The Theory of Relaxation Spectra

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A theoretical analysis of relaxation spectra in condensed media has been made based on energy absorption from an external periodical field by relaxators of various order. Expressions for absorption stripe maximum position in the relaxation spectrum and their widths have been found. Comparison of calculation results with the experimental data have shown that the developed theory adequately describes the basic properties of relaxation spectra in polymers.

KEY WORDS Relaxation, relaxation spectrum, molecular mobility, temperature effects.

THEORY AND DISCUSSION

As relaxation spectroscopy the influence of some external field of forces on a material (electric, magnetic, mechanical, etc.) as well as observation of field energy absorption depending on the field's frequency which is a relaxation spectrum,[1] are understood. Absorption stripes in the relaxation spectrum are conditioned by resonance interaction of a field of forces with material structure elements and characterize their molecular mobility at fixed temperature. Using the principle of temperature/time equivalency[2] temperature relationships of field energy absorption dependencies at the fixed frequencies are usually studied, as this method can be more easily realized experimentally.

By now relaxation spectra of many materials have been studied experimentally (see, for example,[1–6] and the references to it). There were attempts to theoretically describe the obtained spectra proceeding from various models of a solid body[1–6] based on the following ideas about heat motion of structural elements. This motion takes place by way of element transfer from one balance state to the adjacent one, where speed of such transfer depends on a height of potential barrier (U) separating two adjacent balances, on element volume (V) and temperature (T).[2]

In these models each element is characterized by the most probable relaxation time which, according to Frenkel and Eyring, has the following temperature relationship[2]:

$$\tau = B \exp(U/K_B T) \qquad (1)$$

where: K_B is Boltzmann constant, B is preexponential coefficient linked to activation entropy

$$B = V^{5/6}(6K_B T/\rho)^{-0.5} \tag{2}$$

where: ρ is density of substance of which the element consists.

However, attempts to apply relationship (1) in analysing relaxation spectra give in some cases parameter values U and B which have no physical sense. For example, in polymethylmethacrylate (PMMA) for α-process $U = 228$ kcal/mol and $B = 10^{-130}$ s[7] values were got, and stong temperature dependence U was seen.[2,8] This confirms limited application of (1) in an analysis of relaxation spectra and insufficient substantiation of the model views on relaxation processes in a material used in making conclusion.[1]

In contrast to the above mentioned "energetic" approach where τ is to be determined by a height of potential barrier U, we[9] have developed a "space" approach where τ is to be identified by specific accessible fluctuation volume f. In Reference 9 a model of condensed medium was considered consisting of structural elements, i.e., relaxators (oscillators with very long damping) heat motion of which occurs in the following way. Due to heat fluctuations the elements are withdrawn from balance positions and returned to them with the most probable relaxation time

$$\tau = \tau_0 \exp(f^-) \tag{3}$$

where: τ_0 is a minimum relaxation time equal to

$$\tau_0 = (m/K)^{0.5} \tag{4}$$

m, K are mass and elastic coefficient of the element ($2\pi\tau_0$ is a period of oscillator fluctuations in the absence of damping).

Specific accessible fluctuation volume f was found in Reference 9 on the basis of the fluctuation-dissipation theorem[10]

$$f = [(4K_B T/K)^{n/2} - (4K_B T_k/K)^{n/2}]a^{3-n}V^{-1} \tag{5}$$

where: T_k is a critical temperature derived from the condition $\tau \to \infty$ at $T \to T_k$; a is a characteristic linear size of the element ($V = a^3$); n is the order of the relaxator ($n = 1, 2, 3$).

By substituting (5) to (3) we shall have:

$$\tau(T) = \tau_0 \exp \left[\frac{f_k^{-1}}{(T/T_k)^{n/2} - 1} \right] \tag{6}$$

where: f_k is a relative critical free volume of the element

$$f_k = (4K_B T_k/K)^{n/2}a^{3-n}V^{-1} \tag{7}$$

Obtained temperature relationship τ (6) substantially differs from relationship (1): instead of "energetic" parameter U in (1) (6) includes "space" parameter f_k^{-1}; instead of preexponential coefficient B in (1) (6) includes minimum relaxation time τ_0 which has clear physical sense.

Dependencies $\ln\tau$ on T^{-1} sharply differ from (1) in accordance with (6) shown in Figure 1 for relaxators of the various order. In the same figure dependence $\ln$ τ on T^{-1} in accordance with (1) is given for comparison provided that $B = \tau_0$ and $U = K_B T_k f_k^{-1}$. It is seen that for all relaxators ($n = 1, 2, 3$) dependencies $\ln\tau$ on T^{-1} substantially differ from the linear one. The efficient "activation energy" determined by their local curvature

$$U_{\text{eff}} = K_B T_k f_k^{-1} \frac{d(f_k \ln(\tau/\tau_0))}{d(T_k/T)} \tag{8}$$

greatly depends on T for two- and three-dimensional relaxators and relatively weakly for one dimensional ones.
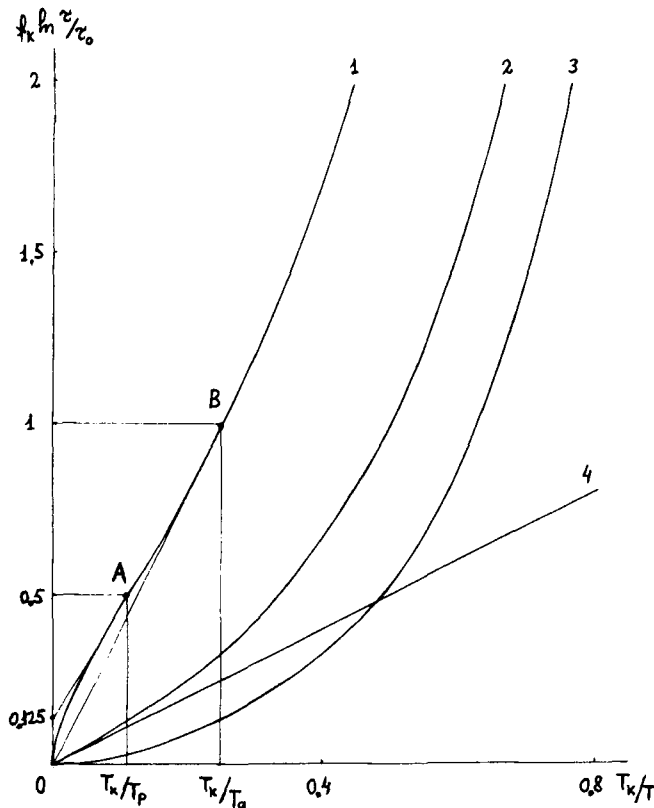

FIGURE 1 Dependencies of the most probable relaxation time τ on inverse temperature T^{-1} (in dimensionless values) for relaxators of various order: 1, $n = 1$; 2, $n = 2$; 3, $n = 3$; 4, is dependence in accordance with (1) at $B = \tau_0$ and $U = K_B T_k f_k^{-1}$. Denominations of f_k, τ_0, T_k, T_p and T_a see in the text.

For three dimensional relaxators which are the segments of macromolecules responsible for α-process of relaxation in polymers,[9] at $T_k < T < 2T_2$ U_{eff} can have any great values and sharply decreases with increase of T, and at $T > 2T_k$ U_{eff} lowers up to $U_{eff} = 0$ at $T \to \infty$ which is seen for α-process.[2,7,8]

For two dimensional relaxators as well as for three dimensional monotonous decrease of U_{eff} is observed with increase of T up to $U_{eff} = K_B T_k f_k^{-1}$ at $T \to \infty$.

For one dimensional relaxators which are links and groups of macromolecules responsible for β- and γ-processes of relaxation in polymers (see below) there are substantial peculiarities seen in dependence $ln\tau$ on T^-. With the increase of T from T_k to $T_p = 9T_k$ U_{eff} decreases up to a minimum value of $U_{min} = 27 K_B T_k f_k^{-1}/8$ and later grows: $U_{eff} \to \infty$ at $T \to \infty$. In other words at $T > T_p$ for one dimensional relaxators there is inverse relationship of U_{eff} and T, which is observed in some cases for β- and γ-processes in polymers.[8]

It should be underlined that the presence of a bend point (A in Figure 1). in dependence $ln\tau$ on T^{-1} is a direct proof that the observed relaxation process is connected with heat movement of the one dimensional relaxators. From the experimentally found U_{min} values, those of T_p, τ_p which correspond to bend point A all parameters characterizing relaxation properties of the element can be found:

$$T_k = T_p/g, \qquad f_k = 0.375 K_B T_p U_{min}^{-1}, \qquad \tau_0 = \tau_p \exp(-4U_{min}/3K_B T_p) \quad (9)$$

In dependence $ln\tau$ on T^{-1} for one dimensional relaxators there is one more characteristic point (B) in which U_{eff} is equal to "Arrenius activation energy" U_a to be determined by slope of OB straight line. From the experimentally found values of U_a, T_a and τ_a (which correspond to point B) T_k, f_k and τ_0 can be calculated

$$T_k = T_a/4, \qquad f_k = K_B T_a U_a^{-1}, \qquad \tau_0 = \tau_a \exp(-U_a/K_B T_a) \quad (10)$$

It should be noted that for one dimensional relaxators in contrast to two- and three-dimensional U_{eff} changes slightly (less than 20%) in a wide range of temperatures: from $3T_k$ to $50T_k$ (where τ changes for a greater amount of vaues), and practically coincides with U_a. The latter occurs, for example, for γ-process in polycyclohexilmethacrylate (PCHMA).[8]

Proceeding from the developed considerations about relaxators let us analyse the relaxation spectra of materials. Energy (Q) dissipated by a relaxator for one period is determined this way:

$$Q = Q_M \frac{2w\tau}{1 + w^2\tau^2} \quad (11)$$

where $w = 2\pi/v$ is an angular frequency of an external field; Q_M is maximum of the absorbed energy which takes place at T_M where:

$$w\tau(T_M) = 1 \quad (12)$$

So, absorption stripes in the relaxation spectrum should be described by equation (11) taking account of temperature dependence $\tau(T)$ in accordance with (6).

Since a modulus of material losses (G'', E'', ε'') functionally depends on w and τ similarly to (II) and characterizes the value of dissipated energy,[2] then experimental relaxation spectra should be read as loss modulus dependencies on T, not as dependencies of the loss angle tangent (logarithmic damping decrement) on T as is usually done.[1-8]

Absorption stripes in the relaxation spectrum are characterized by position of their maxima (T_M) and width (Δ) which are to be determined by frequency of the external field (v) and relaxation characteristics of material structural elements (T_k, f_k and τ_0). Varying the external field frequency in a wide range ($v_1 < v_2 < v_3$, etc.) maxima of absorption stripes ($T_1 < T_2 < T_3$, etc.) can be found, which permit to find relaxator parameters in accordance with (6) taking account of

$$\tau_1(T_1) = (2\pi/v_1)^{-1}, \quad \tau_2(T_2) = (2\pi/v_2)^{-1}, \quad \tau_3(T_3) = (2\pi/v_3)^{-1}, \text{ etc.} \quad (13)$$

By substituting (13) into (6) we can find:

$$T_k^{n/2} = \frac{T_1^{n/2}(T_3^{n/2} - T_2^{n/2})\,\ell n(v_2/v_1) - T_3^{n/2}(T_2^{n/2} - T_1^{n/2})\,\ell n(v_3/v_2)}{(T_3^{n/2} - T_2^{n/2})\,\ell n(v_2/v_1) - (T_2^{n/2} - T_1^{n/2})\,\ell n(v_3/v_2)} \quad (14)$$

$$f_k^{-1} = \frac{(T_1^{n/2} - T_k^{n/2})(T_2^{n/2} - T_k^{n/2})}{T_k^{n/2}(T_2^{n/2} - T_1^{n/2})} \;\ell n(v_2/v_1) \quad (15)$$

$$-\ell n\tau_0 = \ell n 2\pi/v_1 + \frac{T_2^{n/2} - T_k^{n/2}}{T_2^{n/2} - T_1^{n/2}} \;\ell n(v_2/v_1) \quad (16)$$

In case when "activation energies" U_a and U_{eff} are measured at temperature T_2 which corresponds to frequency v_2 for relaxator parameters will be:

$$T_k^{n/2} = (1 - nU_a/2U_{\text{eff}})T_2^{n/2} \quad (17)$$

$$f_k^{-1} = \frac{U_a}{K_B T_2} \frac{nU_a}{2U_{\text{eff}} - nU_a} \quad (18)$$

$$-\ell n\tau_0 = \ell n 2\pi/v_2 + U_a/K_B T_2 \quad (19)$$

Proceeding from (13)–(19) and taking account of the found values of absorption stripe and "energy of activation"[7,8] maximum positions let us calculate the relaxators' characteristics responsible for γ- and β-processes in PCHMA and PMMA, accordingly. Considering that γ-process in PCHMA is connected with one dimensional aperiodical motion of the methylene group of cyclohexil ring near a balance

position of "chair" type ($n = 1$) and taking into account that at $v_2 = 1$ Hz $T_2 = 193$K and $U_a(T_2) = U_{eff}(T_2) = 11.3$ kcal/mol[8] we can find from (17)–(19):

$$T_k = 48.25\text{K}, \qquad f_k^{-1} = 29.48, \qquad \tau_0 = 10^{-13.6}\text{s} \qquad (20)$$

Let us note that a critical volume is 3.4% from a volume of the methylene group. Substituting the found parameter values to (6) considering (13) at $v_1 = 10^{-4}$ Hz and $v_3 = 200$ Hz we can obtain values $T_1 = 149.8$K and $T_3 = 237.6$K which well agree with the values obtained by experiment.[8]

From the values of parameters (20) one can find in accordance with (4) and (7) elasticity coefficient K and height h of the methylene group:

$$K = 3.7 \cdot 10^4 \text{dn/cm}, \qquad h = 2.5 \cdot 10^{-8} \text{ cm} \qquad (21)$$

which well agree with deformation force constant $K_b = 0.37 \cdot 10^5$ dn/cm of C—C—C group[11] and a sum of Van der Vaals radii ($2.4 \cdot 10^{-8}$ cm) of two hydrogen atoms.[12]

To our opinion β-process in PMMA is connected with one dimensional aperiodical movement of the side chain ($COOCH_3$) in a plane going through C—C-bonds which connect side groups into the main chain setting to motion a part of the chain from three monomeric links in the shape of a crankshaft according to Boyer[2] around two colinear bonds. The motion of a torsion relaxator (side chain) is motion of a torsion oscillator with very great attenuation conditioned by interaction of an ester group (COO) of the second monomeric link with adjacent methylene and methyl groups inside the crankshaft.

Such model of β-relaxation in PMMA well explains all experimental data,[8] in particular, the absence of any influence on the maximum position of β-absorption stripe in PMMA plasticization and the nature of ester group R in the side chains COO—R (its length and polarity), and substantial influence on the position of β-stripe in the substitution of methyl group (CH_3) linked to the main chain for other substitutions (H, Cl, etc.).[8]

Taking into account that for β-process in PMMA $T_1 = 233$, $T_2 = 283$ and $T_3 = 307$K at $v_1 = 10^{-3}$, $v_2 = 1$ and $v_3 = 10$ Hz[7,8] we can find from (14)–(16):

$$T_k = 76.2\text{K}, \qquad f_k^{-1} = 26.86, \qquad \tau_0 = 10^{-13.4}\text{s} \qquad (22)$$

It should be noted that the critical volume of the torsion relaxator is 3.7%. From the obtained values (22) in accordance with (4) and (7) will be:

$$K = 5.6 \cdot 10^4 \text{ dn/cm}, \qquad h = 2.33 \cdot 10^{-8} \text{ cm} \qquad (23)$$

which agrees with the fact that β-process in PMMA is conditioned by motion of the side chain linked to deformation of valence angles in the main chain.

As is mentioned above, the absorption stripes in relaxation spectrum are characterized not only with a position of their maxima $T_M(v, T_k, f_k, \tau_0)$, but with their width $\Delta(v, T_k, f_k, \tau_0)$ as well. However, the nature of the latter has not been practically discussed in literature. It is only mentioned that the width of absorption

stripes substantially exceeds the width of a peak with one relaxation time,[8] and this fact is connected with presence of the relaxation time spectrum in materials.[2]

Proceeding from the developed concepts about relaxators let us calculate the width of absorption stripes in a relaxation spectrum. The relaxators must be described with equation (2) taking account of $\tau(T)$ in conformity with (6). One can easily show[9] that an absorption stripe in dimensionless coordinates $X = \ln w\tau$ and $Y = \ln(Q/Q_m) = \ln(G''/G_M'')$ is well described by symmetric curve

$$y = \begin{cases} \ln 2 + X & X < \ln(2 - \sqrt{3}) \\ -X^2/2 + X^4/12 & \ln(2 - \sqrt{3}) < X < \ln(2 + \sqrt{3}) \\ \ln 2 - X & X > \ln(2 + \sqrt{3}) \end{cases} \qquad (24)$$

with width at half-height $(Q_B = 1/2 \cdot Q_M)$

$$b = \ln\frac{2 + \sqrt{3}}{2 - \sqrt{3}} = 2.634 \qquad (25)$$

Apparently the absorption stripe in coordinates $\theta = (T - T_M)/(T_M)$ and $Y = \ln(Q/Q_M) = \ln(G''/G_M'')$ can be described by curve (24) taking account of (6) and (12) at

$$X = \frac{(1 + \theta)^{n/2} - 1}{(1 + \theta)^{n/2} - (T_k/T_M)^{n/2}} \ln w\tau_0 \qquad (26)$$

with width at half-height

$$\Delta = \frac{2b[1 - (T_k/T_M)^{n/2}]}{n \ln w\tau_0} \qquad (27)$$

Attention is attracted by the fact that $\Delta \sim n^{-1}$. It means that absorption stripes for the one dimensional relaxators are much wider (approximately by three times) than for three dimensional ones; this is observed in experiments for β- and γ-processes in comparison with α-process.[7,8]

Substitution to (27) of the obtained values $T_M = 237.6K$, $T_k = 48.25K$, $\tau_0 = 10^{-13.6}$s for γ-stripe in PCHMA and $T_M = 233K$, $T_k = 76.2K$, $\tau_0 = 10^{-13.4}$s for β-stripe in PMMA gives $\Delta_\gamma = 0.12$ and $\Delta_\beta = 0.063$ which are lesser than the measured values approximately by 2 and 5 times, accordingly.[8]

This is conditioned by the fact that at derivation of (27) temperature dependence of the most probable relaxation time (6) was used, i.e., it was supposed that $T_0 = $ const in the whole material volume, and hence all relaxators are to be characterized by single relaxation time $\tau(T_0)$ in accordance with (6). But this is not so, as for a balanced macroscopic body there are fluctuations of the basic thermodynamic values, in particular, of temperature the average fluctuation square of which equals to[10]

$$(\overline{\Delta T})^2 = T^2/C_v = K_B T^2/c_v \rho V_s \qquad (28)$$

where: C_v is dimensionless heat capacity, c_v and ρ are heat capacity and density of the material; v_s is subsystem volume which defines the relaxator's motion.

Energy dissipated by all N relaxators in the material for one period at balance temperature T considering temperature fluctuations can be derived from the following expression:

$$Q(T) = Q_M N \int \left[\frac{2w\tau(t)}{1 + w^2\tau^2(t)} \right] (2\pi T^2/C_v)^{-0.5} \exp\left[-\frac{(t - T)^2}{2T^2/C_v} \right] dt \quad (29)$$

By expanding into Tailor series the expression in square brackets in the vicinity of T_M and estimating integral (29) we can get:

$$Q(\theta) = Q_M N (1 + q^2)^{-0.5} \exp[-B^2\theta^2/(1 + q^2)] \quad (30)$$

where:

$$B^2 = 0.5 \left[\frac{0.5n \; \prime_n w\tau_0}{1 - (T_k/TyM)^{n/2}} \right]^2, \qquad q^2 = 2B^2/C_v \quad (31)$$

It is seen that consideration of temperature fluctuations leads to smearing of the absorption stripes: height of maximum $Q'_M = Q_M(1 + q^2)^{-1/2}$ decreases by $(1 + q^2)^{1/2}$ times and width increases by $(1 + q^2)^{1/2}$ times, but the energy absorbed by all relaxators does not change. It should be noted that due to dependence of c_v on T with the growth of T q^2 lowers and Q'_M grows, which is confirmed experimentally.[8]

It is obvious that B^2 characterizes peak width (Δ_1) with the same relaxation time in absence of temperature fluctuations ($q^2 = 0$) which at height e^{-1} equals to

$$\Delta_1 = -\frac{4\sqrt{2}[1 - (T_k/T_M)^{n/2}]}{n \; \prime_n w\tau_0} \quad (32)$$

and practically coincides with (27).

Hence, homogeneous width (Δ_0) of absorption stripes in material relaxation spectrum determined with temperature fluctuations exceeds by $(1 + q^2)^{0.5}$ times width Δ_1 of absorption peaks of isolated relaxators. Absorption stripes can be expanded heterogeneously ($\Delta_h > \Delta_0$) due to heterogeneity of the material's structure. This is confirmed by dependence of width of β-stripe in PMMA on plasticizer concentration (C_p): Δ_h decreases with an increase of C_p up to Δ_0.[8]

Let us calculate Δ_0 for γ-stripe in PCHMA and β-stripe in PMMA. Using the measured values of V_M monomeric link volume and ρ density[13]

$$V_M = 254 \cdot 10^{-24} \text{ cm}^3, \qquad \rho = 1.098 \text{ g/cm}^3 \text{ for PCHMA}$$
$$V_M = 142 \cdot 10^{-24} \text{ cm}^3, \qquad \rho = 1.17 \text{ g/cm}^3 \text{ for PMMA} \quad (33)$$

and taking into account temperature heat capacity c_v for methacrylates in the range of 100–300K[14]

$$c_v = (10^{-3} \cdot T + 0.04) \text{ cal/g.grad} \qquad (34)$$

we shall have $\Delta_{0\gamma} = 1.65_{1\gamma}$ for γ-stripe at $T_M = 237.6$K and $\Delta_{0\beta} = 5\Delta_{1\beta}$ for β-stripe at $T_M = 233$K. The obtained values $\Delta_{0\gamma}$ and $\Delta_{0\beta}$ well agree with the experimentally measured values.[8]

The calculation of $\Delta_{0\gamma}$ and $\Delta_{0\beta}$ has been made by us in assumption that a volume of subsystem V_s which determines relaxator's motion is: $V_s = 12V_M$ for γ-stripe in PCHMA and $V_s = 3V_M$ for β-stripe in PMMA. Such a choice of V_s is conditioned by geometric considerations for PCHMA and the above mentioned calculations of β-relaxation in PMMA. It is obvious that V_s can be derived from the experimentally measured homogeneous absorption stripe width and, thus, nature of the relaxator explained which is responsible for absorption of energy from an external periodical field.

Thus, this article contains the theory of relaxation spectra in condensed media and well explains the basic features of energy absorption from an external periodical field by materials which include relaxators of various order. The developed theory permits to adequately describe relaxation (viscoelastic, electric, etc.) properties of polymers, liquids and other materials as well as solid phase chemical reactions in them which depend on reagent mobility.

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