

The relaxation function of linear polymers possessing a discrete relaxation time spectrum is analyzed.

Polymers possess a discrete set of principal relaxation times λ_i ($i=1, \dots, N, \lambda_i < \lambda_{i+1}$). A definite relaxation mechanism, associated with the mobility of specific structural elements [1], individual fine-scale sections of macromolecules, free and bound segments in the bulk, and in the adsorbed part of the polymer on the active filler, as well as in microdomains of supermolecular and supersegmental structures and particles of the active filler, corresponds to each principal time λ_i . We considered the shear strain of a polymer which is fundamental to the analysis of more complex kinds of stress state. The magnitude of the contribution of each of the relaxation mechanism to the total system relaxation process during shear is determined by the partial elastic modulus G_i . Any principal i -th process is a multiplet process, i.e., possesses a fine structure of the spectrum. Hence, in addition to the principal relaxation time λ_i , for each relaxation process there is a number of other relaxation times λ_{in} around the principal time λ_{in} ($n = 2, 3, \dots$), to which the partial elastic moduli G_{in} will correspond. This is due to different reasons [1] – the size distribution of structural elements of a given type, the difference in local interactions between a structural element and its neighbors, the cooperative nature of the motion of structural elements, etc. Thus, for example, the presence of a relaxation time spectrum in the Kargin–Slonimskii–Routh [2, 3] and the Doi–Edwards [4] models, respectively, for a dilute and concentrated solution of macromolecules is related to the decomposition of the macromolecule motion into separate components (modes), each of which governs the coordination displacement of parts of the macromolecule.

In the case of small strains (linear viscoelasticity domain), the rheological equation is written as follows

$$\mathbf{T}(t) = 2 \int_{-\infty}^t G(t-\tau) \mathbf{e}(\tau) d\tau, \quad (1)$$

where \mathbf{T} , \mathbf{e} are, respectively, the tensors of the excess stresses and strain rates, and $G(t)$ is the relaxation function determined from tests on stress relaxation. The Newtonian viscosity η equals

$$\eta = \int_0^{\infty} G(t) dt. \quad (2)$$

For a discrete relaxation time spectrum

$$G(t) = \sum_{i=1}^N \sum_{n=1}^{\infty} G_{in} \exp(-t/\lambda_{in}), \quad (3)$$

$$\eta = \sum_{i=1}^N \sum_{n=1}^{\infty} G_{in} \lambda_{in}. \quad (4)$$

As an analysis of many empirical nonlinear viscoelastic models shows [5], Eq. (3) is even applicable in the case of nonlinear processes if their nature is geometric, i.e., a change in structure does not occur. The relaxation function parameters (3) play a decisive role even in the rheological equation for large strains [5] when the relation between the stress and strain rate tensors is nonlinear in nature. The following empirical formulas [5]

$$\lambda_{in} = \lambda_i/n^{\alpha_i}, \quad G_{in} = G_i/n^{\beta_i}, \quad (5)$$

which are most convenient for experimental data processing, are used extensively for the distributions of the relaxation times λ_{in} and the corresponding moduli G_{in} . Analogous power-law expressions are also obtained as a result of a computation

of molecular-kinetic models of polymers. Thus, $\alpha = 2, \beta = 0$ for a free-flowing macromolecule model in a Kargin–Slonimskii–Routh solution, $\alpha \approx 3/2, \beta = 0$ [3] for a Zimm model with hydrodynamic interaction of the macromolecule segments, and $\alpha = 2, \beta = 2$ for the Doi–Edwards [4] and Curtis–Bird [6] models of macromolecules in a concentrated solution and a melt. From the conditions for convergence of the series (4) there follows that $\alpha_1 + \beta_1 > 1$. In the case of applying (5), the expression (3) takes the form

$$G(t) = \sum_{i=1}^N G_i f_i(\theta_i), \quad \theta_i = t/\lambda_i, \quad (6)$$

i.e., for each relaxation mechanism, a partial relaxation function

$$f(\theta) = \sum_{n=1}^{\infty} \frac{1}{n^\beta} \exp(-n^\alpha \theta), \quad \alpha + \beta > 1. \quad (7)$$

is introduced. Other kinds of kernels, e.g., Koltunov, Rabotnov, Rzhantsyn, Slonimskii, etc. (see the appropriate bibliography in [1]), are used extensively in (1) in the mechanics of viscoelastic materials.

By analyzing the asymptotic behavior of the series (7), we have established a connection between the kernel for the discrete time spectrum (6) and the other kinds of kernels used in the mechanics of viscoelastic materials. To do this we apply the Laplace transformation to the function $f(\theta)$

$$\hat{f}(z) = \int_0^{\infty} f(\theta) \exp(-z\theta) d\theta = \sum_{n=1}^{\infty} \frac{n^{-\beta}}{z + n^\alpha}. \quad (8)$$

We use the Mellin transform to find the asymptotic behavior of the series (8) for $|z| \gg 1$ and $|z| \ll 1$. Since [7]

$$g(s) = \int_0^{\infty} \frac{x^{-\beta}}{z + x^\alpha} x^{s-1} dx = \frac{\pi z^{\frac{s-\beta}{\alpha}-1}}{\alpha \sin \frac{\pi(s-\beta)}{\alpha}} \quad \text{for } 0 < \operatorname{Re} \left(\frac{s-\beta}{\alpha} \right) < 1,$$

then by applying the inversion formula for the Mellin transform for the function $g(s)$ and substituting it into the series (8), we obtain (here $j = \sqrt{-1}$)

$$\hat{f}(z) = \frac{1}{2\pi j} \int_{c-j\infty}^{c+j\infty} \frac{\pi z^{\frac{s-\beta}{\alpha}-1}}{\alpha \sin \frac{\pi(s-\beta)}{\alpha}} \left(\sum_{n=1}^{\infty} \frac{1}{n^s} \right) ds = \frac{1}{2\pi j} \int_{c-j\infty}^{c+j\infty} \omega(s) ds, \quad (9)$$

where $\omega(s) = \pi z^{\frac{s-\beta}{\alpha}-1} \zeta(s)/\alpha \sin \frac{\pi(s-\beta)}{\alpha}$, $\zeta(s)$ is the Riemann zeta function. Formula (9) is valid for $\operatorname{Re}(s) > 1, \beta < \operatorname{Re}(s) < \alpha + \beta$.

Let us examine the behavior of the function $\omega(s)$ in the complex plane. The zeta function $\zeta(s)$ has a pole with residue 1 for $s = 1$ [8], $\sin \frac{\pi(s-\beta)}{\alpha} = 0$ for $s = \beta + \alpha n, n = 0, \pm 1, \pm 2, \dots$. For $(1-\beta)/\alpha$ not equal to zero or an integer, the function $\omega(s)$ has just a first-order pole:

$$\operatorname{Res}_{s=1}(\omega(s)) = \pi z^{\frac{1-\beta}{\alpha}-1} / \alpha \sin \frac{\pi(1-\beta)}{\alpha}, \quad \operatorname{Res}_{s=\beta+\alpha n}(\omega(s)) = (-1)^n z^{\frac{\beta-1}{\alpha}} \zeta(\beta + \alpha n).$$

When $(1-\beta)/\alpha$ equals zero or an integer, then the function $\omega(s)$ has a second-order pole at the point $s = 1$. Using the power series expansion of the zeta function at the point $s = 1$ [8], we obtain

$$\operatorname{Res}_{s=1}(\omega(s)) = \gamma z^{-k-1} + \frac{1}{\alpha} z^{-k-1} \ln z, \quad k = \frac{\beta-1}{\alpha},$$

where γ is the Euler constant. Applying the asymptotic formulas for $\zeta(s)$ as $\operatorname{Im}(s) \rightarrow \pm\infty$ [8, 9], we easily show that the function $\omega(s)$ is exponentially small as $\operatorname{Im}(s) \rightarrow \pm\infty$.

Transferring the line of integration in integral (9) to the left with the addition of the residues at the appropriate poles, and letting $c \rightarrow -\infty$ we obtain the asymptotic formula for $f(z)$ as $|z| \rightarrow \infty$:

$$\hat{f}(z) \approx \frac{\pi z^{\frac{1-\beta}{\alpha}-1}}{\alpha \sin \frac{\pi(1-\beta)}{\alpha}} + \sum_{n=0}^{\infty} \frac{(-1)^n \zeta(\beta - \alpha n)}{z^{1+n}}, \quad \frac{\beta-1}{\alpha} \neq k, \quad (10)$$

$$\hat{f}(z) \approx \gamma z^{-k-1} + \frac{1}{\alpha} z^{-k-1} \ln z + \sum_{n \geq 0, n \neq k}^{\infty} \frac{(-1)^n \zeta(\beta - \alpha n)}{z^{1+n}}, \quad \frac{\beta-1}{\alpha} = k.$$

For $\beta - \alpha n < 1$ [8]

$$\zeta(\beta - \alpha n) = \frac{2\Gamma(\alpha n - \beta + 1) \zeta(\alpha n - \beta + 1) \cos\left(\frac{\pi}{2}(\alpha n - \beta + 1)\right)}{(2\pi)^{\alpha n - \beta + 1}}.$$

Analogously transferring the line of integration in (9) to the right with the addition of the appropriate poles and letting $c \rightarrow +\infty$, we obtain the asymptotic formula for $f(z)$ as $|z| \rightarrow 0$:

$$\hat{f}(z) \approx \sum_{n=1}^{\infty} (-1)^{n-1} z^{n-1} \zeta(\beta + \alpha n). \quad (11)$$

Returning to the original in (10) and (11) by using the Laplace transform inversion formulas [7], we obtain

$$f(\theta) \approx \frac{1}{\alpha} \theta^{\frac{\beta-1}{\alpha}} \Gamma\left(\frac{1-\beta}{\alpha}\right) + \sum_{n=0}^{\infty} \frac{(-1)^n \zeta(\beta - \alpha n) \theta^n}{n!}, \quad \frac{\beta-1}{\alpha} \neq k, \quad (12)$$

$$f(\theta) \approx \varphi_k(\theta) + \sum_{n \geq 0, n \neq k}^{\infty} \frac{(-1)^n \zeta(\beta - \alpha n) \theta^n}{n!}, \quad \frac{\beta-1}{\alpha} = k;$$

for $\theta \rightarrow 0$

$$f(\theta) \approx \sum_{n=1}^{\infty} (-1)^{n-1} \delta^{(n-1)}(\theta) \zeta(\beta + \alpha n) \quad (13)$$

for $\theta \rightarrow \infty$. Here

$$\varphi_k(\theta) = \begin{cases} \gamma - \frac{1}{\alpha} \ln \gamma \theta, & k = 0, \\ \frac{\gamma \theta^k}{k!} + \frac{1}{\alpha} \left(1 + \frac{1}{2} + \dots + \frac{1}{k} - \ln \gamma \theta \right) \frac{\theta^k}{k!}, & k \geq 1, \end{cases}$$

$\delta^{(n-1)}(\theta)$ is the n -th generalized derivative of the Heaviside function [10]. The formula (12) obtained for $\beta = 0$ agrees with the result in [9].

In addition to the asymptotic formulas (12) and (13), the asymptotic formulas (10) and (11) for the series (8) are also important for applications. Thus, for instance, the dependence of the shear viscosity on the shear rate is given by a series of the type (8) for many nonlinear rheological models [5]. In this case (10) and (11) determine the dependence of the fluid viscosity for large and small shear rates, respectively. The comparison made in [11] between the results of the numerical computations of the function $f(z)$ for $\alpha = 2\beta$, $\beta = 3.5$ for real values of z by means of (8), (10), (11) displayed good applicability of the first several terms of the asymptotic formula (11) for $z < 20$ and (10) for $z > 20$. Series of the form (8) appear also in the calculation of polymer viscosity under small stationary harmonic oscillation conditions when $e(t) = e_0 \exp(j\omega t)$. In this case we obtain from (1)

$$\mathbf{T} = 2\eta^* e_0 \exp(j\omega t), \quad \eta^* = \int_0^{\infty} G(\tau) \exp(-j\omega\tau) d\tau$$

and for the relaxation function (6)

$$\eta^* = \sum_{i=1}^N G_i \lambda_i^{\beta_i} \hat{f}_i(z_i), \quad z_i = j\omega\lambda_i.$$

Formulas (10) and (11) determine the asymptotic behavior of the functions $\hat{f}_i(z_i)$ for fast $\omega\lambda_i \gg 1$ and slow $\omega\lambda_i \ll 1$ effects, respectively.

For small θ the principal terms in the expansion (12) of the function $f(\theta)$ are

$$f(\theta) \approx \xi(\beta), \quad \beta > 1; \quad f(\theta) \approx \Gamma\left(\frac{1-\beta}{\alpha}\right) \theta^{-\frac{1-\beta}{\alpha}}, \quad \beta < 1;$$

$$f(\theta) \approx -\frac{1}{\alpha} \ln \theta, \quad \beta = 1.$$

Let us consider the behavior of the relaxation functions $G(t)$, (6), and the integral relation (1) for $\lambda_m \ll t \ll \lambda_{m+1}$, i.e., in a certain time interval exceeding the duration of the relaxation processes 1, ..., M and less than for the structures M + 1, ..., N. This corresponds to the conception of the "action pointer" [1]. Applying the asymptotic formulas (12) and (13) for this case and limiting ourselves to the principal term of the expansion for each relaxation mechanism, we have

$$G(t) \approx \sum_{i=1}^M G_i \xi(\beta_i + \alpha_i) \delta\left(\frac{t}{\lambda_i}\right) + \sum_{i \geq M+1, \beta_i > 1}^N G_i \xi(\beta_i) + \sum_{i \geq M+1, \beta_i < 1}^N G_i \Gamma\left(\frac{1-\beta_i}{\alpha_i}\right) \left(\frac{\lambda_i}{t}\right)^{\frac{1-\beta_i}{\alpha_i}} - \sum_{i \geq M+1, \beta_i = 1}^N G_i \ln \frac{t}{\lambda_i}. \quad (14)$$

Substituting (14) into (1) yields

$$\mathbf{T} \approx 2\tilde{\eta}_M \mathbf{e}(t) + \tilde{G}_M \mathbf{e}(t) + \int_{-\infty}^t \tilde{\Psi}_M(t-\tau) \mathbf{e}(\tau) d\tau, \quad (15)$$

where $\mathbf{e}(t) = \int_{-\infty}^t \mathbf{e}(t) dt$ is the strain,

$$\tilde{\eta}_M = \sum_{i=1}^M G_i \lambda_i \xi(\beta_i + \alpha_i), \quad (16)$$

$$\tilde{G}_M = \sum_{i \geq M+1, \beta_i > 1}^N G_i \xi(\beta_i), \quad (17)$$

$$\tilde{\Psi}_M(t) = \sum_{i \geq M+1, \beta_i < 1}^N G_i \Gamma\left(\frac{1-\beta_i}{\alpha_i}\right) \left(\frac{\lambda_i}{t}\right)^{\frac{1-\beta_i}{\alpha_i}} - \sum_{i \geq M+1, \beta_i = 1}^N G_i \ln \frac{t}{\lambda_i}. \quad (18)$$

In asymptotic formulas of the majority of kernels of the integral equation (1) proposed by different researchers (see [1]), the principal (first) term of the expansion as $t \rightarrow 0$ is identical to the power-law:

$$G(t) \sim 1/t^\gamma. \quad (19)$$

In our case the first terms of the function $\tilde{\Psi}_M(t)$ (see (18)) take account of the presence of many relaxation mechanisms. Each component in the first term of (18) here has the same type of singularity as (19). The second term in (18) takes into account the logarithmic singularity that appears for multiplet splitting with $\beta_i = 1$. Each slow relaxation mechanism $i = M + 1, \dots, N$ for the time interval $t \ll \lambda_{M+1}$ is characterized by some value of β_i . Processes with $\beta_i > 1$ hence fall into the sum for \tilde{G}_M (17), with $\beta_i \leq 1$ in the sum for $\tilde{\Psi}_M(t)$ (18), where the mechanisms with $\beta_i < 1$ are in the first component, and with $\beta_i = 1$ in the second. The fast relaxation mechanisms, $i = 1, \dots, M$, yield a contribution to the viscosity $\tilde{\eta}_M$ (16).

The analysis performed shows that the types of singularity in the relaxation function (3) with discrete relaxation time spectrum agree completely with the types of singularities of the integral kernels used in the mechanics of viscoelastic materials, Koltunov, Rabotnov, Rzhantsyn, Slonimskii, etc. [1], that were introduced purely phenomenologically.

LITERATURE CITED

1. G. M. Bartenev, Structure and Relaxation Properties of Elastomers [in Russian], Khimiya, Moscow (1979).
2. G. V. Vinogradov and A. Ya. Malkin, Rheology of Polymers [in Russian], Khimiya, Moscow (1977).
3. T. D. Ferry, Viscoelastic Properties of Polymers, 3rd ed., Wiley, New York (1980).
4. M. Doi and S. F. Edwards, "Dynamics of concentrated polymer systems, I. Brownian motion in the equilibrium state. II. Molecular motion under flow. III. The constitutive equation," J. Chem. Soc. Faraday Trans. II, **74**, No. 10, 1789-1832 (1978); IV, "Rheological properties," J. Chem. Soc. Faraday Trans. II, **75**, No. 1, 38-54 (1979).
5. Z. P. Shul'man, S. M. Aleinikov, B. M. Khusid, and E. É. Yakobson, "Rheological equations of state of flowing polymer media (analysis of the state of the problem)," Preprint No. 3, Inst. of Heat and Mass Transfer, BSSR Academy of Sciences, Minsk (1981).
6. C. F. Curtiss and R. B. Bird, "A kinetic theory for polymer melts. I. The equation for the single-link orientational distribution function. II. The stress tensor and the rheological equation of state," J. Chem. Phys., **74**, No. 3, 2016-2033 (1981).
7. H. Bateman and A. Erdelyi, Tables of Integral Transforms, McGraw-Hill.
8. H. Bateman and A. Erdelyi, Higher Transcendental Functions [Russian translation], Vol. 1, Nauka, Moscow (1965).
9. M. A. Evgafov, Asymptotic Estimates and Entire Functions, Gordan and Breach (1962).
10. M. A. Lavrent'ev and B. V. Shabat, Methods of Complex Variable Function Theory [in Russian], Nauka, Moscow (1965).
11. Z. P. Shul'man, S. M. Aleinikov, and B. M. Khusid, "Rheodynamics and heat transfer in the flow of hereditary media in a circular tube," in: Heat and Mass-Transfer-VI [in Russian], Pt. 2, Inst. of Heat and Mass Transfer, Academy of Sciences of the BSSR, Minsk (1980), pp. 128-139.

THEORY OF THERMAL WAVES

V. A. Bubnov

UDC 532.24.02

An analogy between thermal and electromagnetic waves is established. The conditions under which thermal oscillations can give rise to acoustical oscillations are derived. The coefficients of thermal conductivity in liquid helium are calculated as a function of the temperature below the lambda point.

1. Analogy between Thermal and Electromagnetic Waves. We shall examine the first two Maxwell equations in the case that electric and magnetic conduction currents are absent:

$$\operatorname{rot} \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t}, \quad \operatorname{rot} \mathbf{E} = - \frac{\partial \mathbf{B}}{\partial t}. \quad (1)$$

Let the physical properties of the medium be determined by the following equations:

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}, \quad \mathbf{B} = \mu_0 \mathbf{H} + \mathbf{M}.$$

Substituting these equations into system (1), we rewrite the latter as follows:

$$\operatorname{rot} \mathbf{H} = \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \frac{\partial \mathbf{P}}{\partial t}, \quad \operatorname{rot} \mathbf{E} = - \mu_0 \frac{\partial \mathbf{H}}{\partial t} - \frac{\partial \mathbf{M}}{\partial t}. \quad (2)$$

In these equations, the second terms on the right determine the electric and magnetic displacement current densities which arise as a result of polarization and magnetization, respectively.

In the stationary case, the system of equations (2) goes over into the following:

$$\operatorname{rot} \mathbf{H} = 0, \quad \operatorname{rot} \mathbf{E} = 0, \quad (3)$$

which for a two conductor line has a solution of the form [1]:

$$\mathbf{H} = \mathbf{H}_0 = H_0(x) \mathbf{k}, \quad \mathbf{E} = \mathbf{E}_0 = E_0(x) \mathbf{j}, \quad H_0 = E_0. \quad (4)$$