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Micro-rheology and relaxation phenomena in T_g vicinity

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Abstract

The present paper describes possible forms of relaxation phenomena in T_g vicinity. The individual types of relaxation in amorphous matrix are described in the areas of Vogel's temperature, T_g and crossover temperature. Special emphasis is laid on the difference between Flory's relaxation mechanism and the approach by Di Marzio, Adams and Gibbs. These authors used the common formula of Flory, however, their interpretations of the so-called „configurational phenomena" reflect completely different realities. The theoretical justification of heat capacity as a complex number (recently introduced by Hutchinson, Monserrat and Schawe in T_g vicinity) is provided in detail and compared with the existing experimental evidence quoted by the authors of these contributions as well as with data published in literature. The relation between complex heat capacity and relaxation of internal stress in amorphous matrixes or the effects of ageing are discussed.

Introduction

For the glassy state it is assumed that the individual vibrating particles of about a monomer size[1] are localised in the non-linear potential valleys[2-4], where they perform the oscillations due to the energy of thermal agitation,

$$U - U_0 = \frac{1}{2} f \xi^2 - \frac{1}{3} g \xi^3 - \frac{1}{4} c \xi^4 \tag{1}$$

where $\xi = r - r_0$ is the deviation from the equilibrium position and r_0 is defined as a half of the distance separating the bottoms of two potential valleys. U_0 is the basic level of internal energy. The parameters f, g, c can be determined through the level of bulk modulus $K^* = f / r_0$, the level of thermal expansion coefficient $\alpha = \frac{1}{r_0} \frac{g}{f^2} k_B$ and the level of c_p values[5].

$$c_p = k_B \left[1 + \left(\frac{3}{2} \frac{c}{f^2} + \frac{15}{9} \frac{g^2}{f^3} \right) k_B T \right] \tag{2}$$

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The parameters f, g, c in Eq. (1) are usually considered as constants[2-4]. However, Hlaváček and co-workers[5, 6] have started to consider the variability of c in the vicinity of Vogel's temperature and the variability of f, g, c in T_g vicinity.

The variability of these constants has been achieved due to the interaction of a particle with its neighbours. The integral effect of action of vicinity has been expressed through the F_{ext} in Eq. (3),

$$m\frac{\partial^2 \xi}{\partial t^2} + \frac{\partial U}{\partial \xi} = F_{ext} \tag{3}$$

where m is the mass of vibrating particle.

Adding the F_{ext} to Eq. (3) and allowing the constants f, g, c to vary, depending on F_{ext}, the authors[5, 6] have arrived at the non-autonomous system. Such systems can mathematically be investigated by using the deterministic chaos theories[7-9]. The theories of glassy transitions have a common treatment, and it does not matter whether we deal with the organic or inorganic glasses or polymers.

In the following text we will discuss the time related phenomena in α and c_p. For this purpose the approach toward the problem through Eq. (3) seems to be highly convenient, because every term, with the exception of particle mass in that equation, can be considered as time dependent.

Theory

Every thermodynamical function is well defined with respect to the partition function, as is for example the entropy:

$$S = k\ln Z + kT\left(\frac{\partial \ln Z}{\partial T}\right)_V \tag{4}$$

The partition function is formed by two integrals[10],

$$Z = Z_{ph}Z_{cf} \tag{5}$$

$$Z = \frac{1}{(2\pi\hbar)^{3N}}\frac{1}{N!}\int e^{-\frac{\tilde{K}(p)}{k_B T}}dp\int e^{-\frac{U(\bar{g})}{k_B T}}d\bar{g} \tag{6}$$

where the term Z_{ph} is the integral over a phase space[10] where $\tilde{K}(p)$ represents the summation over all moments of N particles, and $U(\bar{g})$ represents the overall interactive energy of all the particles.

$$\widetilde{K}(p) = \frac{1}{2m}\left(p_1^2 + p_2^2 + \ldots + p_{3N}^2\right) \tag{7}$$

$$U(\overline{g}) = \sum_{j>k} \mu_{jk} \tag{8}$$

where μ_{jk} represents the mutual interactive energy between a pair of particles

$$dp = dp_{1x} dp_{1y} \ldots dp_{Nz} \tag{9}$$

$$d\overline{g} = dx_1 dy_1 dz_1 \ldots dx_N dy_N dz_N \tag{10}$$

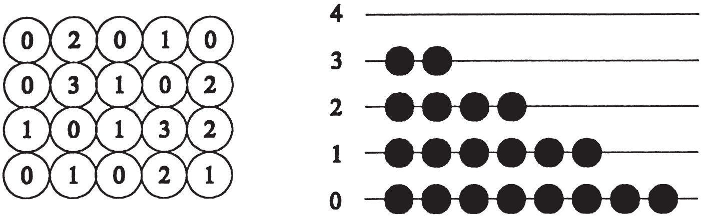

Fig. 1 A *schematic picture of thermal (vibration) contribution of entropy. The individual particles on the left are localised in constant positions and vibrate on different energy levels. The entropy* $S = k \cdot \ln W_{th}$ *is determined through the overall arrangements of vibration positions (on the right). For example, on the basic energy level there are 8 particles while on level 3 there are only 2 particles.*

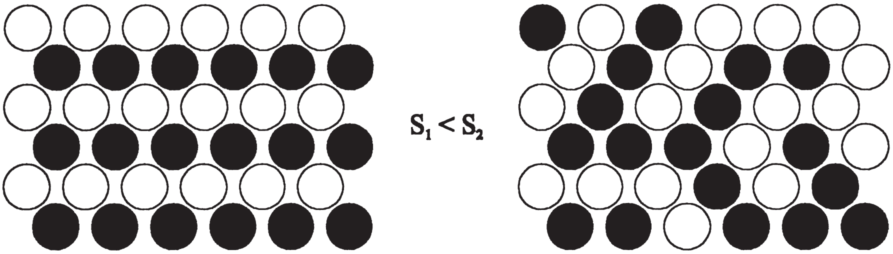

Fig. 2 *A schematic view of configurational entropy enlargement, materialised through the spatial displacements.*

Both the forms of partition function will play an important role in our problem definition. The fact that both parts of entropy, the thermal (Fig. 1) and configurational (Fig. 2) entropies, can play an important role in the studies of phenomena in T_g vicinity has been recognised for the first time by Goldstein[11, 12]. In the theories of solid state physics one of the integrals in Eq. (6) has been often disregarded.

So for example Debye[13], while calculating the specific heat of crystals, has been able to disregard the configurational part of integral (6), assuming that there are no changes in the average particle positions till the melting point. Debye has calculated the integral over the moments while taking $dp = \frac{h}{\mathrm{v}_s} d\nu$ where $p = m \cdot \mathrm{v} = \frac{h}{\lambda} = \frac{h\nu}{\mathrm{v}_s}$, where v_s is the velocity of sound and ν is the vibrational frequency, h is Planck's constant.

For the internal energy Debye obtained

$$E = \frac{12\pi V}{\mathrm{v}_s} \int_0^{\nu\max} \frac{\rho(\nu) h\nu}{\exp(h\nu / k_B T) - 1} d\nu \tag{11}$$

where $\rho(\nu) \cong \nu^2$, as suggested by Debye, and V is the molar volume.

Debye essentially considered an indefinite crystal, where the individual vibrating units can be connected as the lump elements, providing thus the first example of the problem definition which in this decade is well known as the mode coupling theory[14, 15].

This integral can be modified for amorphous bodies by considering different forms of degeneracy, or two Debye's θ temperatures[16-19], but basically it can be stated that the basic form of integral (11) holds in very similar form till Vogel's temperature for amorphous bodies as well as for crystals. Because the cohesive energy of crystals represents an extra bonding force, Eq. (11) holds for crystals till T_m.

As it has been shown by Wunderlich[20] for the amorphous bodies the c_p value starts to be larger than the c_p value for crystals above T_V mainly because the level of vibrations reaches the level where it starts to have an influence on the individual constants f, g, c in Eq. (4), and the individual vibrating units start to move in space. So in our approach we consider that the level of integral (11) has the major effect on the time average value of F_{ext} in Eq. (3).

Above T_V for the amorphous bodies and above T_m for crystals we assume that the configurational part of integral (6) starts to play a role, and the individual constants f, g, c have to be considered as time and temperature variables.

$$f = f_1\left[x_1(t), y_1(t) \ldots z_n(t); F_{ext}(T,t)\right] \tag{12}$$

$$g = f_2\left[x_1(t), y_1(t) \ldots z_n(t); F_{ext}(T,t)\right] \tag{13}$$

$$c = f_3\left[x_1(t), y_1(t) \ldots z_n(t); F_{ext}(T,t)\right] \tag{14}$$

where f_1, f_2, f_3 are symbols of functional dependence, and T is the temperature.

Just an opposite approach has been taken by Gibbs[21], who avoided the vibrational part Z_{ph} completely, and through the subsequent works of many authors[22-25] this insufficiency has been laboriously corrected.

In our approach the vibrational modes can influence the structure of the polymeric matrix in the isolated areas below the Vogel's temperature. Usually we talk about the islands of mobility in the sense of Johari–Goldstein β-maxima[26-28] or about the γ-maxima. Then at T_V the vibrational energy is big enough, and the main frame of amorphous body starts to move[29] (Fig. 2).

Moreover, the motions in the „islands of mobility“ will cause a change in $U(\bar{g})$ function in those particular areas and, further more, a high damping of mechanical disturbances will develop in these particular areas. Obviously the integral (11) can not involve the waves of long wavelengths, and in such a case integral (11) should have the form:

$$E = \frac{12\pi V}{\mathrm{v_s}} \int_{\nu\min}^{\nu\max} \frac{\rho(\nu)h\nu}{\exp(h\nu / k_B T) - 1} d\nu \tag{15}$$

when the system is passing through α, β, γ maxima and also for the shear mode vibrational interactions above T_g for low-molecular substances, the later being a result of the presence of vacancies which are interfering with shear mode vibrations (the second Lamme's coefficient μ on the local level quickly approaches zero above T_g)[30].

Our basic idea is that the vibrational part of Eq. (6) starts to influence the configurations of particles and therefore the configurational integral as well. The changes in the configurational integral will act as a feedback and will affect the vibrational integral in the sense of Eq. (15).

If we avoid the tunnelling state and boson peaks phenomena (as a results of low number of particles involved in these effects[2-4]), then we can say that the entropy of amorphous matrices is realised by rearrangements in the vibrational levels (Fig. 1) till Vogel's temperature. If no-degenerencies are considered, the particle vibrational arrangements should have an exponential form[10] (Fig. 3a).

Then the thermal partition function will be

$$P = e^{-\frac{\varepsilon_0}{kT}} + e^{-\frac{\varepsilon_1}{kT}} + e^{-\frac{\varepsilon_2}{kT}} + \ldots \tag{16}$$

where the local non-equilibria will manifest themselves either in a shift of energy levels (this will be connected to local stresses; Figs 3b, c) or in local fluctuations of heat demonstrated by irregular numbers of particles on the individual energy levels which do not have to fit the exponential form (Fig. 1), while keeping the separations of energy levels unchanged. Above Vogel's temperature the time-related phenomena in the relaxation of local stresses from the non-equilibrium situation (Figs 3b, 3c) toward the equilibrium (Fig. 3a) start to play an important role. The same can be stated about the configurational part of entropy, and the internal stresses can be relaxed, through the changes in particles positions. Because the parameter „*c*" is not involved in the definition of α, the development of α with time proceeds differently from the development in c_p or, in other words, the developments of volumetric changes do not have to coincide with the developments in entropy or enthalpy changes. For periodically variable external conditions we can talk about c_p and α as about complex numbers. So the procedures introduced by Schawe[31], Hutchinson[32], and Málek[33] can be fully justified.

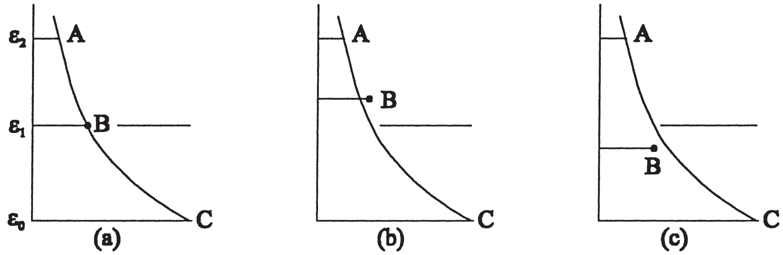

Fig. 3 *a) The equilibrium distribution of particles on three different vibrational energy levels.*

b,c) The non-exponential non-equilibrium vibrational distribution caused by the energy level shift generated by local stresses.

Recently Málek[34] has succeeded in introducing the general and universal theory of relaxation phenomena, dealing with speeds of recovery toward the equilibria in areas of temperatures between T_V and T_g.

Even higher changes in matrix structure start to develop in T_g vicinity and above at higher temperatures, where the huge vacancies start to develop. The vacancies size is reaching the size of critical volume $V_c \approx 3b$ for $T > 1.2T_g = T_{cr}$, where T_{cr} is the so-called crossover temperature.

In a liquid or rubber-like state, such vacancies can be envisaged (Fig. 4) as being created by the highly excited particle which is able to switch its vibrational amplitude to a higher level and push the particles in its vicinity aside[5-6]. The ability to perform the amplitude of vibrations on a completely different level is the basic property of non-autonomous vibrational systems. As shown by many PASCA measurements[35-43] the vacancy expansion coefficient is about 10 times to 100 times larger than the expansion coefficient of the remaining matrix. The agitated particle will be in semievaporated state, and it even can be considered to move in a space allowing several energy levels for one particle, like in a gas phase. In the system the highly activated particles will behave as new and completely mechanically different species.

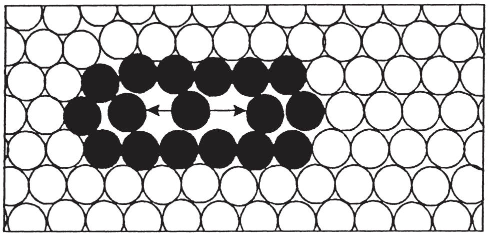

Fig. 4 *A schematic view of vacancy creation through the vibrational amplitude switch.*

This appearance of new species in the system, which will disappear if the system is cooled down below T_g temperature, is the main cause of non-existence of Kauzman[44] paradox in our approach.

Another interesting aspect should be mentioned: The liquid state starts at T_g and the substance, through the presence of vacancies, starts to increase its surface from inside, because the molecules on the surface will always be on the higher level of internal energy than are the molecules in bulk. The evaporation from bulk will lead, for the low-molecular weight substance, eventually to the boiling point. The restructuring of Eq. (6) can proceed further, which eventually leads to virial development and equation of state for real gases.

The T_g area is characterised also by high damping connected with the so-called α-transition[20, 29].

Above T_g the entropy has three parts

$$S = k \ln W_{th} + k \ln W_{cf} + k \ln W_{conf} \qquad (17)$$

where W_{th} is connected with the overall displacements of particles on thermal vibrational levels (Fig. 1, Eq. (15), Eq. (16)). This term is dominant under T_V. The term W_{cf} is then related to the microdisplacements of particles (without heterogeneities) in the sense of Fig. 2 which occur above T_V and finally the term W_{conf} involving the changes of entropy of long distance interaction in the sense of Rouse theories[45] and to rubber-like elasticity. This term plays a very important role in the case of polymers above T_g. For low-molecular substances it is connected to Eyring's type[46] of diffusion and to transfer of several particles from the Bose–Einstein statistics to the Boltzmann like statistics which always have to accompany the process of sublimation or evaporation.

All three types of entropies lead to complete by different time dependencies of relaxations phenomena. Every system which deviates somehow from the equilibrium, from the most probable state, shows different ageing as well. All three types of entropy contributions should be discerned in every study of ageing or relaxation phenomena in T_g vicinity.

Finally, we should mention the connection of our theory which puts emphasis on the amplitude jump in areas of α-transition, with the theories by Johari and Goldstein[26-28], which deal with the explanation of β-maxima, and we should provide some discussion concerning the very successful theories of Gibbs, Di Marzio and Adams.

THE JOHARI–GOLDSTEIN β-RELAXATION PROCESS

The major difference between the β-slow process and α-process is in that the β-slow process does not have a pronounced effect on measurable volume; therefore, it can start below the T_g temperature inside a rigid matrix frame. It will contain a couple of co-operating units in a form of motion creating no vacancies.

The number of co-operating units in this type of motion is relatively small and not much influenced if the temperature declines below T_{cr}. As an example, we can quote rotational movements in the side chains which appear in the main frame matrix below T_g.

The α-process will involve an infinite amount of units as the temperature declines below T_g. [For a purely elastic body, the interacting sequence of particles is limited to a whole sample ($\lambda \rightarrow \infty$ and $\omega = 0$ in Debye's[13] integral)]. Above T_g the number of units involved in displacement will be reduced sharply as the temperature rises. The increasing number of vacancies will add to the shortening of the sequence of interacting particles in α-process in space because the liquid state is connected with the interception of couplings lumped in its shear mode vibrations. Finally, note that the general type of interaction usually considered for the lumped elements, in the form of:

$$m\frac{d^2u_n}{dt^2} = f\left[\left(u_{n+1} + u_{n-1}\right) - 2u_n\right] \tag{18}$$

where m is the mass of the particle and f is the constant of elasticity, and u_n stands for the displacement of „n“ particles out of equilibrium position, can be incorporated. This type of interaction, which was used (in a modified form) by Rouse[45], will always bring a sharp increase in the relaxation times as the number of interacting elements „*n*“ increases.

The increase stems from the properties on the three main diagonals of the matrix involved, expressed through the numbers 1, –2, 1.

GIBBS–DI MARZIO–ADAMS THEORY[21-25]

Gibbs[21] was the first to consider the T_g transition by using substantially simplified Flory's[47] formula for investigation of T_g transition. Flory[47] originally followed the entropy changes of rigid macromolecules in solvents which had about 10^{13} times lower viscosity than that at T_g. These entropy changes were connected in Flory's theory with finite changes of macromolecular orientation as it is shown in Fig. 5.

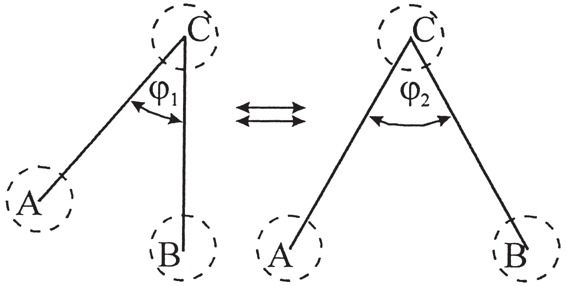

Fig. 5 *The entropy changes according to Flory[46] connected with the finite changes of angles* $\varphi_1 \neq \varphi_2$ *of rod-like type of macromolecules. The points of flexibility selected by Di Marzio and followers[21-25], which are prone to enhance the configurational changes in their vicinities. (See Fig. 6)*

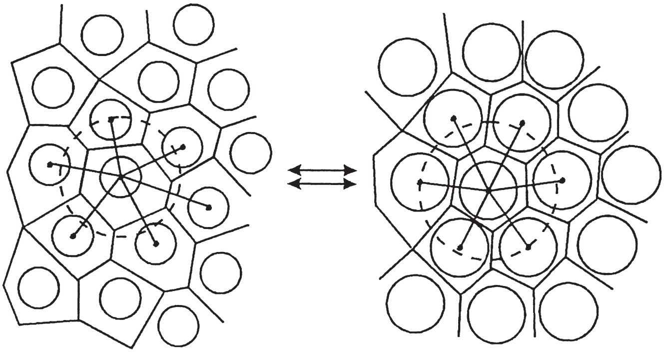

Fig. 6 *The microdisplacements created in the vicinity of more easily agitable parts of macromolecules. (See the points (A), (B), (C) in Fig. 5).*

If we take the frequency of jumps according to Kauzman[44] as

$$k = \frac{V\eta}{RT} \tag{19}$$

where η is the viscosity and V is the molar volume, we can see that even for the molecules of the size of styrene units it will take about 3 hours to perform a jump in the sense of Eyring's theory[46]. Therefore the macromolecule will have almost a fix position inside the urrounding matrix at T_g.

It was the rigorous localisation of the points of macromolecule prone to the different type of vibrations which Gibbs, Di Marzio and Adams[21-25] did properly. (The ends points of macromolecule and the points of flexibility.) There seems to be major reason for the abnormal success of those theories. On these points (A), (B) and (C) shown in Fig. 5 the activation of particles in vicinity could happen and cause the microconfigurational displacements of positions of particles in the neighbourhood (Fig. 6). Although they counted with the presence of vacancies, they were never able to incorporate the dynamic creation of vacancies into their approach and, therefore, their approach is mainly configurational and unable to predict the amplitude jumps or even the evaporation from bulk, or chain ruptures.

Conclusions

We have presented the explanations and spin-offs stemming from the consideration of non-linear, non-autonomous system of vibrating particles. Special attention was given to the area in the vicinity of T_g and T_V temperatures. Seemingly, the entropy of polymers in the T_g vicinity consists of three parts. The major part is associated with vibrations of particles. The vibration of particles can cause the structural configurational changes above Vogel's temperature.

Above the T_g temperature the „new“ mechanical units with complete different properties start to appear as the result of excitation of the non-linear oscillating units to upper level of amplitudes. The time-related phenomena in enthalpy and volume can be fully discerned and treated separately in the T_g vicinity.

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