form of cluster and molecular spectra superposition. Peaks corresponding to various temperatures are enumerated in ascending order of temperature. T_1 and T_2 are transition area boundaries. *a* is the total spectrum, *b*, *c* is the cluster and molecular spectra, respectively.

(Fig. 3, *b*) occur in the transition area as a result of free molecule absorption by clusters, which in turn leads to a decrease in the molecular peaks amplitude (Fig. 3, *c*). It is also obvious that with the appearance of clusters, new types of internal friction occur, due to molecule–cluster and cluster–cluster interactions. The $\alpha\beta$-area has a single type of interaction: molecule–molecule.

Consider the evolution of molecular peaks ($1''$-$13''$) shown in Fig. 3, *c*. In the high-temperature area, molecular peaks $12''$, $13''$ are slightly narrower than for the α-relaxation. Peaks in the transition area significantly decrease in amplitude, it is caused by the decrease in molecule concentration due to free molecules absorption by clusters. At the same time, there is significant broadening of molecular peaks ($1''-10''$). It is known that an increase in friction leads to broadening of loss peaks; accordingly, broadening of peaks $1''-10''$ is caused by the appearance of a new type of friction: molecules with emerging clusters.

Thus, formation of clusters induces wide low-amplitude secondary β-peaks ($1''-7''$) caused by free molecules motion. These peaks are within the frequency range corresponding to the transition area. Position of β-peaks either is weakly dependent on temperature (for example, sorbitol [31]), or is almost temperature-independent (epoxy resin [28–30]). Low amplitude is a consequence of low concentration of free molecules due to absorption of the latter by clusters; large peak width is caused by high friction. A question arises: why are not all free molecules absorbed by clusters? Two explanations can be proposed:

(i) free molecules appear as a result of dynamic cluster formation–decay process induced by energy fluctuations;

(ii) β-relaxation is caused by impurity molecules, which cannot be included in clusters.

Both proposed mechanisms probably exist simultaneously. Discussion of these assumptions is beyond the scope of this work.

The fact that the β- and $\alpha\beta$-type relaxations are caused by free molecule motion is their common feature. Differences in behavior are caused by different types of interactions; $\alpha\beta$-relaxation is due to the intermolecular interaction, β-relaxation is induced by the molecule–cluster interaction. It follows from Fig. 2 that the activation energy for the β-relaxation is lower than the one for the $\alpha\beta$-process. It is obvious that this is a consequence of differences in the molecule–molecule and molecule–cluster interaction mechanisms.

Next, consider the behavior of cluster peaks $1'-10'$ shown in Fig. 3, *b*. Clusters in the transition area result from association of free molecules followed by occurrence of cluster peaks. As the number of absorbed molecules increases, the amplitude of α-peaks increases and peaks are broadened. In the α-area ($T < T_1$), the cluster peaks amplitude and width increase as the temperature decreases; positions of peaks substantially depend on the temperature. It is suggested that the width of cluster peaks is mainly affected by the cluster–cluster interaction, while the cluster–molecule interaction has no any substantial effect.

It may be suggested that cluster formation with a decrease in temperature occurs because this becomes energetically favorable, i.e. the cluster structure gives the minimum of thermodynamic potentials for a fragile substance.

3. Discussion

In this study the crossover point is considered as a transition from the strong to fragile relaxation. The new approach explains processes taking place in the neighborhood of this point, strong-to-fragile transition mechanism and the nature of the secondary relaxation.

For a substance demonstrating the S-F transition, frequency spectra can be divided into three areas by the type of processes in them: molecular, transition and cluster (Figs. 2, 3). The S-F transition takes place in the transition area in a quite wide frequency (temperature) range. It is shown that a change in substance structure occurs in the transition area. Appearance of the structural (α) and secondary (β) relaxations is a consequence of molecules association into clusters.

Also internal friction nature varies in the transition area. Association of molecules into clusters in the neighborhood of T_C leads to the fact that, besides the molecule–molecule interaction, new types of cluster-related interactions occur: cluster–cluster and molecule–cluster. Features of molecular and cluster peaks are to a great extent provided by various types of friction. Above the S-F transition area boundary (T_1), only the molecule–molecule interaction is possible and, consequently, only the Arrhenius relaxation is possible. Below T_1 , the cluster–cluster and molecule–cluster interactions are observed. The molecule–cluster interaction plays an important role only in the transition area. Note that these statements are true only for pure substances, but not for mixtures, where two or more types of clusters may exist. The presence of irregular loss peaks and wide low-amplitude β-peaks is the key feature of the transition area.

This work provides better understanding of the nature of the secondary relaxation. It is shown above that the secondary relaxation results from the S-F transition, it is caused by free molecules motion and molecule–cluster interaction. The key difference between the β- and $\alpha\beta$-relaxations is in different types of interaction. It should be emphasized that the presence of clusters and free molecules is a prerequisite for the secondary β-type relaxation. This means that the secondary β-relaxation is not a precursor of the α-relaxation as is reported by some authors (for example, in work [35]). The primary and secondary relaxations — two interconnected processes, the β-process can not occur without the α-relaxation. As mentioned above, α- and β-relaxations occur simultaneously in the same frequency range, the $\alpha\beta$-relaxation is their precursor.

Since the substance structure changes during the S-F transition, the transition has signs of a phase transition. Therefore, a change in the substance heat capacity can be presumable observed during the S-F transition. Measurements performed in [22], confirm this assumption.

The S-F transition in epoxy resin is described above. This material is suitable for consideration because the S-F transitions are clearly pronounced and visible. This study investigates crossover with strong relaxation splitting into two branches: primary α-relaxation and secondary β-relaxation. This is not the only possible type of crossover, there are other more complex options, see, for example, [36], etc. Nevertheless, the results obtained above are also basically true for other substances and can serve as the basis for explanation of processes occurring in them.

Finally, note that this article poses a set of questions, answers to which are beyond the scope of this work. Questions about the nature , properties, causes of clusters, etc., are important.

Conclusion

The study uses a new approach: crossover phenomenon in glass-forming substances is treated as a transition from the strong to fragile relaxation. Processes occurring during this transition have been explored and explained. It is shown that the substance structure changes in the transition area; free molecules are associated into clusters as the temperature decreases. Assumption that molecules are associated into clusters makes it possible to explain processes occurring in the transition area. It is shown that the secondary β-relaxation is induced by the transition. The presence of free molecules and molecule–cluster interaction is the prerequisite for the secondary relaxation.

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Conflict of interest

The author declares no conflict of interest.

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