115. R.A.Keller and G.H.Stewart, Analyt.Chem., 36, 1184 (1964).
116. A.T.James and A.J.P.Martin, Biochem.J., 50, 679 (1952).
117. M.S.Vigdergauz and M.I.Afanas'ev, Zhur.Anal.Khim., 19, 1122 (1964).
118. A.Waksmundzki and Z.Suprynowicz, J.Chromatog., 18, 232 (1965).
119. R.S.Porter, H.L.Hinkins, L.Tornheim, and J.F.Johnson, Analyt.Chem., 36, 260 (1964).
120. B.D.Blaustein, C.Zahn, and G.Pantages, J.Chromatog., 12, 104 (1963).
121. M.S.Vigdergauz and M.I.Afanas'ev, Khim.i Tekhnol. Topliv i Masel, No.5, 55 (1965).
122. H.Kelker, Ber.Bunsen Gesellschaft Phys.Chem., 67, 698 (1963).
123. H.Kelker, Z.analyt.Chem., 198, 254 (1963); 220, 1 (1966); see Ref.5, p.271.
124. M.J.S.Dewar and J.P.Schroeder, J.Amer.Chem.Soc., 86, 5235 (1964); J.Org.Chem., 30, 3485 (1965).
125. J.C.Giddings, Analyt.Chem., 32, 1707 (1960).
126. J.C.Giddings, Analyt.Chim.Acta, 27, 207 (1962).
127. C.Hishta, J.P.Messerly, and R.F.Rescnke, Analyt. Chem., 32, 880 (1960); 32, 1730 (1960).
128. "Standard Perkin-Elner Columns and Their Application", Publications of Perkin-Elmer Corp., Norwalk, Conn., USA.
129. S.J.Hawkes and J.C.Giddings, Analyt.Chem., 36, 2229 (1964).
130. S.J.Hawkes and E.F.Mooney, Analyt.Chem., 36, 1473 (1964).
131. W.Gerrard, S.J.Hawkes, and E.F.Mooney, "Gas Chromatography. Proceedings of the Third International Symposium on Gas Chromatography in Edinburgh" (Translated into Russian), Izd.Mir, Moscow, 1964, p.267.
132. "Materials for Gas Chromatography", May and Baker Ltd., Dagenham, England, 1961.
133. N.M.Turkel'taub, A.A.Zhukhovitskii, L.N.Vasil'eva, and A.I.Karymova, Symposium, "Gazovaya Khromatografiya" (Gas Chromatography), NIITEKhIM, Moscow, No.1, p.30.
134. J.J.Duffield and L.B.Rogers, Analyt.Chem., 32, 340 (1960).
135. W.J.de Wet and V.Pretorius, Analyt.Chem., 32, 340 (1960).

Synthetic Alcohols and Organic Products
Research Institute, Novokuibyshevsk

U. D. C. 539.67

STUDY OF MOLECULAR MOTION IN SOLID POLYMERS BY THE INTERNAL FRICTION METHOD

V. S. Postnikov

CONTENTS

I. Introduction 787
II. Methods of measurement of internal friction 788
1. Methods of free and forced vibrations 788
2. Method of wave propagation 790
III. Experimental results 791
1. Temperature dependence 792
2. Frequency dependence 794
IV. Theory of internal friction 794
1. Phenomenological theory 794
2. Molecular-kinetic description 800
V. Comparison of the results of studies on molecular motion in polymers, obtained by different methods 801
1. Mechanical and dielectric losses 801
2. Mechanical losses and nuclear magnetic resonance 802

I. INTRODUCTION

Various properties of solid polymers depend decisively on the nature of the motion of the individual groups and segments of the molecular chains from which they are built up. Therefore it is both of practical and theoretical importance to know the type of molecular motion occurring in the given polymer and the dependence of the type of motion on the composition, structure, molecular weight, temperature, and other factors. One of the most useful physical methods for the investigation of the internal motion of polymeric chains is the internal friction method, the essential features of which are as follows.

When a body is deformed, internal forces (or stresses) arise, due to the change in the distribution of molecules or atoms in it. If the stresses and the relative deformations throughout the period of operation of external forces remain constant and fall to zero instantaneously when the operation of such forces ceases, then we are dealing with a perfectly elastic substance. The isothermal state of such a substance, if the latter is isotropic, is known to be described by the generalised Hooke's law[1]:

$$\sigma_{ik} = 2G\left(u_{ik} - \frac{1}{3}\delta_{ik}u_{ll}\right) + K \cdot u_{ll} \cdot \delta_{ik}\,, \qquad (1)$$

where $\dot{u}_{ik} = 0$ when the external forces are constant. Here σ_{ik} is the elastic stress tensor, u_{ik} the deformation tensor, and G and K are the moduli of shear and bulk elasticity respectively.

It is possible also to imagine another ideal case, where the relative deformations of the substance are not constant under the action of constant external forces, but increase continuously at a particular constant rate which is proportional to the stress. The behaviour of such an ideally viscous isotropic material is described[1] by the generalised Newton equation:

$$\sigma'_{ik} = 2\eta\left(\dot{u}_{ik} + \frac{1}{3}\delta_{ik}\dot{u}_{ll}\right) + \zeta\dot{u}_{ll} \cdot \delta_{ik}\,, \qquad (2)$$

where σ'_{ik} is the dissipative stress tensor, $\dot{u}_{ik}$ the derivative of the deformation tensor with respect to time, and η and ζ are the shear and bulk viscosities.

However, in no real substance with a definite structure can stresses exist indefinitely or decrease instantaneously, since during deformation the structure of the substance changes continuously (and in a complex manner) at a certain finite velocity, determined by the nature of the substance. Therefore the behaviour of a real material is in fact described by more complex relations than Eqns. (1) and (2).

The nature of these relations is most readily elucidated using the state of idealised linear stress as an example. Since shear deformations are of the greatest importance in mechanical problems associated with polymers and plastics, we shall consider homogeneous shear deformation. For this case,

$$u = u_y \text{ and } u_{yz} = \frac{1}{2}\frac{\partial u_y}{\partial z} .$$

For non-zero components of the stress tensor, we find from Eqns. (1) and (2)

$$\sigma_{yz} = G\frac{\partial u_y}{\partial z},\ \sigma'_{yz} = \eta\frac{\partial u_y}{\partial z} . \qquad (3)$$

The behaviour of an ideally viscous material described by Newton's equation [Eqn. (3)] can be represented schematically by a section of a $\partial\dot{u}_y/\partial z - \sigma_{yz}$ straight line passing through the coordinate origin (Fig. 1, curve I). The direct proportionality of the flow rate gradient $\partial\dot{u}_y/\partial z$ to the stress σ_{yz} implies that the shape and state of the structural elements of the object do not undergo any changes and that the shear stress increases and decreases instantaneously.

The flow of high polymers and plastics does not usually[2] obey Newton's equation [Eqn. (3)]. Their flow rate gradient can increase with shear stress either faster (Fig. 1, curve II) or more slowly (Fig. 1, curve III). Apart from fluidity, polymers and plastics exhibit a certain elasticity and therefore the onset of non-elastic deformation (flow) does not as a rule coincide with the origin of the coordinates (Fig. 1, curves IV–VI) of the $\partial\dot{u}_y/\partial z - \sigma_{yz}$ curve. Therefore the total deformation in a solid under the influence of a mechanical load can be represented by the sum of two terms: the reversible† (elastic) deformation u'_y propagated at the velocity of sound and the irreversible (plastic) deformation u''_y. The latter type of deformation in a real substance is not established instantaneously but increases gradually when an external constant load is applied. Its experimental time dependence $u''_y = \Phi(t)$ is very complex and is related to the previous history of the specimen. As a result, when the external load is changed periodically there is a phase lag between the total deformation and the stress, which entails energy dissipation by vibrations. The capacity of a substance to transform the energy of mechanical vibrations into heat is known as mechanical losses or internal friction‡. The following quantity can serve as a measure of internal friction:

$$\delta = \Delta E/E , \qquad (4)$$

where ΔE is the energy dissipated during the cycle and E the vibrational energy. The physical cause of internal friction is the rearrangement in the solid occurring at a finite rate under the influence of mechanical stresses. Five types of this kind of rearrangement are known: thermal rearrangement (thermoelastic effects), electrical rearrangement (electron redistribution, ion migration, rotation of electrical dipoles, and other effects), magnetic rearrangement (magnetomechanical hysteresis, relaxation of the magnetic flux as a result of the appearance of macro- or micro-fluxes, rotation of magnetic dipoles, and other effects), atomic rearrangement (ordering of the atoms under the influence of the stress, the appearance, redistribution, and migration of dislocations, etc.), and molecular rearrangement (relative-displacement of groups, segments, and the entire molecules).

In the present review special attention is given mainly to the last type of rearrangement which has been least investigated§. The first four types of internal rearrangement and the mechanisms of internal friction associated with them have been fairly thoroughly examined at various times by numerous investigators (see the review articles [7–11]).

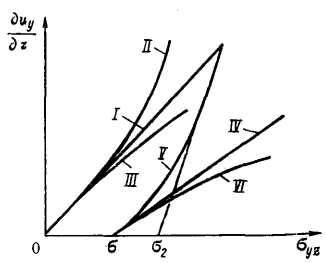


Fig. 1. Principal types of flow curves: I) viscous Newton substance; II) and III) "quasi-viscous" substance; IV) Bingham's "plastic" substance; V) and VI) "quasi-plastic" substance; σ_2—conventional limit of fluidity.

† If the substance exhibits rubberlike elasticity, it is essential to take into account also the rubberlike deformation.

II. METHODS OF MEASUREMENT OF INTERNAL FRICTION

Internal friction can be measured by different methods: (1) from the temperature variation of the substance during deformation; (2) from the variation of the phase shift angle between the stress and the deformation; (3) from the amplitudes of free and forced vibrations at various frequencies; (4) from the decay of elastic waves. The first [12,13] and the second [14–16] methods have not been widely used. The third and fourth methods are the most extensively applied and therefore we shall in fact consider them, leaving aside methods developed for rubberlike materials (see, for example, the review by Bartenev et al. [17]).

1. Methods of Free and Forced Vibrations

The third group of methods is usually divided into two parts. The first part includes all the low-frequency methods and the second all the high-frequency methods. We shall consider briefly the methods in each subsection of this group separately.

a. Low-frequency methods. The low-frequency methods include all known methods based on torsional, bending, longitudinal, and transverse vibrations in the range between 10^{-3} and 10^2 c/s. At vibration frequencies above 2 c/s the variation of the amplitude with vibration frequency is usually recorded automatically. At lower frequencies it is possible (and very convenient) to make visual observations.

‡ In earlier studies [3] internal friction was erroneously identified with the viscosity.

§ It has been partially described by Kolsky [4] and Ferry [5]. Molecular motion in polymers has been described by Mikhailov and Borisova [6].

The oldest and the simplest of all the low-frequency methods for the measurement of internal friction is that of the torsional pendulum. As early as 1837, Weber[18] used the torsional pendulum to solve the problem of the non-elastic behaviour of silk threads, whereby he initiated the studies of internal friction by this method. The torsional pendulum method received general recognition in subsequent years. The method has been used particularly extensively during recent years after its very successful application[19-21] in the study of the viscous behaviour of grain boundaries in metals.

The principal disadvantages of the method of low-amplitude torsional vibrations, which otherwise has many advantages[21], are the inhomogeneity of the deformation of the specimen (the relative amplitude of deformation varies from a maximum of 10^{-5}–10^{-4} on the surface of the specimen to zero at its axis) and the presence of a constant extensive load due to the weight (of the order of 30–50 g) of the inertial system attached to the lower end of the specimen. A torsional pendulum free of the last defect was proposed in 1954 by Ang and Wert[22] and in the same year by Jenckel[23]. It is known as the "reversible torsional pendulum". Its most successful version was developed and constructed in 1960 by Piguzov[24]. This apparatus permits the measurement of internal friction and the modulus of shear in the temperature range between 80° and 770°K. In its design provision is made for the irradiation of the specimen with ultraviolet and X-rays and for the deformation of the specimen directly during the measurement.

Other versions of the torsional pendulum with different design features are also known[25-31]. A novel apparatus, permitting the measurements of the internal friction in polymers and plastics in the frequency range between 10^{-3} and 10^{2} c/s during bending vibrations has been described by Maxwell[33] and apparatus for the measurement of internal friction during torsional vibrations in the infrared frequency range has been described by Illers and Breuer[34] (see also Refs. 35 and 36). Illers[35] described a novel method for the measurement of mechanical losses at a frequency of about 1 c/s.

A simple shear pendulum has been proposed by Rorden and Grieco[37]. Methods in which longitudinal vibrations are used[38,39] have been developed predominantly for materials with rubberlike elasticity. A very interesting method, for materials of the same type, using longitudinal vibrations excited electrically has been described by Hutton and Nolle[40]. The logarithmic decay decrement θ, or the quantity Q^{-1}, which is smaller by a factor of π, serve as measures of the internal friction in this method. The last symbol was introduced by analogy with the decay of electromagnetic oscillations in electrical circuits[9]; Q is the Q-factor of the system in which the mechanical vibrations are excited.

We may note that materials with a very small internal friction (of the order of 10^{-5}) cannot be investigated with the aid of a torsional pendulum (of whatever design), for example, since under these conditions the decay resulting from the losses in the apparatus has an effect.

b. High-frequency methods. These methods are characterised by the absence of a special inertial system linked with the specimen. The specimen in the form of a rod executes torsional, longitudinal, transverse, or bending vibrations at one of its natural frequencies. Steady forced vibrations (resonance method) and the decay of natural vibrations (the method of free vibrations) can be used for the measurements. In the first case the internal friction is measured by the quantity

$$B = \frac{\Delta\nu}{\nu_0}, \qquad (5)$$

where $\Delta\nu$ is the half-width of the resonance peak. In the second method the internal friction is measured, as in the low-frequency methods, by the logarithmic decay decrement θ or Q^{-1}.

The frequency range depends on the type of vibrations excited and the size and shape of the specimens. For example, in torsional, longitudinal, and transverse vibrations the frequency is usually between about 10^2 and 10^6 c/s. In bending vibrations the frequency is in the range approx. 10^2–10^4 c/s.

High-frequency vibrations can be excited and recorded in different ways. However, most investigators use the same methods for both purposes. Depending on the way in which the forced vibrations are excited, all the high-frequency methods can be divided into electrical, piezoelectric, electromechanical, and electromagnetic.

In the electrostatic method (Fig. 2*a*) mechanical vibrations are excited by applying an alternating potential to a condenser, one plate of which is the end of the specimen (covered by a conducting layer in the case of polymer) and the end is a stationary plate. To record the vibrations, it is possible to use the same type of condenser at the other end of the specimen, operating as a capacitive microphone. The electrical method is suitable for longitudinal, bending, and torsional vibrations. The method was used for the first time by Bancroft and Jacobs[41] to excite longitudinal and bending vibrations in metallic rods. It was then used by Parfitt[42] for polymers. A description of the subsequent use and development of this method can be found in Refs. 14, 43–49, etc.

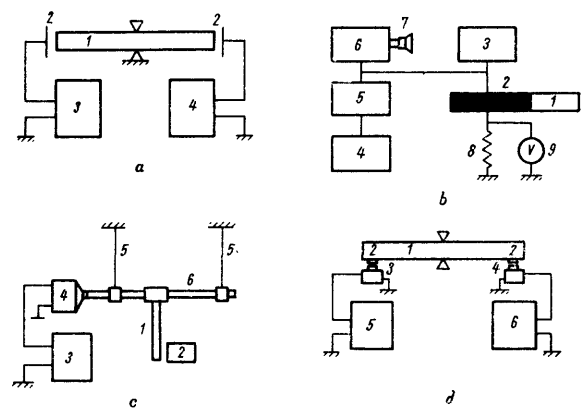


Fig. 2. Schematic representation of high-frequency methods for the measurement of internal friction:
a): 1) specimen; 2) condenser plates; 3) oscillator; 4) detector;
b): 1) specimen; 2) quartz; 3) constant amplitude and alternating frequency generator; 4) constant frequency generator; 5) multivibrator; 6) amplifier; 7) reproducer (beat detector); 8) resistance; 9) valve voltmeter;
c): 1) specimen; 2) "detector"; 3) oscillator; 4) electromechanical transducer; 5) flat springs; 6) connecting rod;
d): 1) specimen; 2) pole pieces; 3) and 4) electromagnetic transducer and receiver; 5) oscillator; 6) detector.

In the piezoelectric method (Fig. 2*b*) the specimen of the test material in the form of a rod is attached by a cement to the end-face of the piezo-quartz rod. When an alternating potential is applied to the piezo-quartz rod, the specimen and the quartz begin to vibrate as a single body (compound vibrator), executing longitudinal or torsional vibrations. From the variation of the current flowing through the quartz, measured by means of a valve voltmeter *9* (or determined from the changes in the resonance curve), it is possible to determine the internal damping of the system, which yields the overall internal friction of quartz and the specimen. The internal friction of quartz can be determined separately and allowed for. The vibration frequencies of the compound vibrator are measured by the method of beats.

Quimby[50,51] and then Zacharias[52] were the first to use this method to measure the internal friction in solids. The compound vibrator method has been applied to the investigation of polymers in Refs. 53–56 and other investigatons. It has been found[57] that, as a resutl of the differences between the coefficients of linear expansion of quartz and the specimen, the internal friction is greatly influenced by the deformations in the cementing layer. This effect is small if the specimen and the quartz rod are selected to ensure that they have similar natural vibrations so that a vibration node is located at the point of attachment. This requirement cannot always be satisfied and therefore the method is not suitable for the investigation of internal friction as a function of temperature. Using a number of precautions, Mikhailov and Solov'ev[54,56] and Wada and Yamamoto[55] nevertheless succeeded in investigating the temperature vibration (in the range between 100° and 360°K) of the internal friction of certain polymers by the compound vibrator method.

In the electromechanical method the vibrations of the specimen are excited by an electromechanical transducer of special design[14,58,59] or simply with the aid of a loudspeaker[60,61], as shown in Fig. 2*c*. In the earliest studies[60,62] the amplitude of the vibrations of the specimen was measured visually using a microscope.

A photoelectric method has been employed for recording the vibrations of specimens[14,58]. Robinson's work[58] is particularly interesting, since he developed a method whereby it is possible to measure the internal friction in the temperature range between 20° and 600°K at vibration frequencies between 10^2 and 10^3 c/s.

Capacitive and inductive methods have been employed for the recording of vibrations[63,64]. An improved capacitive method has also been described[61] for the measurement of the vibration amplitudes in the frequency range between 6 and 6000 c/s. The temperature during the measurements could vary between −50° and +300°C.

In the electromagnetic method (Fig. 2*d*) a disc of a ferromagnetic material is attached to each end of the specimen by means of a special cement. A coil (supplied with power from an oscillator) located near one of the ends of the specimen sets up an alternating magnetic field which interacts with the ferromagnetic disc and gives rise to the vibration of the specimen. In a second coil (near the second disc) an e.m.f. is induced and then amplified and recorded. The relative positions of the coils and discs determine the type of vibration: depending on the relative positions, the vibrations can be longitudinal[65,66], bending[22,67,68], and torsional[69]. The method is not very suitable for the measurement of low internal frictions, since the discs can move at their points of attachment causing additional energy losses. Forster[70] eliminated this defect by modifying the method. In his procedure the vibrations of the specimen are transmitted via a wire suspension. They are then transmitted through another wire suspension to the recording device. This method is suitable for the measurement of internal friction at high temperatures: the wires emerge from the furnace and the entire electrical section is at room temperature. After some design modifications; Kline[71] used Forster's method to investigate the internal friction in polymers at temperatures between 4° and 600°K and frequencies between 50 and 5000 c/s.

Borovitskaya[72] used an optical interference-modulation method[73] to investigate the internal friction in rubberlike materials at frequencies between 10^2 and 10^5 c/s.

2. Method of Wave Propagation

This method for the investigation of internal friction consists in the measurement of the decay of the stress wave during its propagation in the solid. Under certain conditions[4] it is possible to compare this decay with the internal friction determined by the methods examined above. It can be shown that the absorption coefficient α and the quantity δ are related to the wavelength λ as follows:

$$\alpha = \frac{1}{2\lambda}\delta \ . \qquad (6)$$

Using the case where only one relaxation process, characterised by one relaxation time τ, takes place in the solid, Zener[74,75] showed that the parameters (examined above) defining internal friction are simply related¶, regardless of the exact mechanism of energy dissipation, provided that the internal friction is low (for example, $\tan\varphi \leqslant 0.1$). This relation is as follows:

$$\tan\varphi = \frac{\theta}{\pi} = \frac{\delta}{2\pi} = \frac{B}{\sqrt{3}} = \frac{\lambda}{\pi}\frac{\alpha}{\pi} \ . \qquad (7)$$

Bearing in mind the above relation, it is possible to express the absorption coefficient in terms of any parameter used as a measure of internal friction. However, one must not forget that in fact the decay of the pulse is not due solely to absorption but also to a large extent to dissipation at inhomogeneities. The decay of the stress waves is particularly pronounced when the average size of an individual inhomogeneity is comparable to the wavelength. Under these conditions the decay of stress waves is caused not so much by absorption, whose mechanism is similar to that of internal friction, as by diffusive scattering of stress waves by the inhomogeneities.

The method of wave propagation can be subdivided into two separate procedures: the method of "travelling waves" and the pulse method. The method of travelling waves was first used by Ballow and Silverman[79] and then by Nolle[80],

¶ Eqn. (7) breaks down when $\tan\varphi > 0.1$; it depends on the mechanism of energy dissipation[76]. In the region of very high internal friction the logarithmic decay decrement cannot serve as a reliable characteristic and in the region of aperiodic motion the concept of a logarithmic decrement loses all significance. Therefore in the aperiodic region and in the adjacent regions (see Figs. 7, 8, and 10) of rapid decay of the vibrations, it is necessary to use other quantities as characteristics of internal friction, for example the absorption coefficient[77] α or the coefficient of mechanical losses, which in this case is related to $\tan\delta$ in a different way[78].

Kuznetsov[81], and others. The theory of this method and the calculation of the dynamic characteristics of the material have been discussed[82-84]. The method has been developed most completely (Fig. 3*a*) by Volodin[85].

This method for the measurement of α can be used only in a restricted frequency range (approx. 10^3-10^5 c/s) and for materials with values of α which are neither unduly large nor unduly small[81,85].

The pulse method (Fig. 3*b*) consists in the excitation of a short high-frequency vibration pulse ($\nu \simeq 10^5-5\times10^8$ c/s) and the measurement of its propagation and decay times during passage through the specimen. In the earliest studies[86-88] the pulses lasted between 1 and 15 μs with vibration frequencies of the order of 10^8 c/s. The pulse passes back and forth through a liquid (transmitting medium) and along the specimen *1* and is detected by the receiving crystal *3*. The relative amplitudes of the successive pulses determined with a valve voltmeter *8* provide a measure of the decay and the time intervals between them, determined by an oscilloscope *7*, give the rate of propagation.

The method was developed further by other workers[89-94]. In their study of the intrinsic piezo-effect of quartz, Merkulov and Yakovlev[94] measured the absorption coefficient of quartz (for shear and longitudinal waves) by the pulse method up to hypersonic frequencies ($\nu \simeq 10^9$) in the temperature range between −200° and +200°C.

As shown above, the results obtained by the pulse method must be interpreted with some caution. It is necessary to take into account the "spreading" of the pulse during its propagation in the absorbing medium (due to the dispersion of the velocity of sound) and also the fact that the overall weakening of the pulse is due not only to absorption but also to a large extent to scatter by inhomogeneities.

A pulse method for hypersonic frequencies (approx. 10^9-10^{10} c/s) has been described[95,96]. This method, which is a development of Baranskii's method[97], is based on hypersonic excitation in a quartz rod with the aid of an electromagnetic cavity resonator. The quartz rod is the test specimen. Hypersonic vibrations of higher frequencies ($\nu \simeq 10^{12}-10^{13}$ c/s) cannot be excited artificially. We may note that the limit of natural thermal hypersonic frequencies is of the order of $10^{12}-10^{13}$ c/s even in crystalline materials. The study of the rate of propagation and absorption of natural hypersonic vibrations in crystals is possible only by indirect methods, namely optical[98] and X-ray[99-103] methods.

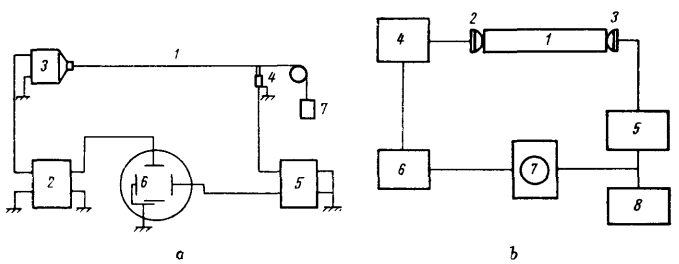


Fig. 3. Schematic representation of the "travelling wave" and pulse methods for the measurement of the rates of propagation and absorption of vibrations in solids:
a): 1) threadlike specimen; 2) oscillator; 3) electromechanical transducer; 4) piezoelectric rod; 5) amplifier; 6) double-beam oscilloscope;
b): 1) specimen; 2) piezoelectric transducer; 3) piezoelectric receiver; 4) pulse generator; 5) amplifier; 6) synchronisation unit; 7) oscilloscope; 8) valve voltmeter.

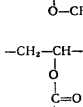
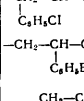
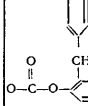
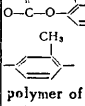
III. EXPERIMENTAL RESULTS

The solid polymers and plastics which have been investigated are listed in the Table which indicates the range of conditions investigated, the method of investigation, and the literature sources available to the author of the review. It is evident from the Table that technically important polymers such as polyethylene, polystyrene, poly(vinyl chloride), polyamides, and acrylic acid polymers have been most completely investigated. Few studies have been made on plastics.

TABLE.

No.	Polymer	Monomer unit	Range investigated: temperature, °K	Range investigated: frequency, c/s	Method	Refs.
1	polyethylene	$-CH_2-CH_2-$	110—400	~1	torsional vibrations	104—108
			85—400	~1	shear vibrations	109
			80—450	10^2-10^3	transverse vibrations	110—116
			50—550	10^2-10^3	ditto	117,118
			170—350	10^2-10^3	»	119
			300—425	10^2-10^3	shear vibrations	120,121
			190—425	10^3-10^4	longitudinal vibrations	14,49, 122—127
			110—370	10^4-10^5	ditto	128—130
			210—340	~10^6	shear waves	128—130
			275—360	~10^6	longitudinal waves	55,92,128, 130,131
2	polyoxymethylene	$-CH_2O-CH_2O-$	100—450	~1	torsional vibrations	132—134
3	poly-α-olefins	$-CH_2-CH(R)-$	80—350	10^2-10^3	transverse vibrations	135
4	polypropylene	$-CH_2-CH(CH_3)-$	50—450	10^2-10^3	transverse vibrations	136
			190—275		longitudinal vibrations	49
			230—400		longitudinal waves	137
5	polyisobutylene	$-CH_2-C(CH_3)_2-$	110—415	~1	torsional vibrations	104
			300	$30-5\cdot10^3$	shear vibrations	138
			230—375	10^2-10^3	ditto	139
			290	~10^6	longitudinal waves	92
6	poly(vinyl chloride)	$-CH_2-CH(Cl)-$	~300	$10^{-3}-10^2$	bending vibrations	33
			125—425	1—10	torsional vibrations	27,60,101, 140
			25—350	10^2-10^3	transverse vibrations	111
			255—300	10^2-10^3	shear vibrations	138
			285—375	10^6	longitudinal waves	55,92,141
			175—475	10^6	ditto	142
7	poly(vinylidene chloride)	$-CH_2-C(Cl)_2-$	110—470	~1	torsional vibrations	104
8	poly(vinyl alcohol)	$-CH_2-CH(HO)-$	175—475	~1	torsional vibrations	142
			290—450	10^2-10^3	transverse vibrations	143
9	polyacrylonitrile	$-CH_2-CH(C\equiv N)-$	110—500	~1	torsional vibrations	104
10	polystyrene	$-CH_2-CH(C_6H_5)-$	100—210	~1	torsional vibrations	144
			135—425	~1	ditto	23,104,107 145,146
			50—500	10^2-10^3	transverse vibrations	61,110,111, 147,148
			50—300	10^3-10^4	longitudinal vibrations	49,149,150
			210—365	10^4-10^5	ditto	125,127
			290	10^6	»	92
			175—475	10^6	»	142
			210—370	10^6	»	58
11	polyvinylstyrene	$-CH_2=CH-CH_2-CH(C_6H_5)-$	~300	10^2-10^3	shear vibrations	129
12	poly(methyl acrylate)	$-CH_2-CH(CH_3O-C=O)-$	~315	$10^{-1}-10^3$	torsional and transverse vibrations	151

TABLE (contd.)

No.	Polymer	Monomer unit	Range investigated: temperature, °K	Range investigated: frequency, c/s	Method	Refs.
13	poly(methyl α-chloroacrylate)		220—430	10^2—10^3	transverse vibrations	152
14	poly(methyl methacrylate)		250—350	10^{-3}—10^2	bending vibrations	153
			30—300	10^3—10^4	ditto	154
			150—435	~1	torsional vibrations	155,156
			4.2—100	~1	ditto	157
			190—400	1—10^2	»	28,158-160
			200—400	10^2—10^3	transverse vibrations	28,158,160
			290—370	10^2—10^3	longitudinal vibrations	48
			225—385	10^3—10^4	ditto	49
			225—355	10^4—10^5	»	125
			290—380	~10^6	longitudinal waves	55,92,161, 162
15	poly(ethyl methacrylate)		4.2—100	~1	torsional vibrations	157
			225—285	~1	ditto	151
			~315	10^{-1}—10^3	torsional and transverse vibrations	151
16	poly(cyclohexyl methacrylate)		~315	10^{-1}—10^3	torsional and transverse vibrations	151
17	poly(methyl α-cyanoacrylate)		220—430	10^2—10^3	transverse vibrations	152
18	poly(tributyl methacrylate)		~315	10^{-1}—10^3	torsional and transverse vibrations	151
19	poly(isobutyl vinyl ether)		110—370	1—10	torsional vibrations	104,163
20	poly(vinyl acetate)		125—460	$2 \cdot 10^6$	longitudinal waves	164
21	poly-p-chlorostyrene		100—210	10^{-1}—1	torsional vibrations	144
22	poly-p-bromostyrene		100—210	10^{-1}—1	torsional vibrations	144
23	polyvinyl carbazole		120—525	~1	torsional vibrations	104,163
24	polybutylene		210—285	10^3—10^4	longitudinal vibrations	49
25	polytetrafluoroethylene		125—435	~1	torsional vibrations	155,165
			20—560	~1	ditto	30,31,106, 163,166
			4.2—100	~1	transverse vibrations	111,112
			50—600	10^2—10^3	shear vibrations	120
			300	10^2—10^3		
26	polychlorotrifluoroethylene		150—500	~1	torsional vibrations	158
			110—470	~1	ditto	104,163
27	phenol formaldehyde resins		200—360	10^3—10^4	longitudinal vibrations	49
			200—450	10^4—10^5	ditto	125,127
			290—360	10^6	»	55
28	poly(di-o-cresyl carbonate)		100—510	~1	torsional vibrations	167
29	polyester resins	polymer of complex structure	220—520	~1	torsional vibrations	104,163
			210—360	10^4—10^5	longitudinal vibrations	
30	polyamides	ditto	100—485	~1	torsional vibrations	168,169
			110—525	~1	ditto	104,106
			50—600	10^2—10^3	transverse vibrations	111,170,171
			235—535	10^3—10^4	longitudinal vibrations	49
			210—290	10^4—10^5	ditto	125
			265—335	10^6	longitudinal and shear waves	128
			290—360	10^6	longitudinal waves	55
31	polyesters	»	210—525	~1	torsional vibrations	27
32	polyurethanes	»	101—425	~1	torsional vibrations	23,106, 172—174
33	celluloid	plastic	200—450	~1	torsional vibrations	27
			300	10^3—10^2	bending vibrations	33
			290—360	10^6	longitudinal waves	55
34	ebonite	ditto	290—450	10^2—10^3	transverse vibrations	175
			290—360	~10^6	longitudinal waves	53,55
35	Novolak plastics	»	290—700	~1	torsional vibrations	21

We shall consider briefly the principal results of studies on the temperature and frequency dependence† of the internal friction in polymers and plastics on various factors: structure, impurity content, thermal and mechanical treatment, irradiation, etc., using as examples the macromolecular compounds which are technically the most important.

1. Temperature Dependence

Figs. 4*a*, 4*b*, and 5 show the temperature variation of the internal friction of polyethylene, polystyrene, and poly(methyl methacrylate) of technical purity at various frequencies. The results demonstrate that the Q^{-1}–T curves for all the polymers examined have one or several maxima whose positions along the temperature axis may depend on the vibration frequency (as can be seen in Fig. 5). Fig. 5 shows that, with increasing frequency, the internal friction peak is displaced towards higher temperatures, degenerates into a point of inflection, and finally disappears altogether. However, the peaks on the polyethylene Q^{-1}–T curve, for example, do not disappear when the frequency is increased from 1 to 10^6 c/s and their position along the temperature axis changes little, although their shape does alter appreciably. The shape is very sensitive to the number of methyl groups in the polyethylene macromolecule [117].

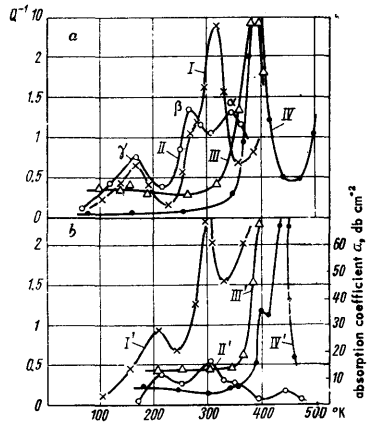
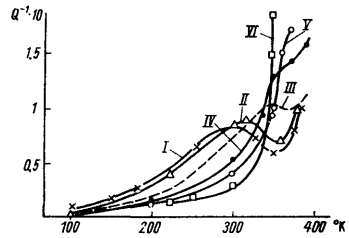


Fig. 4. Temperature variation of the internal friction and of the absorption coefficient α of polyethylene (curves I and II) and polystyrene (curves III and IV):
a) frequencies: 1 c/s for curves I and III and about 10^3 c/s for curves II and IV;
b) frequencies: about 10^4 c/s for curves I and II and about 2×10^6 c/s for curves III and IV.

† For low deformation amplitudes, which usually obtain in measurements of internal friction, the variation of internal friction with the experimental temperature and vibration frequencies is of fundamental importance (see the theory). Various factors (preceding treatment, impurities, irradiation, etc.) alter $Q^{-1}(T)$ and $Q^{-1}(\nu)$. By studying these changes, we are able to assess the nature of molecular motion in solid polymers.



CHEMICAL SOCIETY
REFERENCE
LIBRARY
N HOUSE, W.1

Fig. 5. Temperature and frequency dependence of the internal friction of poly(methyl methacrylate);[49,158] frequency (ν, c/s):
I) 0.4; II) 2; III) 20; IV) 200; V) 2×10^3; VI) 3×10^4.

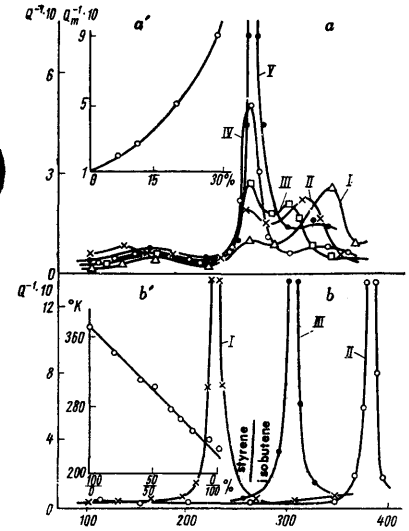


Fig. 6. Effect of chlorine on the shape of the $Q^{-1}-T$ curve for polyethylene:
a) frequency $\nu \sim 1$ c/s:[104] I) 0 wt.% Cl; II) 5.8 wt.% Cl; III) 10.4 wt.% Cl; IV) 12.3 wt.% Cl; V) 28.2 wt.% Cl;
a') variation of the height of the 270°K peak on the $Q^{-1}-T$ curve with the chlorine content;
b) temperature variation of the internal friction of a mixture of polyisobutylene and polystyrene at $\nu \sim 1$ c/s:[104]
I) polyisobutylene; II) polystyrene; III) 50% polystyrene–50% polyisobutylene mixture;
b') temperature variation of the Q_m^{-1} maximum with the ratio of styrene and isobutene in the mixture.

The shape of the peaks depends significantly also on other factors, in the first place on the relative amounts of the amorphous and crystalline phases in the solid polymer. Thus the low-temperature peak on the $Q^{-1}-T$ curve for Teflon decreases in height with increasing degree of crystallinity, while the height of the peak in the region of 300°K actually increases with increasing crystallinity[31,165]. The high-temperature peak on the Teflon $Q^{-1}-T$ curve (at about 400°K) varies in a more complex manner.

Another factor which influences significantly the shape of the peak is impurities. Fig. 6*a* shows this effect in polyethylene containing various amounts of chlorine atoms. It is seen that for technically pure polyethylene there is a point of inflection near 270°K instead of the peak. With increasing percentage content of chlorine atoms in polyethylene, the peak not only becomes distinct but also increases rapidly in height (Fig. 6*a'*). The high-temperature peak (340°K) also varies appreciably on introduction of chlorine atoms into polyethylene but the variation of its height and position is more complex. The effect of chlorine atoms on the position and height of the low-temperature peak (at about 170°K) is slight.

The position of the maximum in the $Q^{-1}-T$ curve can also depend on the molecular weight of the polymer. For example, increase of the molecular weight of polystyrene[104] from 80 000 to 120 000 causes a displacement of the peak (without significant change in its height) towards higher temperatures by about 16 deg, but effects of this kind are not always observed. For example, a change of the molecular weight of polyisobutylene from 500 000 to 1 750 000 changes neither the position nor the height of the peak on the curve[104].

According to Fig. 6*b*, the $Q^{-1}-T$ curves for polyisobutylene and polystyrene have distinct maxima. A mixture‡ of these polymers also gives rise to a peak (Fig. 6*b*, curve III) on the $Q^{-1}-T$ curve, whose position on the temperature axis (Fig. 6*b'*) depends on the relative amounts of styrene and isobutene in the mixture.

It has been shown[104] that heat treatment influences the form of the $Q^{-1}-T$ curve for a mixture of poly(vinyl chloride) and poly(vinylidene chloride). In the first place the authors draw attention to the fact that, in contrast to pure amorphous polymers which have no peaks on the $Q^{-1}-T$ curve, the curve for a mixture of amorphous homogeneous polymers has an internal friction peak at approximately 300°K. Crystallisation of the mixture (as a result of the heat treatment) leads to the appearance of a second peak on the $Q^{-1}-T$ curve, whose height increases slightly with increasing amount of the crystalline phase, while the peak characteristic of the amorphous phase decreases sharply.

Irradiation has a significant effect on the shape of the $Q^{-1}-T$ curve. Irradiation with γ-rays emitted in the decomposition of radioactive cobalt-60 nuclei at a selected dose (about 100 mr) does not give rise to an appreciable change[111] of the shape of the $Q^{-1}-T$ curve for non-irradiated polyethylene. The situation changes markedly when polyethylene is irradiated with a neutron beam of the order of 10^{18} neutron cm^{-2} s^{-1}.[111,115,118] With increasing intensity of the neutron beam, the low-temperature γ-peak initially broadens and increases in height and then begins to be displaced towards higher temperatures with a simultaneous decrease in height. At the same time the β and α peaks merge into a single, broad peak, which then vanishes altogether.

Summarising, one may say that the $Q^{-1}-T$ curve characterises a given polymer under concrete conditions. Each change in the specimen, be it a change in molecular weight, composition, degree of crystallinity, etc., is reflected in

‡ For more detailed information on the composition of the polymers see, for example, Bartenev et al.[35]

a characteristic change in the shape of the internal friction–temperature curve. We shall see below that theoretical and experimental studies of these changes provide information about the characteristic features of the mechanism of certain processes in polymers.

2. Frequency Dependence

The variation of the internal friction of polymers over a wide range of frequencies has not been investigated. This is due to the experimental difficulties involved in such experiments. Fig. 7*a* shows the frequency dependence of the internal friction of polyethylene and poly(methyl methacrylate) at 30°C based on the results of several investigators [28,55,119,125,128,142,153,176].

Examination of Fig. 7 shows that in the frequency range between 10^{-3} and 10^{6} c/s poly(methyl methacrylate) has a single maximum and polyethylene two maxima in the $Q^{-1}-\nu$ curve. The origin and nature of these maxima will be discussed below. Here attention is drawn to the possible dependence of the positions of the maxima along the frequency axis and their shape on various factors. The results of the investigations presented in Fig. 7*b* make it possible to follow the effect of temperature on the shape of the $Q^{-1}-\nu$ curve. It is readily evident that an increase of temperature entails a displacement of the maximum towards higher frequencies (see also Fig. 5) and an increase in its height.

It has been shown [28] that the introduction of a plasticiser into the polymer [28] almost does not alter the position of the maximum in the $Q^{-1}-\nu$ curve for poly(methyl methacrylate) but does increase somewhat its height. However, if the molecular structure of the polymer is altered, for example by copolymerisation, the shape of the $Q^{-1}-\nu$ curve can change significantly [28]. Comparison of the $Q^{-1}-\nu$ and $Q^{-1}-T$ curves shows that in the first case the frequency must be varied within very wide limits (at least by 5–6 powers of ten, see Fig. 1) in order to detect the required maxima, while in the second case it is sufficient to vary the temperature by less than 1–2 powers of ten (see Fig. 4).

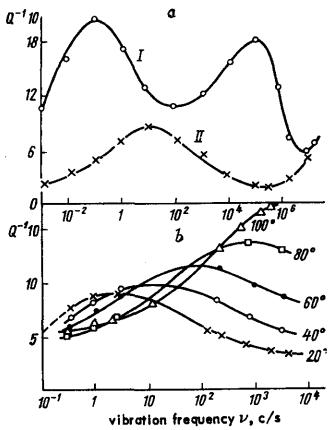


Fig. 7. *a*) Frequency dependence of the internal friction of polyethylene (curve I) and poly(methyl methacrylate) (curve II) at 30°C;
b) frequency and temperature dependence of the internal friction of poly(methyl methacrylate).

IV. THEORY OF INTERNAL FRICTION

It was noted above that in a real solid deformation does not follow exactly the stress applied to the substance from outside but lags behind it by a certain angle φ. As a result, in a periodic deformation of such a substance at a frequency ν, elastic vibration energy is dissipated. Investigations show (see Figs. 4–7) that the relative amount of energy dissipated in one cycle (or internal friction) depends on the vibration frequency and the experimental temperature. The nature of the temperature and frequency dependence of internal friction depends in turn on a multiplicity of various factors, some of which have been examined above.

The theory of internal friction should provide an answer to three questions at least: (1) why there are maxima in the $Q^{-1}-\nu$ and $Q^{-1}-T$ curves and what is their nature; (2) why certain amorphous substances do not have maxima in the $Q^{-1}-T$ curve; (3) how various factors affect the nature of the $Q^{-1}-\nu$ and $Q^{-1}-T$ curves. The modern theory of internal friction cannot yet provide an exhaustive answer to these questions but many of aspects are now fairly clear.

The theory has developed in two main directions: one involving the phenomenological description of the principal laws governing internal friction and one involving the development of its various mechanisms on the basis of the molecular-kinetic theory. We shall examine briefly the principal results of the theory obtained in these two ways.

1. Phenomenological Theory

The phenomenological approach to the solution of the problem of the dissipation of the elastic energy of a real vibrating solid may be twofold. It is possible to solve the problem within the framework of the thermodynamics of irreversible processes after making certain simplifying assumptions about the properties of real substances. Another approach (purely formal) is based on the replacement of the real substance by a model, which reflects some definite property of the real substance. The mechanical properties of real solids, including internal friction, can be described more or less fully by a set of models. We shall begin with the latter procedure, since it has had some success [177] because of the clear-cut nature of the results obtained.

a. The model theory. We shall examine a substance which undergoes elastic deformation under stress and which can also flow. The total deformation of such a substance under the influence of a shear stress, for example, is equal to its elastic deformation and degree of flow, i.e.

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \text{ or } \dot{\varepsilon} = \dot{\varepsilon}_1 + \dot{\varepsilon}_2 \qquad (8)$$

where a dot over a symbol denotes differentiation with respect to time. The rate of elastic displacement is determined from Hooke's law and the rate of viscous flow from Newton's law [see Eqn. (3)].

Hence we have from Eqn. (8)

$$\dot{\varepsilon} = \frac{\sigma}{\eta} + \frac{\dot{\sigma}}{G} . \qquad (9)$$

Let the specimen, the material of which obeys the Maxwell equation [Eqn. (9)] undergo a deformation ϵ_0 and then remain in this state. Then $\dot{\epsilon}_0 = 0$ and Eqn. (9) reduces to the following relation:

$$\frac{\dot{\sigma}}{G} + \frac{\sigma}{\eta} = 0 .$$

The solution of this differential equation has the form

$$\sigma = \sigma_0 \, e^{-\frac{G}{\eta}t} . \qquad (10)$$

Thus the decrease (relaxation) of stress in the specimen with time is exponential and is characterised by the relaxation time

$$\tau = \eta/G . \qquad (11)$$

As will be shown later, the relaxation time is a very convenient characteristic of the rate of relaxation processes in both simple and complex systems.

The behaviour of a substance which obeys the Maxwell equation can be represented by the mechanical model shown in Fig. 8. When stress is applied at a certain instant t_1, the spring is instantly extended by an amount σ/G and the piston begins to be uniformly displaced at a rate σ/η. When at another instant t_2 the stress is discontinued, the spring instantly contracts but the piston remains in the displaced state. As a result, the motion of the lower end of the model [or the deformation $\epsilon(t)$] is of the form shown in Fig. 8.

When a stress $\sigma(t) = \sigma_0 e^{i\omega t}$, which varies periodically, is applied to a Maxwell substance, dissipation of vibration energy is observed. Indeed, on substituting $\sigma(t)$ in the Maxwell equation [Eqn. (9)] and integrating the latter, we find

$$\varepsilon = l^* \sigma ,$$

$$l^* = \frac{1}{i\omega\eta} + \frac{1}{G} , \qquad (12)$$

where l^* is the reciprocal of the complex shear modulus G^* or the pliability. The following quantity is adopted as a measure of internal friction:

$$Q^{-1} = \tan\varphi = \frac{\mathrm{Im}\,(G^*)}{\mathrm{Re}\,(G^*)} = \frac{\mathrm{Im}\,(l^*)}{\mathrm{Re}\,(l^*)} . \qquad (13)$$

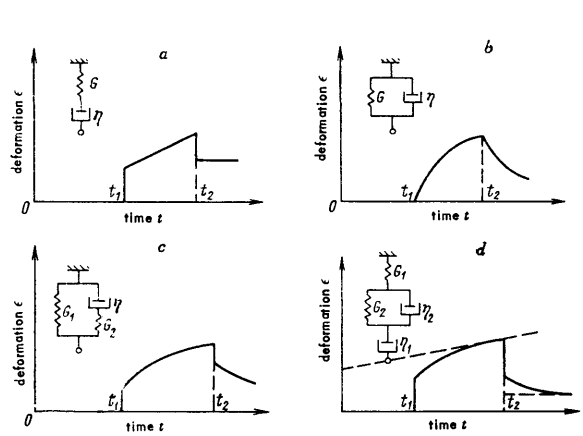


Fig. 8. Variation of the deformation with time for different types of substance (model):
a) Maxwell substance; *b*) Voigt substance; *c*) "standard linear substance"; *d*) Alfrey–Kobeko substance.

Bearing in mind Eqn. (13), we find

$$Q^{-1} = \frac{1}{\omega\tau} . \qquad (14)$$

Since the viscosity of amorphous objects is known [2,177] to decrease rapidly with temperature [in accordance with Eqn. (14)], the internal friction of a Maxwell substance should increase steadily with the temperature of the measurements. The low-frequency internal friction of certain amorphous polymers (K-18-2 resin), polypropylene, etc., does indeed increase steadily with experimental temperature, but this by no means implies that the properties of a Maxwell substance describe a real polymer satisfactorily. It was assumed above that elastic deformation takes place instantly, i.e. that the substance exhibits ideal elasticity (as well as ideal viscosity). A real substance may show a lagging elastic response, which can be represented by the mechanical model in Fig. 8*b*. This device differs from that in Fig. 8*a* in that the spring and the piston are linked in parallel and not in series. There is a significant difference between Voigt and Maxwell elements. In contrast to a Maxwell substance, the behaviour of a Voigt substance is described by the following differential equation:

$$\sigma = G \cdot \varepsilon + \eta \cdot \dot{\varepsilon} . \qquad (15)$$

It can be readily shown that the lag time (retardation) is defined by the same equation [Eqn. (11)] as the relaxation time.

In a cyclic deformation of a Voigt substance the deformation is a periodic function of time, which can be written thus:

$$\varepsilon = \varepsilon_0^* \cdot e^{i\omega t} , \qquad (16)$$

where ϵ_0^* is the complex amplitude. When Eqn. (16) is substituted in Eqn. (15), we obtain $\sigma = G^*\epsilon$, where $G^* = G + i\omega\eta$ is the complex shear modulus. We find from Eqn. (13)

$$Q^{-1} = \omega\tau . \qquad (17)$$

Comparison of Eqns. (14) and (17) shows that the variation of the internal friction of a Voigt substance with temperature [$\tau = \tau(T)$] and frequency is precisely the opposite type and therefore it does not correspond in the least to the experimental variation Q^{-1} with T and ω.

We shall now assume that the solid is a mixture of two phases, one of which is viscous [obeying Eqn. (9)] and the other is purely elastic. The mechanical model representing such an object is shown in Fig. 8*c*. If we put $G_1 = 0$ in the model, the latter becomes a Maxwell model, and if we put $G_2 = \infty$, the Voigt model is obtained.

It is not difficult to show that the differential equation corresponding to the mechanical model in Fig. 8*c* is of the form

$$\sigma + \frac{\eta}{G}\dot{\sigma} = G_1 \cdot \varepsilon + \eta\dot{\varepsilon} . \qquad (18)$$

Since this is the most general linear homogeneous equation, relating the stress, deformation, and their first derivatives with respect to time, the solids which obey Eqn. (18) are called "standard linear substances". If it is assumed that $\dot{\epsilon}$ is zero, Eqn. (18) is converted into the equation $\sigma + (\eta/G_2)\dot{\sigma} = G_1\epsilon_0$, which has a solution of the form

$$\sigma(t) = G_1 \cdot \varepsilon_0 + (\sigma_0 - G_1 \cdot \varepsilon_0)\, e^{-t/\tau_\varepsilon} ,$$

where $\tau_\epsilon = \eta/G_2$ is the relaxation time of the stress under conditions of constant deformation.

If it is assumed that $\dot{\sigma}$ is zero, then, on the basis of similar considerations, we obtain from Eqn. (18) the solution

$$\varepsilon(t) = G_1^{-1}\sigma_0 + (\varepsilon_0 - G_1^{-1}\ \sigma_0)\ e^{-t/\tau_\sigma},$$

where $\tau_\sigma = \eta/G$ is the retardation time.

Introducing the new constants τ_ϵ and $\tau_{\dot{\sigma}}$ into Eqn. (18), we obtain

$$\sigma + \tau_\varepsilon\ \dot{\sigma} = G_1(\varepsilon + \tau_\sigma\ \dot{\varepsilon}) . \qquad (19)$$

We now find the relation between the stress and deformation in standard linear substances when these quantities vary periodically with time. For this purpose, we substitute in Eqn. (19)

$$\sigma = \sigma_0\ e^{i\omega t} \text{ and } \varepsilon = \varepsilon_0^*\ e^{i\omega t}.$$

As a result we have $\sigma = G^*\epsilon$, where the complex modulus G^* is represented by the expression

$$G^* = \frac{1 + i\omega\tau_\sigma}{1 + i\omega\tau_\varepsilon}\ G_1 . \qquad (20)$$

The internal friction is now found thus:

$$Q^{-1} = \frac{\omega(\tau_\sigma - \tau_\varepsilon)}{1 + \omega^2\tau_\varepsilon\ \tau_\sigma} \qquad (21)$$

The last expression loses its significance only when $\tau_{\dot{\sigma}} - \tau_\epsilon > 0$, i.e. when the retardation time is greater than the relaxation time, As will be shown below, this does happen in real solids.

In order to represent the variation of the internal friction of a standard linear substance with angular frequency as clearly as possible, we introduce the geometrical mean§ of the times τ_ϵ and τ_σ: i.e. $\bar{\tau} = (\tau_\epsilon\tau_\sigma)^{1/2}$, and the geometrical mean of the moduli G_1 and G_2, i.e. $\bar{G} = (G_1G_2)^{1/2}$.

Then, using the equation

$$\frac{\tau_\sigma}{\tau_\varepsilon} = \frac{G_2}{G_1} , \qquad (22)$$

it is possible to transform Eqn. (21) into the following form:

$$Q^{-1} = \frac{G_2 - G_1}{\bar{G}}\ \frac{\omega\bar{\tau}}{1 + (\omega\bar{\tau})^2} . \qquad (23)$$

Eqn. (23) agrees fully with the familiar expression for Q^{-1} obtained by Zener[75] by a formal generalisation of Hooke's law, provided that we put $G_2 = M_n$ and $G_1 = M_r$, where M_n and M_r are the non-relaxation and relaxation moduli¶ respectively.

For an isotropic substance, M is understood as one of three quantities: the modulus of elasticity E, the modulus of shear G, and the modulus of bulk compressibility K. In this case the first multiplier on the right-hand side of Eqn. (23) defined the degree of relaxation of the modulus M. However, as will be shown below, for simple exponential relaxation it is more convenient to estimate the degree of relaxation of the modulus M by the quantity

$$\Delta = \frac{M_n - M_r}{M_r} , \qquad (24)$$

which is called the defect of the modulus.

§ This artificial procedure was introduced by Zener[75]. As will be seen later, $\bar{\tau}$ is in fact the really significant time, since in many cases a single average retardation time is sufficient to describe the frequency (or temperature) dependence of the decay.

¶ The final value of the stress/deformation ratio which is attained at the end of the relaxation process for the chosen mechanism with a single relaxation time.

The internal friction defined by Eqn. (23) has a maximum given by

$$Q^{-1}_{max} = \frac{1}{2}\frac{G_n - G_r}{\bar{G}} \qquad (25)$$

when

$$\omega\bar{\tau} = 1 , \qquad (26)$$

i.e. when the vibration frequency ω is equal to the reciprocal of the relaxation time $\bar{\tau}$. On either side of this maximum the internal friction decreases asymptotically to zero.

Thus a standard linear substance, i.e. a substance consisting of an elastic matrix in which viscous regions are embedded, dissipates elastic energy during periodic deformation to an appreciable extent only when Eqn. (26) holds. The relaxation time τ depends on the physical nature of the viscous region and also on its size and shape. If different amorphous regions are embedded in the elastic matrix (the basic material of the solid), then each region will have its own relaxation time τ_i and the behaviour of such a solid will be determined by the complete set of relaxation times τ_i, which leads to some "spreading" of the maximum (if the relaxation times are fairly close to one another).

Numerous experiments have shown that the relaxation time for relaxation phenomena associated with atomic and molecular rearrangement (in the field of internal forces) induced by periodic external forces varies with temperature largely according to the law

$$\tau = \tau_0 \cdot e^{H/RT} , \qquad (27)$$

where H is the heat of activation for the process, R the gas constant, and T the absolute temperature.

Since according to Eqn. (23) the internal friction Q^{-1} varies with frequency and the relaxation time in terms of the parameter $\omega\tau$, it is possible to keep the frequency ω constant and vary τ by varying the temperature. At a certain temperature T Eqn. (26) is satisfied and an internal friction maximum due to the occurrence of the relaxation phenomenon discussed above will be observed in the $Q^{-1}\omega - T$ curve.

Thus the rheological model examined makes it possible to explain the peak on the $Q^{-1} - T$ curve but it does not account for the appearance of an internal friction background, i.e. the increase of the internal friction beyond (with continuous increase of temperature) the high-temperature maximum (Fig. 4). An attempt will be made to describe the relaxation peak and the background by a model based on a series combination of Maxwell and Voigt materials, i.e. an Alfrey–Kobeko substance† (Fig. 6*d*).

The differential equation relating ϵ and σ can be obtained in this case from the following considerations. The overall deformation of an Alfrey–Kobeko substance, under the influence of shear stress for example, is equal to the sum of the deformations of the Maxwell and Voigt elements, i.e. $\epsilon = \epsilon_M + \epsilon_V$ or $\dot{\epsilon} = \dot{\epsilon}_M + \dot{\epsilon}_V$, where according to Eqn. (9) the rate of change of the deformation $\dot{\epsilon}_M$ is

$$\dot{\varepsilon}_M = \frac{\dot{\sigma}}{G_1} + \frac{\sigma}{\eta_1}$$

and according to Eqn. (15) that of $\dot{\epsilon}$ is

$$\dot{\varepsilon}_V = \frac{\sigma}{\eta_2} - \frac{G_2}{\eta_2}\ \varepsilon_V . \qquad (28)$$

† This model is sometimes called the four-element model.

On adding together ϵ_M and $\dot{\epsilon}_V$, differentiating the resulting equation once more with respect to time, and eliminating ϵ_V and $\dot{\epsilon}_V$ from these two equations, we obtain with the aid of Eqn. (33) the required differential equation in the following form:

$$\ddot{\sigma}+\left(\frac{1}{\tau_1}+\frac{G_2+G_1}{G_2}\cdot\frac{1}{\tau_2}\right)\dot{\sigma}+\frac{\sigma}{\tau_1\tau_2}=G_1\ddot{\varepsilon}+\frac{G_1\dot{\varepsilon}}{\tau_2} \quad , \qquad (29)$$

where the relaxation times are

$$\tau_1=\eta_1/G_1; \quad \tau_2=\eta_2/G_2 \quad . \qquad (30)$$

On substituting in Eqn. (29)

$$\sigma=\sigma_0\ e^{i\omega t} \text{ and } \varepsilon=\varepsilon_0^*\ e^{i\omega t} \quad ,$$

we obtain

$$\sigma=G^*\varepsilon,$$

where

$$G^*=\frac{-G_1\omega^2+i\omega G_1/G_2}{-\omega^2+i\omega\left(\frac{1}{\tau_1}+\frac{G_2+G_1}{G_2}\ \frac{1}{\tau_2}\right)+\frac{1}{\tau_1\tau_2}} \quad . \qquad (31)$$

According to Eqn. (13),

$$Q^{-1}=\frac{1+\omega^2\tau_2^2+\frac{G_1}{G_2}\omega^2\tau_1\tau_2}{\omega\tau_1\left(\frac{G_2+G_1}{G_2}+\omega^2\tau_2^2\right)} \quad . \qquad (32)$$

Internal friction at a constant frequency depends significantly on the relation between η_1 and G_1 on the one hand and η_2 and G_2 on the other. If, for example, $G_2 \gg G_1$, then the deformation of an Alfrey–Kobeko substance will be determined mainly by the deformation of the Maxwell element and therefore the internal friction must be calculated in this case from a formula analogous to Eqn. (14). Indeed, if $G_2=\infty$, it follows from Eqn. (32) that $Q^{-1}=1/\omega\tau_1$, i.e. Eqn. (14) obtains. If, on the other hand, $G_1 \gg G_2$ and $\eta_1 \gg \eta_2$, the deformation of an Alfrey–Kobeko substance is determined almost entirely by the deformation of the Voigt element. In the limit, when $G_1=\infty$ and $\eta_1=\infty$, we obtain from Eqn. (32) $Q^{-1}=\omega\tau_2$, i.e. Eqn (17), which applies to a Voigt substance.

For other relations between G_1 and G_2 and between η_1 and η_2, a maximum and a background can appear on the Q^{-1}_{ω}–T curve. Fig. 8*a* confirms this. The average relaxation time τ_2 was found from the data of Nolle et al. [178] (Fig. 5). The ratio $G_1/G_2=0.16$ was obtained from Eqn. (32) on the assumption that the maxima on the theoretical and experimental Q^{-1}–T curves are of the same magnitude. We now find that an Alfrey–Kobeko substance does indeed reflect the properties of real solids more fully than a standard linear substance. With its aid, it is possible to explain qualitatively‡ the temperature variation for certain polymers. However, many polymers have not one but several broad and narrow maxima on the Q^{-1}–T curve (Fig. 4).

‡ No model with a single relaxation time can describe satisfactorily a real Q^{-1}–T curve whatever the relations between the moduli G_i and the viscosities η_i, since only absolutely rigid molecules can have a single relaxation time. The molecules of a real polymer are flexible. As a result of their flexibility, the relaxation processes in polymers can be described only with the aid of an extensive set or a continuous spectrum of relaxation times. However, when the maxima on the Q^{-1}–T curve are fairly narrow, they can be described satisfactorily also with a single average (or most probable) relaxation time. See also Refs. 6 and 179.

The introduction of a large number of elastic and viscous elements makes it possible to set up complex rheological models, which are consistent with many relaxation times and which provide the best approximation to various properties of a real polymer [2,5,177,180–183]. A one-dimensional complex rheological model characterised by n relaxation times with a zero equilibrium stress leads to $n-1$ maxima and an internal friction background curve. However, while it is still possible to attribute some definite physical significance to the elements of an Alfrey–Kobeko substance [177], this cannot be done for the elements of a complex rheological model§. Furthermore, a linear rheological model cannot be used to find the temperature variation of the square of the frequency, from which the temperature variation of the modulus of shear is estimated and therefore it cannot yield the correct temperature variation of internal friction, since the latter depends on the frequency.

A less formal approach, which is to some extent free of the above defects, whereby it is possible to solve from the very beginning the three-dimensional problem of the dissipation of the energy of elastic vibrations, is provided by the thermodynamics of irreversible processes.

b. Thermodynamic theory. The principle of the thermodynamic theory of relaxation phenomena in solids (isothermal case) was put forward by Finkel'shtein and Fastov [184]. Later this theory was extended to the case of non-isothermal deformations [185–189]. The following expression has been obtained for the stress tensor for a homogeneous isotropic body [188]:

$$\sigma_{ik}=K\cdot\varepsilon_{ll}\cdot\sigma_{ik}+2G\left(\varepsilon_{ik}-\frac{1}{3}\varepsilon_{ll}\cdot\delta_{ik}\right)+\eta_2/\tau_2\int_{-\infty}^{t}\dot{\varepsilon}_{ll}(t')\,e^{\frac{t'-t}{\tau_2}}dt'+\frac{2\eta_1}{\tau_1}\int_{-\infty}^{t}\left[\dot{\varepsilon}_{ik}(t')-\frac{1}{3}\dot{\varepsilon}_{ll}(t')\,\delta_{ik}\right]e^{\frac{t'-t}{\tau_1}}dt'-C\cdot\delta_{ik}\cdot C_v\int_{-\infty}^{t}\dot{T}(t')\,e^{\frac{t'-t}{\tau_3}}dt'-K\cdot\alpha\cdot\delta_{ik}\int_{-\infty}^{t}\dot{T}(t')\,e^{\frac{t'-t}{\tau_3}}dt' \quad . \qquad (33)$$

Here K is the isothermal modulus of all-sided compression, G the modulus of shear, η_2 the bulk viscosity, η_1 the coefficient of the shear relaxation of the viscosity, τ_2 and τ_1 are the relaxation times of the bulk and shear viscosities C is a constant, C_v the heat capacity per unit volume of the substance at constant volume, α the thermal conductivity, and τ_3 the thermal relaxation time defined by the expression

$$\tau_3\simeq\frac{C_l^2}{\varkappa'\omega^2} \quad , \qquad (34)$$

where $\varkappa'$ is the thermal diffusivity, C_l the velocity of longitudinal sound waves, and ω the angular frequency. The variation of τ_3 with frequency can be accounted for by the fact that an increase of the frequency entails an increase in the size of the regions between which the relaxation of the thermal flux takes place. For polymers (as for metals), temperature relaxation need be taken into account only in the hypersonic region [as is readily evident from Eqn. (34)]. In the region of sonic and ultrasonic frequencies $\omega\tau_3 \gg 1$.

For adiabatic deformation in this frequency range we have [188]

$$\sigma_{ik}=K^{ad}\cdot\varepsilon_{ll}\sigma_{ik}+2G\left(\varepsilon_{ik}-\frac{1}{3}\varepsilon_{ll}\cdot\delta_{ik}\right)+\eta_2^{ad}/\tau_2\cdot\delta_{ik}\int_{-\infty}^{t}\dot{\varepsilon}_{ll}(t')\,e^{\frac{t'-t}{\tau_2}}dt'+\frac{2\eta_1}{\tau_1}\int_{-\infty}^{t}\left[\varepsilon_{ik}(t')-\frac{1}{3}\varepsilon_{ll}(t')\,\delta_{ik}\right]e^{\frac{t'-t}{\tau_1}}dt', \qquad (35)$$

§ For a physical justification of rheological models, see Zelenev and Molotkov [181,182].

where

$$K^{ad} \equiv K + T_0\alpha^2\frac{K^2}{C_v} \qquad (36)$$

$$\eta_2^{ad} = \eta_2 + CT_0\alpha K\cdot\tau_2 \quad . \qquad (36')$$

We now use Eqn. (35) for the stress tensor to calculate the internal friction and the absorption coefficient of longitudinal and transverse elastic waves.

For a pure shear, for example low-amplitude torsional vibrations, $\epsilon_{ll} = 0$, and therefore

$$\sigma_{ik} = 2G\cdot\varepsilon_{ik} + \frac{2\eta_1}{\tau_1}\int_{-\infty}^{t}\varepsilon_{ik}(t')e^{\frac{t'-t}{\tau_1}}dt' \quad .$$

If the deformation is a periodic function of time, then

$$\varepsilon_{ik} = \varepsilon_{ik}^{(0)}\cdot e^{i\omega t} \quad ,$$

and the generalised Hooke's law is written in the following form:

$$\sigma_{ik} = G^*\cdot\varepsilon_{ik} \quad ,$$

where the complex modulus of shear is

$$G^* = G + \frac{i\omega\eta_1}{1+i\omega\tau_1}$$

or

$$G^* = G + \frac{(\omega\tau_1)^2}{1+\omega^2\tau_1^2}\cdot\frac{\eta_1}{\tau_1} + \frac{i\omega\tau_1}{1+\omega^2\tau_1^2}\cdot\frac{\eta_1}{\tau_1} \quad . \qquad (37)$$

The real component of the complex modulus is usually employed as the dynamic modulus, i.e.

$$G_\omega = G + \frac{(\omega\tau_1)^2}{1+\omega^2\tau_1^2}\cdot\frac{\eta_1}{\tau_1} \quad . \qquad (38)$$

We find from the last expression (if the temperature relaxation at hypersonic frequencies is disregarded, as was done above)

$$G_\infty = G + \eta_1/\tau_1 \quad G_0 = G \quad . \qquad (39)$$

Taking into account Eqns. (38) and (39), we obtain the modulus of shear which determines the degree of relaxation:

$$\Delta'_\omega = \frac{G_\infty - G_\omega}{G_0} = \frac{\Delta'_0}{1+\omega^2\tau_1^2} \quad , \qquad (40)$$

where

$$\Delta'_\omega = \frac{G_\infty - G_\omega}{G_0}$$

is the maximum defect of the shear modulus. Bearing in mind Eqn. (13), we find from Eqn. (37)

$$Q^{-1} = \frac{\Delta'_0\,\omega\tau_1}{1+\frac{G_\infty}{G_0}\omega^2\tau_1^2} \quad . \qquad (41)$$

Eqn. (41) is identical, to within the multiplier G_∞/G_0 in its denominator, with Eqn. (23) obtained above from model hypotheses for a standard linear body, if G_2 is identified with G_∞ and G_1 with the modulus G_0. Therefore all that has been said above about Eqn. (23) applies also to Eqn. (41). Furthermore, one may say that the moduli G_2 and G_1 now acquire a completely definite physical significance, defined by Eqn. (39).

Repeating the above reasoning and operations, we find for bulk compression

$$Q^{-1} = \frac{\Delta''_0\,\omega\,\tau_2}{1+\frac{K^{ad}}{K_0^{ad}}\omega^2\tau_2^2} \quad , \qquad (42)$$

where

$$\Delta'' = \frac{K_\infty^{ad} - K_0^{ad}}{K_0^{ad}} \quad . \qquad (43)$$

Evidently the nature of the variation of Q^{-1} with the parameter $\omega\tau$ does not change.

We now find the absorption coefficient α. Suppose that a transverse wave with frequency ω has the wave vector $\vec{k}$ ($k_x = k$, $k_y = 0$, $k_z = 0$), i.e. it is planar and is propagated along the x axis. It will be assumed that the wave is propagated in an infinite relaxing medium, described by the stress tensor (35). On substituting the non-zero components σ_{xy} and σ_{xz} is the equation of motion

$$\rho\frac{\partial^2\varepsilon_i}{\partial t^2} = \frac{\partial\sigma_{ik}}{\partial x_k} \quad , \qquad (44)$$

we find

$$\left.\begin{aligned} -\rho\omega^2A_y &= -k^2GA_y + i\frac{k^2A_y\,\omega\eta_1}{1-i\omega\tau_1} \\ -\rho\omega^2A_z &= -k^2GA_z + i\frac{k^2A_z\omega\eta_1}{1-i\omega\tau_1} \end{aligned}\right\} \quad . \qquad (45)$$

The square of the wave vector, obtained with the aid of Eqns. (45), is

$$k^2 = \frac{\rho\omega^2}{G}\frac{1+2\omega^2\tau_1^2+i\omega\tau_1}{1+4\omega^2\tau_1^2} \quad . \qquad (46)$$

In the limiting case of low frequencies ($\omega\tau_1 \ll 1$), i.e. when the period of the sound wave is large compared with the relaxation time, Eqn. (46) yields the following result:

$$k = \omega\sqrt{\rho/G} + i\frac{\omega^2\tau_1}{2}\sqrt{\rho/G} \quad , \qquad (47)$$

i.e. decay takes place, due to the presence of shear viscosity with the coefficient

$$\alpha'_t = \frac{\omega^2\tau_1}{2}\sqrt{\rho/G} \quad , \qquad (48)$$

which is proportional to the square of the frequency, in agreement with the familiar expression for the absorption coefficient[1]: $\alpha_t = \omega^2\eta_1/2\rho C_t^3$, provided that one puts $\eta_1 = G\tau_1$.

As was to be expected, the rate of propagation of the wave

$$C'_t = \frac{\omega}{\mathrm{Re}\,(k)} = \sqrt{G/\rho} \qquad (49)$$

is independent of frequency. In the opposite limiting case of high frequencies ($\omega\tau_1 \gg 1$), we find from Eqn. (46) for the absorption coefficient

$$\alpha''_t = \frac{1}{4\tau_1}\sqrt{\rho/2G} = \frac{1}{4\tau_1 C''_t} \quad , \qquad (50)$$

where the velocity of sound C''_t is

$$C''_t = \sqrt{\frac{2G}{\rho}} \quad . \qquad (51)$$

Both the absorption coefficient and the velocity of sound are to a first approximation independent of frequency at

high frequencies. In a more accurate expression the frequency dependence of both quantities is taken into account by the multiplier $1 - 1/8\omega^2\tau_1^2$, and the first expression in Eqn. (50) should be used for α_t''.

We shall now consider the propagation of a longitudinal sonic wave in an infinite relaxing medium. The only non-zero terms, the component of the displacement vector ϵ_x and the component of the deformation tensor $\epsilon_{xx} = ik\epsilon_x$, yield the following expression for the corresponding component of the stress tensor (33):

$$\sigma_{xx} = ik\varepsilon_x \cdot K + {}^4/_3 iG \cdot K \cdot \varepsilon_x + \frac{k\omega\eta_2^{ad}}{1-i\omega\tau_2}\varepsilon_x + {}^4/_3\frac{k\omega\eta_1}{1-i\omega\tau_1}\varepsilon_x + \frac{k\omega\chi}{1-i\omega\tau_3}\varepsilon_x, \quad (52)$$

where the conversion from the temperature function to the deformation function is performed with the aid of Eqn. (1), with χ defined thus:

$$\chi \equiv \tau_3\ \alpha^2 K T_0/C_v\,. \quad (53)$$

On substituting Eqn. (52) in the equation of motion (44), we find the square of the wave number:

$$k^2 = \rho\omega^2\left[K + {}^4/_3 G - i\left(\frac{\omega\eta_2^{ad}}{1-i\omega\tau_2} + {}^4/_3\frac{\omega\eta_1}{1-i\omega\tau_1} + \frac{\omega\chi}{1-i\omega\tau_3}\right)\right]. \quad (54)$$

At low frequencies $\omega\tau_1$ and $\omega\tau_2$ are both much less than 1 and, as pointed out earlier, $\omega\tau_3 \gg 1$. Bearing this in mind, we obtain the following expression for the wave number:

$$k \simeq \sqrt{\frac{\rho\omega^2}{K^{ad}+{}^4/_3 G}}\left(1 + \frac{i\omega}{2}\frac{{}^4/_3\eta_1 + \eta_2^{ad} + \chi/\omega^2\tau_3^2}{{}^4/_3 G + K^{ad}}\right). \quad (55)$$

The rate of propagation of longitudinal waves is found from the real part of this expression:

$$C_l' = \sqrt{\frac{K^{ad}+{}^4/_3 G}{\rho}}\,. \quad (56)$$

The imaginary part of Eqn. (55) yields the absorption coefficient for longitudinal waves:

$$\alpha_l' = \frac{\omega^2}{2}\frac{\sqrt{\rho}}{(K^{ad}+{}^4/_3 G)^{3/2}}\left({}^4/_3\eta_1 + \eta_2^{ad} + \frac{\chi}{\omega^2\tau_3^2}\right). \quad (57)$$

In the region of high but not hypersonic frequencies the condition $\omega\tau_1 \gg 1$ holds for all relaxation times. In this case we obtain from Eqn. (54)

$$k \simeq \frac{\omega\sqrt{\rho} + \frac{i\sqrt{\rho}}{2}(\eta_2^{ad}/\tau_2^2 + {}^4/_3\eta_1/\tau_1 + \chi/\tau_3^2)}{[K^{ad} + \eta_2^{ad}/\tau_2 + {}^4/_3(G + \eta_1/\tau_1)]^{1/2}}\,, \quad (58)$$

whence

$$C_l'' = \frac{1}{\sqrt{\rho}}[K^{ad} + \eta_2^{ad}/\tau_2 + {}^4/_3(G + \eta_1/\tau_1)]^{1/2} \quad (59)$$

and

$$\alpha_t'' = \frac{1}{2(C_l'')^3}\left(\eta_2^{ad}/\tau_2^2 + {}^4/_3\eta_1/\tau_2 + \frac{\alpha^2 K^2 T_0 \varkappa'}{C_v (C_l'')^2}\omega^2\right). \quad (60)$$

Thus the viscosity component of the absorption coefficient yields a constant term to a first approximation and the component due to the principal thermal conductivity yields a quadratic relation in frequency which does not differ from the corresponding additional term in the expression for α_l', as in both cases the condition $\omega\tau_3 \gg 1$ holds.

Summarising, one may say that at frequencies between 10^{-3} and 10^8 c/s, which we examined above (Figs. 4 and 5), the important factor is viscous relaxation (shear or bulk), which in the case of homogeneous isotropic solids is characterised by a single relaxation time. Consequently, according to Eqns. (41) and (42), a homogeneous isotropic body is characterised by a peak on the Q^{-1}–$\omega\tau$ curve and the absence of background. The Q^{-1} background can appear only if the body is inhomogeneous, i.e. has two (or more) relaxation times. An example of such a body is a mixture of amorphous polymers, partially crystalline polymers, cross-liked polymers, polymers containing impurities, etc.

A thermodynamic examination of the problem for the case of an inhomogeneous body with two relaxation times has been made by Shermergor and Meshkov[190]. The results of the theory have been examined using polycrystalline aluminium as an example. The form of the Q^{-1}–T curve is similar to that of the analogous curve which the present author obtained for poly(methyl methacrylate) on the basis of model hypotheses (Fig. 9*a*).

Under conditions of cyclic deformation, relaxation processes occur at different rates and at different sites of an inhomogeneous polymer and therefore its behaviour is described by a whole spectrum (discrete or continuous) of relaxation times. However, the spectrum of relaxation times in a solid polymer can be due not only to different rates of the relaxation process in different regions of the inhomogenous body but can also be caused by the presence of various relaxation mechanisms resulting from the flexibility of the molecules[2,7–11,75]. If several independent relaxation processes, each characterised by its own relaxation time τ_i, take place simultaneously in the polymer, the internal friction of the latter, for example in the presence of shear vibrations, is defined by the expression[8,9,75]

$$Q^{-1} = \sum_{i=1}^{n}\frac{\Delta_i^{(0)}\cdot\omega\tau_i}{1 + \left(\frac{G_\infty}{G_0}\right)_i(\omega\tau_i)^2}\,. \quad (61)$$

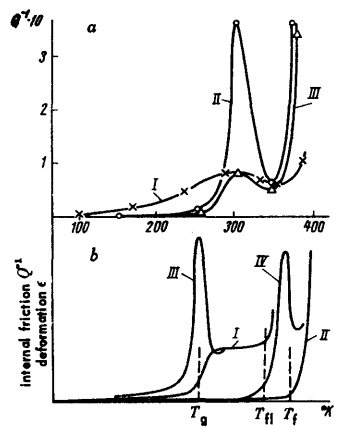


Fig. 9. *a*) Temperature dependence of the internal friction of poly(methyl methacrylate): I) experimental curve[18] for $\nu = 0.4$ c/s; II) and III) theoretical curves [II) $G_1/G_2 = 1$; III) $G_1/G_2 = 0.16$; $\tau_1 = 100\tau_2$; $\nu = 0.4$ c/s];
b) schematic representation of the temperature dependence of the deformation (curves I and II) and internal friction (curves III and IV) of polymers: I) and III) amorphous polymers; II) and IV) crystalline polymers.

Finally, for a continuous distribution of the relaxation constants, which frequently obtains in inhomogeneous materials, the internal friction is defined by the expression[9,75]

$$Q^{-1}=\int_{-\infty}^{+\infty}\frac{\psi(\tau)\,\omega\tau}{1+\left(\frac{G_\infty}{G_0}\right)_{cp}\omega^2\tau^2}\,d(\ln\tau)\ , \qquad (62)$$

where $\Psi(\tau)$ is an unknown distribution function difficult to determine experimentally. It can be found from the condition

$$(\Delta_0)_{cp}=\int_{-\infty}^{+\infty}\psi(\tau)\,d(\ln\tau)\ , \qquad (63)$$

where $(\Delta_0)_{av}$ is the average defect of the modulus found experimentally; this requires the inversion of the integral, which introduces a considerable inaccuracy into the final result.

It is evident from all that has been said above that the phenomenological theory describes fairly completely the frequency and temperature dependence of internal friction in homogeneous and inhomogeneous isotropic solids. The theory of internal friction in anisotropic materials has only just begun to be developed. For example, an expression has been obtained[191] for the stress tensor in a homogeneous anisotropic crystal and it has been shown that the stress tensor components σ_{ik} undergo relaxation to their equilibrium values $\bar{\sigma}_{ik}$, but the relaxation does not involve a simple exponential decay to the equilibrium value, as happens for an isotropic medium, but is determined by the entire set of relaxation times τ_{ik}. In the general case (crystals of the triclinic system) the relaxation of stresses in an isotropic medium is determined by six relaxation times τ_{ik} corresponding to six independent components of the stress tensor.

2. Molecular-Kinetic Description

In contrast to the phenomenological theory, in which the processes responsible for the dissipation of energy by the vibrating body are not considered in detail, the molecular-kinetic theory of internal friction should account for the principal features of the temperature and frequency dependence of the internal friction of solids (and the effect of various factors on the variation of Q^{-1} with T and ν) by a detailed analysis of the molecular processes which constitute its basis. However, the extremely complex structure of polymer molecules, the wide variety of possible types of polymers with the same chemical composition and molecular weight, and other distinctive features, compared with low-molecular compounds and metals, led to considerable difficulties in the development of a molecular-kinetic theory of internal friction.

The starting point of the molecular-kinetic description of the relaxation phenomena consists of hypotheses about the structure of the molecule and about the existence of polymers in various physical states—three amorphous and one crystalline. A clear idea about these physical states is obtained by plotting the deformation of the polymer (developing in a definite period at a given temperature and with specified stress) against temperature. For an amorphous substance, this plot[2], which has been called the thermomechanical curve, should have the form shown schematically by curve I in Fig. 9*b*. The two vertical dashed lines corresponding to temperatures T_g and T_{fl} divide curve I into three regions. The first (from 0°K to T_g) corresponds to the solid vitreous state of the substance, the second to the rubberlike state, and the third to the viscous state.

Since on cooling the polymers solidify (are converted into a glass) in the temperature range arbitrarily denoted by the temperature T_g, the latter has been called the glass point. At temperatures much lower than T_g the polymer molecules cannot change their shape and relative positions. The conformation of the molecular chain is "frozen". However, below T_g individual groups of atoms, which usually form part of the side-chain but can be linked also to the main chain, retain their mobility[192-195].

Near the temperature T_g and above it (but below T_{fl}) a change in the shape of the molecules is observed but not their mutual displacement, the latter being possible near the flow temperature T_{fl} and above it. The temperature range between T_g and T_{fl}, in which the polymer is a rubberlike material, is greater with higher molecular weights. We may note that the same amorphous polymer at the same temperature is capable of exhibiting the properties of vitreous, rubberlike, and viscous-fluid materials, depending on the rate of deformation. Therefore the temperatures T_g and T_{fl} are not physical constants but depend on the rate of deformation or the frequency of the changes in deformation. For example, at a low rate of deformation ($\nu \simeq 1$ c/s) $T_g \simeq 315$°K for poly(methyl methacrylate)[177]. The maximum in the internal friction of poly(methyl methacrylate) occurs at approximately the same temperature (Fig. 9*a*). This relation (schematically shown by curve III in Fig. 9*b*) is observed also for other amorphous polymers. This finding led to the hypothesis[104,107,117,119] that the high-temperature maximum (α-peak) in the internal friction of amorphous polymers is due to a change in the segmental mobility¶ of the molecule.

Similarly the first internal friction peak (or the sharp rise of the Q^{-1}–T curve near the melting point) of crystalline polymers (Fig. 4 and the schematic curve IV in Fig. 9*b*) is attributed[104,117,145] to the increase in the segmental mobility of the polymer molecule on fusion of the individual crystallites.

The nature of the remaining Q^{-1}–T peaks located below the first along the temperature axis may be extremely varied. For example, the second peak (the β-peak) on the Q^{-1}–T curve for poly(methyl methacrylate) is thought to be caused[152,158] by the rotation of the O=C–OCH_3 side-groups between positions of relative stability via an energy barrier, which reflects the steric hindrance due to the methyl groups attached to the same chain atoms. The study of copolymers of variable composition[158] shows that the elimination of the steric hindrance on replacing methacrylate by acrylate results in the disappearance of the loss mechanism; the replacement of the methyl ester group by any rigid and bulky ester group leads to the same effect, which can be explained by the hindrance to the rotation of these groups. On the other hand, the substitution of a more flexible ester group displaced the effect of this mechanism towards higher frequencies and raises the slope of the curves. Although the steric hindrance associated with the existence of two substituted chain atoms is probably responsible for the second peak on the curve for polymethacrylates, secondary loss mechanisms are also observed for polymers whose chains contain monosubstituted atoms

¶ In some cases it can consist of the sum of the contributions Q_α^{-1} and Q_β^{-1} due to the motion of side-groups[196].

but these are usually shown at higher frequencies or at lower temperatures and have smaller maxima. For example, the second peak on the Teflon and poly(vinyl chloride) curves is attributed to an amorphous phase [31]—to conformational changes in the amorphous phase relative to short polar chains [111]. The nature of such local motion is obscure.

The second peak (β-peak) on the polyethylene curve is associated either with the presence of an amorphous phase or with branching of the polyethylene molecules [107,117,126]. The third polyethylene peak (γ-peak) is attributed to the rearrangement of adjacent CH_2 groups [5].

The motion of methyl groups gives rise to the peak on the $Q^{-1}-T$ curve for polypropylene (at about 13°K). [197] Other cases are also known where the side-groups can be involved in motion at low temperatures, while the main skeleton of the molecules shows little mobility, which gives rise to peaks on the $Q^{-1}-T$ curve [104,192,198].

The cases examined above suggest that the observed maxima on the $Q^{-1}-T$ curves for solid polymers can be divided into two groups: the group of the so called principal maximum (α-peak in polyethylene and other substances) and the group of secondary maxima (β-, γ-, etc., peaks)†. The principal maximum is due to change in the mobility of the side-groups or individual small atomic groups of the main chain or the side-chains, which take part in thermal motion as independent elements. The position of the principal maximum is significantly influenced by the size of the side-groups. It has been shown [104] that, as the volume of the side-groups increases, the mobility of the main molecular chain falls and therefore at a constant frequency the principal maximum is displaced towards higher temperatures. At a constant temperature the maximum occurs at lower frequencies.

All these findings demonstrate that the temperature and frequency dependence of internal friction is indeed determined by the type of molecular motion. The type of molecular motion in turn depends on the composition and structure of the polymer and also on external factors (temperature, pressure, radiation, the medium surrounding the polymer, etc). Therefore, in their studies of the effect of composition, structure, and the factors indicated above on the nature of the temperature and frequency dependence of internal friction, various investigators [31,104,107,111,117,119,197,198] were able to arrive at the conclusions discussed above. However, even for a relatively simple molecular system such as polyethylene, it is impossible to make a unique interpretation of the results obtained. This also applies to other polymers which have been investigated [31,104,111]. This ambiguity can be eliminated to some extent by comparing the results of studies of mechanical and dielectric losses with those obtained by the nuclear magnetic resonance method.

V. COMPARISON OF THE RESULTS OF STUDIES ON MOLECULAR MOTION IN POLYMERS, OBTAINED BY DIFFERENT METHODS

1. Mechanical and Dielectric Losses

The first study in which mechanical properties were investigated in order to compare them with dielectric properties is that of Mikhailov and Kirilina [200] more than 25 years ago. They established that at a frequency of about 500 c/s the temperature maxima in Q^{-1} and tan φ_e for ebonite approximately coincide. A similar result was obtained by other investigators [175,201], for ebonite, rubber, and polyisobutylene. Comparison of these results, obtained at low deformation amplitudes, reveals a direct relation between mechanical and electric relaxation (see also Refs. 164, 202, 203).

Fig. 10 presents the results of a study of the temperature variation of the mechanical and dielectric losses for polyethylene [131] and poly(vinyl chloride) [204]. Evidently the $Q^{-1}-T$ and tan φ_e-T curves are of similar form. The form is similar but not identical, since even at the same frequencies (Fig. 10*b*) there is a perceptible difference in the positions of the maxima in Q^{-1} and tan φ_e along the temperature axis [164]. At a frequency of 2×10^6 c/s the tan φ_e maximum (not shown in Fig. 10*b*) is 27 deg below [204] the maximum in Q^{-1}. At a frequency of 3×10^5 c/s the temperature difference is 11 deg and at a frequency of 10^3 c/s only 8 deg. The difference for ebonite at 500 c/s is 3 deg. Such a slight difference suggests that at low deformation amplitudes (when we deal mainly with orientation relaxation), dielectric and mechanical relaxations have a common mechanism. The mechanical and dielectric losses are probably associated with the same form of thermal motion in the polymer [6]. This is shown by the agreement between the activation energies and between the relaxation times [175,200,201,204,205].

It is readily seen (Fig. 10*b*) that at high frequencies (above 10^4 c/s) the maximum in dielectric losses is higher than the maximum in mechanical losses, while at low frequencies (below 10^4 c/s) the opposite relation holds. The opposite variation of the heights of the maxima in Q^{-1} and tan φ_e with frequency is due to the fact that the maximum in dielectric losses is determined by the polarity of the vibrating side-groups or radicals while the maximum in mechanical losses is due to their mass.

The polarity of the side-groups determines not only the frequency but also the position of the maximum along the

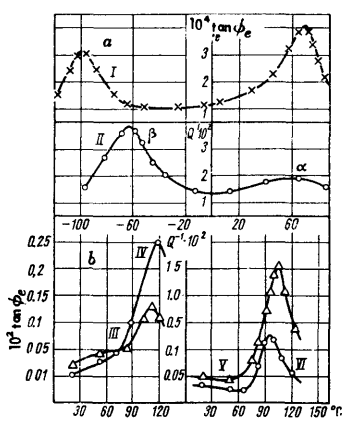


Fig. 10. Temperature dependence of the dielectric loss factor (curves I, IV, and VI) and internal friction (curves II, III, and V) of low-pressure polyethylene (*a*) and poly(vinyl chloride) (*b*):
I) $\nu \sim 5 \times 10^3$ c/s; II) $\nu = 2 \times 10^6$ c/s; III) and IV) $\nu = 3 \times 10^5$ c/s; V) and VI) $\nu = 10^3$ c/s.

† The same subdivision obtains also for rubberlike polymers [59,199].

temperature axis. With increasing dipole moments of the groups, the maximum in tan φ_e is displaced towards higher temperatures, which corresponds to a decrease of mobility with polarity [205]. An increase of the length of the racicals bound chemically to the main chain, while leaving the dipole moment virtually unaltered, causes a diplacement of the tan φ_e maximum towards lower temperatures [206].

Molecular relaxation observed by the dielectric loss method can be divided (like the mechanical relaxation examined above) into two main types: the relaxation of polar groups and the relaxation of the same polar groups together with sections of the main chain, i.e. the relaxation of segments [6,193,207,208]. This has been established for polymers with a wide variety of structures (linear and branched, polymers containing rings in the chain, partially crystallised polymers, and fully amorphous polymers [6,193,208,208]). The losses due to the first type of relaxation are called dipole-radical losses and those due to the second type are called dipole-elastic losses. Usually losses of the first type are observed in a definite temperature range corresponding to the vitreous state of the polymer, while losses of the second type occur above the glass point T_g‡. However, the dipole-radical losses are not a feature of the relaxation of the vitreous state of polymers but can be observed in the rubberlike state, if the period of application of the electric field is comparable with the relaxation time for losses of this type at the chosen temperature [193].

Thus dipole-radical losses reflect the molecular relaxation process which is due to the motion of polar side-groups, while the main chain remains stationary during a period comparable to the vibration period of the applied electric field. If the period of the applied field is sufficiently high, then at certain temperatures it is possible to observe the dipole-elastic losses caused by the displacement of segments together with the polar side-groups. In linear polymers a segment may consist of 2–4 methylene groups [209,210].

The characteristics of losses of the first and second types are also determined by the factors described above. For example, the positions of the temperature and frequency maxima in tan φ_e for dipole-radical losses are independent of the presence of low-molecular impurities [211], but the positions for dipole-elastic losses do depend considerably on such impurities. The relaxation times of the corresponding process decrease under these conditions. The cross-linking of the macromolecules, which impedes their motion and increases the relaxation time of the dipole-elastic losses, has the opposite effect [212,213]. According to the few data available in the literature, the extension of polymer specimens, leading to the orientation of the main chain, increases the relaxation time of dipole-elastic losses but does not affect the relaxation time of dipole-radical losses [214]. Losses of both kinds are considerably influenced by a change in the chemical structure of the monomer unit of the polymer chain. Both polar and non-polar groups, which can be attached either directly to the main chain or to a side-radical, have an effect. For example in a comparative study of mechanical and dielectric losses it has been shown [152] (see Table, entries 13 and 17) that the replacement of the methyl group in the α-position in poly(methyl methacrylate) by a polar group such as CCl, which occupies approximately the same volume, greatly inhibits the segmental motion of the macromolecules. The effects of polarity are enhanced when CH_3 groups are replaced by CN. Comparative study of the temperature variation of Q^{-1} and tan φ_e for low-pressure polyethylene (Fig. 9*a*) [56,131,193] permits the preliminary conclusion that the low temperature β-maximum is due to the "unfreezing" of segmental motion and the high-temperature α-maximum is due to the incipient fusion of poorly formed crystals. The nature of the maxima in Fig. 10*b*, which have been described in detail [204], is not sufficiently clear. The maximum in tan φ_e is due to dipole-elastic losses, i.e. the motion of segments. However, the number of molecular units in the segment remains unknown. The situation is the same as regards the explanation of the γ-maximum on the Q^{-1}–T curve for high-pressure polyethylene, the macromolecules of which are much more branched than for low-pressure polyethylene. The dielectric method does not yield the required information concerning the nature of this maximum. Some workers have simply attributed this maximum to the thermal motion of the parts of macromolecules constituting the amorphous regions of the polymer [215-217].

As mentioned above, the NMR method is very suitable for the investigation of molecular motion. Using this method, one of the first direct demonstrations of rotation of groups about bonds in polymer chains has been achieved [248]. Bearing this in mind, an attempt will be made to resolve, with the aid of the NMR method, the obscure problems concerning the nature of the Q^{-1} maxima, for example on the curves for high-pressure polyethylene and poly(vinyl chloride).

2. Mechanical Losses and Nuclear Magnetic Resonance

The application of nuclear magnetic resonance in the study of molecular motion is based on the observation of changes in the width of the absorption line, which becomes narrower with increasing rate of molecular motion [219-222]. Using nuclear magnetic resonance [223], it is possible to determine both the nature of the mobile group in the polymer and the mode and rate of its motion.

The first comparison of NMR data with results obtained by the internal friction method was made for rubber [224] soon after the discovery of NMR. Some investigators [225-229] have examined the relation between NMR data and the internal friction of polyisobutylene, poly(methyl methacrylate), poly(vinyl chloride), polyethylene, and other polymers. Much work has been done on the relation between mechanical, dielectric, and nuclear resonance absorption in many polymers (see, for example, Refs. 224, 225).

Fig. 11 presents the results of studies on the temperature variation of the internal friction [104,117,119,230] and the nuclear resonance absorption line width [231,232] of high-pressure polyethylene and poly(vinyl chloride) [104,231]. It is seen (Fig. 11*b*) that the absorption line width ΔH varies with temperature similarly to the shear modulus G. In the range 350–360°K, corresponding to the glass point of poly(vinyl chloride), a sharp change in G and ΔH and a distinct maximum in Q^{-1} are observed. The sharp change in ΔH takes place near the transition temperatures which are observed refractometrically [233,234] and by heat capacity measurements [235]. The correlation between the transitions observed by the NMR method and the conversion to the vitreous state observed by other methods makes it possible to relate these transitions to the onset of motion of main-chain segments [194]. However, the number of monomer units in a segment has not been determined with adequate precision. We may note

‡ Sometimes "degeneracy" of the dipole-elastic processes is observed at high temperatures [6].

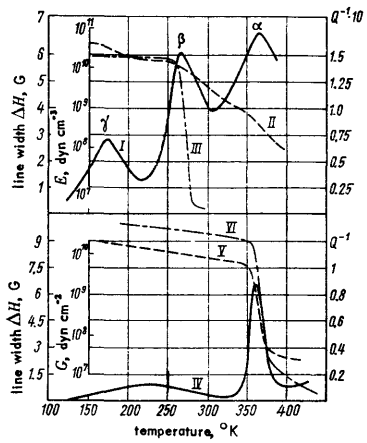


Fig. 11. Temperature dependence of the internal friction (curves I and IV), modulus of elasticity E (curve II), absorption line width (curves III and VI), and modulus of shear G (curve V) of high-pressure polyethylene (a) and poly(vinyl chloride) (b): I) and II) $\nu \sim 10^3$ c/s; IV) and V) $\nu \sim 1$ c/s.

that the agreement between the transition temperatures measured by the NMR and internal friction methods probably cannot be regarded as proof that the same molecular mechanism operates in both cases. It is difficult to imagine the existence of any close relation between molecular motions responsible for the Q^{-1} maximum, which occurs in poly(vinyl chloride) at 330°K and frequencies of the order of 1 c/s, and the motion responsible for the narrowing of the NMR line, which occurs in the same temperature range but at magnetic field frequencies of the order of 10^5 c/s §. Nevertheless the above correspondence between the transitions is observed very frequently [194,195] and therefore there is no reason to believe that this correlation is fortuitous.

A second broad maximum is clearly seen on the Q^{-1}–T curve for poly(vinyl chloride) at about 240°K. It also exists on the tan φ_e curve [237]. However, in the region of this temperature there are no significant changes in the NMR line width. This second Q^{-1} maximum is probably due to slight vibration of methylene groups in the main chain [194].

Fig. 11a shows that the appearance of the low-temperature internal friction maximum (γ-peak) is not accompanied by a sharp change in the width of the NMR resonance line. But the second maximum (β-peak) is satisfactorily correlated with the change in the width of the absorption line. The transition at about 265°K was first observed by the internal friction method [104,114,117,230], but its nature was elucidated by the NMR method. It is due to the rotation of CH_2 side-groups.

Comparison of the second moment of the absorption line with internal friction data suggests that the γ-peak is due to a reorientation of CH_2 groups [108,194]. It has also been suggested [238] that the γ-peak is due to a change in the nature of stereoregularity as a result of cooperative *trans–cis* transitions in polymeric chains. The high-temperature Q^{-1} maximum (α-peak) was discussed above. It is associated with the transition from the state where the main chain is "frozen" to one where its deformation is possible. The corresponding narrowing of the NMR line is almost imperceptible [194]. The study of molecular motion in polymers at these temperatures is best made with the aid of the internal friction and dielectric loss methods. The internal friction method is also preferable in the observation of secondary transitions in the amorphous regions, associated with the motion of individual atomic groups, for example low-temperature transitions in polymers [49,55,104,106,111,125,128,169-171,202].

§ For a more detailed discussion, see Ref. 236.

1. L.D. Landau and E.M. Lifshits, "Mekhanika Sploshnykh Sred" (The Mechanics of Continuous Media), Gostekhizdat, 1953.
2. V.A. Kargin and G.L. Slonimskii, "Kratkie Ocherki po Fiziko-Khimii Polimerov" (A Brief Outline of the Physical Chemistry of Polymers), Izd. Moskov. Gos. Univ., 1960.
3. V.D. Kuznetsov, "Fizika Tverdogo Tela" (Physics of the Solid State), Izd. Poligrafizdat, Tomsk, 1947, Vol. 4.
4. H. Kolsky, "Stress Waves in Solids" (Translated into Russian), GIITL, 1955.
5. J.D. Ferry, "Viscoelastic Properties of Polymers" (Translated into Russian), Inostr. Lit., Moscow, 1963.
6. G.P. Mikhailov and T.I. Borisova, Uspekhi Fiz. Nauk, 83, 63 (1964).
7. K. Mišek, Cesk. Casopis Fys., 2, 65 (1952).
8. A.S. Nowick, "Progress in Metal Physics", Pergamon Press, London, 1953, Vol. 4, p. 1.
9. V.S. Postnikov, Uspekhi Fiz. Nauk, 53, 87 (1954); 66, 43 (1958); Symposium, "Relaksatsionnye Yavleniya v Metallakh i Splavakh" (Relaxation Phenomena in Metals and Alloys), Metallurgizdat, 1963, p. 15.
10. G. Löschner, Technik (Berlin), 11, 299 (1956).
11. B.N. Finkel'shtein, Symposium, "Relaksatsionnye Yavleniya v Metallakh i Splavakh" (Relaxation Phenomena in Metals and Alloys), Metallurgizdat, 1960.
12. B. Hopkinson and G.T. Williams, Proc. Roy. Soc., A87, 502 (1912).
13. O. Föppl, J. Iron Steel Inst., 134, 393 (1956).
14. H.S. Sack, J. Motz, H.L. Raub, and R.N. Work, J. Appl. Phys., 18, 450 (1947).
15. T.S. Kê and M. Ross, Rev. Sci. Instr., 20, 795 (1949).
16. C. Boulanger, Rev. Met. (Paris), 46, 321 (1949).
17. G.M. Bartenev, V.E. Gul', and Yu.V. Zelenev, Vestnik TEI NIITEKhIM, 6, 28 (1962).
18. W. Weber, Pogg. Ann., 34, 29 (1837).
19. T.S. Kê, Phys. Rev., 71, 533 (1947).
20. V.S. Postnikov and Yu.V. Piguzov, Institut Tekhnikoekonomicheskoi Informatsii (ITEIN) Akad. Nauk SSSR, 1955, Pribory i Stendy, PS-55-448.
21. V.S. Postnikov, Plasticheskie Massy, No. 11, 60 (1960).
22. C. Ang and C. Wert, J. Appl. Phys., 25, 1061 (1954).
23. E. Jenckel, Kolloid Z., 136, 142 (1954).
24. Yu.V. Piguzov, Institut Tekhnikoekonomicheskoi Informatsii (ITEIN) Akad. Nauk SSSR, 1961, Pribory i Stendy, PS-61-87/13.
25. V.S. Postnikov and I.V. Zolokukhin, "Referaty Dokladov Nauchnoi Konferentsii Posvyashchennoi 30-Letiyu Voronezhskogo Tekhnologicheskogo Instituta" (Abstracts of Reports at the Scientific Conference Commemorating the 30th Anniversary of the Voronezh Technological Institute), Voronezhskoe Knizhnoe Izd., 1961.
26. L.E. Nielsen, Rev. Sci. Instr., 22, 690 (1951).
27. K. Schmieder and K. Wolf, Kolloid Z., 127, 65 (1952).

28. J.Heijboer, P.Dekking, and A.J.Staverman, "Proceedings of the Second International Congress on Rheology", 1954, p.123.
29. S.L.Blum, J.Amer.Ceram.Soc., 38, 205 (1955).
30. K.M.Sinnott, J.Appl.Phys., 29, 1433 (1958).
31. N.G.McCrum, J.Polymer Sci., 34, 355 (1959).
32. W.A.Hewett and F.E.Weir, J.Polymer Sci., A1, 1239 (1963).
33. B.Maxwell, Amer.Soc.Testing Mater., Spec.Tech.Publ., 215, 76 (1956).
34. K.H.Illers and H.Breuer, Kolloid Z., 176, 110 (1960).
35. G.I.Bartenev, Yu.V.Zelenev, and A.P.Aivazov, Uch.Zap. Moskov.Obl.Ped.Inst., 147, Obshchaya Fizika, No.8, 129 (1965).
36. K.H.Illers, Rheol.Acta, 3, 185 (1964).
37. H.C.Rorden and A.Grieco, J.Appl.Phys., 22, 842 (1951).
38. Yu.S.Lazurkin, Zhur.Tekh.Fiz., 9, 1261 (1939).
39. G.Sawaragi and H.Tokumaru, "Proceedings of the Fourth Japanese National Congress on Applied Mechanics, 1954", 1955, p.399.
40. A.Q.Hutton and A.W.Nolle, J.Appl.Phys., 25, 350 (1954).
41. D.Bancroft and R.B.Jacobs, Rev.Sci.Instr., 9, 279 (1938).
42. G.G.Parfitt, Nature, 164, 489 (1949).
43. P.G.Bordoni, Nuovo cim., 4, 177 (1947).
44. I.Barducci and G.Pasqualini, Nuovo cim., 5, 416 (1948).
45. P.G.Bordoni and M.Nuovo, Ricerca sci., 24, 560 (1954).
46. K.Mišek, Cesk.Casopis Fys., 4, 67 (1954).
47. R.Cabarat, Congr.Internat.Aluminium, Paris, 1, 271 (1954).
48. L.Verdini, Nuovo cim., 14, 648 (1957).
49. M.Baccaredda and E.Butta, Chimie e Industria, 40, 6 (1958).
50. S.L.Quimby, Phys.Rev., 25, 558 (1925).
51. S.Siegel and S.L.Quimby, Phys.Rev., 49, 663 (1936).
52. J.Zacharias, Phys.Rev., 44, 116 (1933).
53. M.Kornfel'd, Zhur.Eksper.Teor.Fiz., 13, 116 (1943).
54. I.G.Mikhailov and V.A.Solov'ev, Akust.Zhur., 1, 343 (1955).
55. Y.Wada and K.Yamamoto, J.Phys.Soc.Japan, 11, 887 (1956).
56. I.G.Mikhailov and V.A.Solov'ev, Akust.Zhur., 3, 65 (1957).
57. C.A.Wert, J.Appl.Phys., 20, 29 (1949).
58. D.W.Robinson, J.Sci.Instr., 32, 2 (1955).
59. Yu.V.Zelenev, G.M.Bartenev, and G.K.Demishev, Zavod. Lab., 7, 868 (1963).
60. L.E.Nielsen, Amer.Soc.Testing Mater., Spec.Tech.Publ., 165, 48 (1950).
61. S.Newman, J.Polymer Sci., 30, 333 (1959).
62. A.W.Nolle, J.Appl.Phys., 19, 753 (1948).
63. C.S.Duckwald, Mod.Plastics, 33, 143 (1956).
64. S.Srella, Amer.Soc.Testing Mater., Spec.Techn.Publ., 214, 57 (1956).
65. E.Ptacnik, Acta Phys.Austriaca, 8, 28 (1953).
66. C.Zener and R.H.Randall, Trans.AIME, 137, 41 (1949).
67. T.S.Kê, J.Appl.Phys., 20, 1226 (1949).
68. E.Fukada, J.Phys.Soc.Japan, 5, 321 (1950).
69. R.L.Wegel and H.Waltner, Physica, 6, 141 (1935).
70. F.Forster, Z.Metallk., 29, 109 (1937).
71. D.E.Kline, J.Polymer Sci., 22, 449 (1956).
72. N.M.Borovitskaya, Dokl.Akad.Nauk SSSR, 109, 923 (1956); Zhur.Tekh.Fiz., 28, 2689 (1958).
73. G.S.Gorelik, Dokl.Akad.Nauk SSSR, 83, 549 (1952).
74. C.Zener, J.Appl.Phys., 18, 1022 (1947).
75. C.Zener, Symposium, "Uprugost' i Neuprugost' Metallov" (Elasticity and Anelasticity of Metals) (Translated into Russian), Inostr.Lit., Moscow, 1964.
76. S.I.Meshkov, V.S.Postnikov, and T.D.Shermergor, Izv. Akad.Nauk SSSR, Mekhan.i Mashinostr., No.3, 104 (1964).
77. S.I.Meshkov, T.D.Shermergor, and V.S.Postnikov, Symposium, "Rasseyanie Energii pri Kolebaniyakh Uprugikh Sistem" (Energy Dissipation in the Vibrations of Elastic Systems), Izd.Akad.Nauk SSSR, 1963, Vol.4, p.357.
78. G.M.Bartenev and Yu.V.Zelenev, Kauchuk i Rezina, 8, 18 (1960).
79. J.W.Ballow and J.Silverman, J.Acoust.Soc.Amer., 16, 113 (1944).
80. A.W.Nolle, J.Acoust.Soc.Amer., 19, 194 (1947).
81. V.A.Kuznetsov, Kauchuk i Rezina, 3, 20 (1961).
82. K.W.Heller and H.Kolsky, Proc.Phys.Soc., B62, 111 (1949).
83. K.W.Heller, Proc.Phys.Soc., 62, 701 (1949).
84. J.W.Ballow and J.C.Smith, J.Appl.Phys., 20, 481 (1949).
85. V.P.Volodin, Pribory i Tekh.Eksper., 3, 142 (1961).
86. W.P.Mason and H.J.McSkimin, J.Acoust.Soc.Amer., 19, 464 (1947); J.Appl.Phys., 19, 940 (1948).
87. W.J.Roth, J.Appl.Phys., 19, 901 (1948).
88. D.G.Ivey, B.A.Mpowka, and E.Cuth, J.Appl.Phys., 20, 486 (1949).
89. P.Hatfield, Brit.J.Appl.Phys., 1, 252 (1950).
90. T.A.Litovitz, T.Lyon, and L.Peselnick, J.Acoust.Soc. Amer., 26, 566 (1954).
91. S.P.Kabin, Zhur.Tekh.Fiz., 26, 2628 (1956).
92. I.V.Bushuev, Symposium, "Primenenie Ul'trazvuka k Issledovaniyu Veshchestv" (Application of Ultrasonics in the Study of Materials), Moskov.Obl.Ped.Inst., No.5, 101 (1957).
93. M.Auberger and J.S.Rinehart, J.Appl.Phys., 32, 219 (1961).
94. L.G.Merkulov and L.A.Yakovlev, Akust.Zhur., 5, 374 (1959).
95. E.H.Jacobsen, Phys.Rev.Letters, 2, 249 (1959).
96. H.E.Bommel and K.Drausfeld, Phys.Rev.Letters, 2, 298 (1959); Phys.Rev., 117, 1245 (1960).
97. K.N.Baranskii, Dokl.Akad.Nauk SSSR, 114, 517 (1957).
98. M.V.Vol'kenshtein, "Molekulyarnaya Optika" (Molecular Optics), Inostr.Lit., Moscow–Leningrad, 1951.
99. G.N.Ramachandran and W.A.Wooster, Acta Cryst., 4, 335, 431 (1951).
100. E.Prince and W.A.Wooster, Acta Cryst., 6, 450 (1953).
101. W.P.Binnie and A.M.Liebsehutz, "Proceedings of the Conference on Nuclear Engineering", E-26, 1953.
102. S.C.Prasad and W.A.Wooster, Acta Cryst., 8, 361, 507, 614, 682 (1955).
103. S.Annaka, J.Phys.Soc.Japan, 11, 937 (1956).
104. K.Schmieder and K.Wolf, Kolloid Z., 134, 149 (1953).
105. L.E.Nielsen, J.Appl.Phys., 25, 1209 (1954).
106. K.H.Hellweye, R.Kaiser, and K.Kuphal, Kolloid Z., 157, 27 (1958).
107. L.E.Nielsen, Soc.Plastics Engrs.J., 16, 525 (1960).
108. H.A.Flocke, Zolloid Z., 180, 118 (1962).
109. K.H.Illers, Rheol.Acta, 3, 202 (1964).
110. J.A.Sauer and D.E.Kline, J.Polymer Sci., 18, 491 (1955).
111. J.A.Sauer and D.E.Kline, Actes IX Congr.Internat. Mecan.appl., Bruxelles, 5, 368 (1957).
112. R.Kubo and K.Tomito, J.Phys.Soc.Japan, 9, 888 (1954); 12, 1082 (1957).
113. J.A.Sauer, N.Fuschillo, C.W.Deely, and A.E.Woodward, "Low Temperature Physics and Chemistry", Madison, 1958, p.608.
114. C.W.Deely, J.A.Sauer, and A.A.Woodward, J.Appl. Phys., 29, 1415 (1958).
115. L.J.Merrill, J.A.Sauer, and A.E.Woodward, Polymer, 1, 351 (1960).
116. W.Pechhold, S.Blasenbrey, and S.Woerner, Kolloid Z., 189, 13 (1963).
117. D.E.Kline, J.A.Sauer, and A.E.Woodward, J.Polymer Sci., 22, 455 (1956).
118. N.Fuschillo and J.A.Sauer, J.Appl.Phys., 28, 1073 (1957).
119. W.G.Oakes and D.W.Robinson, J.Polymer Sci., 14, 505 (1954).

120. E.R. Fitzgerald, J.Chem.Phys., 27, 1180 (1957).
121. E.R. Fitzgerald and M.T. Watson, J.Acoust.Soc.Amer., 32, 584 (1960).
122. E. Butta, J.Polymer Sci., 25, 239 (1957).
123. E. Butta and A.Charlesby, J.Polymer Sci., 35, 119 (1958).
124. M. Baccaredda and E. Butta, J.Polymer Sci., 22, 217 (1956).
125. K. Yamamoto and Y. Wada, J.Phys.Soc.Japan, 12, 374 (1957).
126. V.A. Solov'ev, Vestnik Leningrad.Univ., 4, 30 (1958).
127. Y. Wada and H. Hirose, J.Appl.Phys.(Japan), 27, 652 (1958).
128. W.P. Mason and H.J. McSkimin, Bell System Tech.J., 31, 122 (1952).
129. S.P. Kabin, Vysokomol.Soed., 1, 829 (1959).
130. H.J. McSkimin, J.Acoust.Soc.Amer., 23, 429 (1951).
131. G.P. Mikhailov, S.P. Kabin, and T.A. Krylova, Zhur. Tekh.Fiz., 27, 2050 (1957).
132. N.G. McCrum, J.Polymer Sci., 54, 561 (1961).
133. B.E. Read and G. Williams, Polymer, 2, 239 (1961).
134. L. Bohn, Kolloid Z., 201, 20 (1965).
135. A.E. Woodward, J.A. Sauer, and R.A. Wall, J.Polymer Sci., 50, 117 (1961).
136. J.A. Sauer, R.A. Wall, N. Fuschillo, and A.E. Woodward, J.Appl.Phys., 29, 1385 (1958).
137. B.I. Sazhin, V.S. Skurikhina, and Yu.A. Il'in, Vysokomol. Soed., 1, 1383 (1959).
138. E.R. Fitzgerald and J.D. Ferry, J.Colloid Sci., 8, 1 (1953).
139. E.R. Fitzgerald, L.D. Grandine, and J.D. Ferry, J.Appl. Phys., 24, 650 (1955).
140. S. Wintergerst, Kunststoffe, 50, 277 (1960).
141. Y.J. Maeda, J.Polymer Sci., 18, 87 (1955).
142. H. Thurn, Z.angew.Phys., 7, 44 (1955).
143. N. Tokita and H. Kowai, J.Phys.Soc.Japan, 6, 367 (1951).
144. K.H. Illers and E. Jenckel, J.Polymer Sci., 46, 528 (1959).
145. K.H. Illers and E. Jenckel, Kolloid Z., 165, 73 (1959).
146. G. Adam, Kolloid Z., 172, 132 (1960).
147. C. Schuerch, J.Polymer Sci., 35, 351 (1959).
148. R.A. Wall, J.A. Sauer, and A.E. Woodward, J.Polymer Sci., 35, 281 (1959).
149. S.G. Turly, J.Polymer Sci., C1, 101 (1963).
150. M. Baccaredda, E. Butta, and V. Frosini, J.Polymer Sci., B3, 189 (1965).
151. J. Heijboer, Makromol.Chem., 35A, 87 (1960).
152. K. Deutsch, E.A.W. Hoff, and W. Reddish, J.Polymer Sci., 13, 565 (1954).
153. B. Maxwell, J.Polymer Sci., 20, 551 (1956).
154. P.G. Bordoni, M. Nuovo, and L. Verdini, Nuovo cim., 20, 667 (1961).
155. A.K. Schulz, J.Chim.phys., 53, 93 (1956).
156. W.G. Gall and N.G. McCrum, J.Polymer Sci., 50, 489 (1961).
157. K.M. Sinnott, J.Polymer Sci., 35, 273 (1959).
158. J. Heijboer, Kolloid Z., 148, 36 (1956).
159. E. Fukada, J.Phys.Soc.Japan, 6, 254 (1951).
160. E. Fukada, J.Phys.Soc.Japan, 9, 786 (1954).
161. Y. Wada, J.Appl.Phys.(Japan), 24, 159 (1955).
162. P. Hatfield, Nature, 174, 1186 (1954).
163. K.H. Illers and E. Jenckel, Kolloid Z., 165, 84 (1959).
164. H. Turn and K. Wolf, Kolloid Z., 148, 16 (1956).
165. K.H. Illers and E. Jenckel, Kolloid Z., 160, 87 (1958).
166. N.G. McCrum, Makromol.Chem., 34, 50 (1959).
167. F.P. Reding, J.A. Faucher, and R.D. Whitman, J.Polymer Sci., 54, 56 (1961).
168. K.H. Illers and R. Kosfeld, Makromol.Chem., 42, 44 (1960).
169. K.D. Lawson, J.A. Sauer, and A.E. Woodward, J.Appl. Phys., 34, 2492 (1965).
170. E.A. Woodward, J.M. Crissman, and J.A. Sauer, J.Polymer Sci., 44, 23 (1960).
171. C.W. Deely, A.E. Woodward, and J.A. Sauer, J.Appl. Phys., 28, 1124 (1957).
172. H. Jacobs and E. Jenckel, Makromol.Chem., 43, 132 (1961).
173. J. Herbert and E. Jenckel, Makromol.Chem., 47, 72 (1961).
174. H.A. Flocke, Kolloid Z., 188, 114 (1963).
175. L.T. Ponomarev, Zhur.Tekh.Fiz., 10, 588 (1940).
176. P. Hatfield, Research, 9, 388 (1956).
177. T. Alfrey, "Mechanical Behaviour of Polymers" (Translated into Russian), Inostr.Lit., Moscow, 1952.
178. A.W. Nolle, P.W. Sieck, and S.C. Mowry, J.Acoust.Soc. Amer., 20, 432 (1948).
179. G.M. Bartenev and Yu.V. Zelenev, Vysokomol.Soed., 4, 66 (1962).
180. V.L. Akulov, Yu.V. Zelenev, and I.G. Novikova, Izv.Vys. Ucheb.Zaved., Tekhnol.Legkoi Prom., No.2, 154 (1961).
181. Yu.V. Zelenev, Vysokomol.Soed., 4, 1486 (1962).
182. Yu.V. Zelenev and A.G. Molotkov, Uch.Zap.Moskov.Obl. Ped.Inst., 147, Obshchaya Fizika, No.8, 151 (1965).
183. M. Reiner, "Rheology" (Translated into Russian), Izd. Nauka, Moscow, 1965.
184. B.N. Finkel'shtein and N.S. Fastov, Dokl.Akad.Nauk SSSR, 71, 875 (1950).
185. N.S. Fastov, Probl.Metalloved.i Fiz.Metal., Inst.Metalloved.i Fiz.Metal., Sbornik Trudov, 5, 550 (1958).
186. T.D. Shermergor, Zhur.Tekh.Fiz., 28, 647 (1958).
187. N.S. Fastov, Dokl.Akad.Nauk SSSR, 130, 541 (1960).
188. T.D. Shermergor and V.S. Postnikov, Symposium, "Relaksatsionnye Yavleniya v Metallakh i Splavakh" (Relaxation Phenomena in Metals and Alloys), Metallurgizdat, 1963, p.27.
189. N.S. Fastov, Fiz.Metallov i Metalloved., 12, 431 (1961).
190. T.D. Shermergor and S.I. Meshkov, see Ref.188, p.46.
191. T.D. Shermergor, Izv.Vys.Ucheb.Zaved., Ser.Fiz., 1, 78 (1958).
192. E.A.W. Hoff, D.W. Robinson, and A.H. Wilbourn, J.Polymer Sci., 18, 161 (1955).
193. G.P. Mikhailov and T.I. Borisova, Uspekhi Khim., 30, 895 (1961) [Russ.Chem.Rev., 386 (1961)].
194. J.A. Sauer and A.E. Woodward, Rev.Mod.Phys., 32, 88 (1960).
195. A.E. Woodward, Trans.N.Y.Acad.Sci., 24, 250 (1962).
196. W.C. Child and J.D. Ferry, J.Colloid.Sci., 12, 327 (1957).
197. L.T. Muns, N.G. McCrum, and F.C. McGraw, Soc. Plastics Engrs.J., 15, 368 (1959).
198. L.E. Nielsen, J.Amer.Chem.Soc., 75, 1435 (1953).
199. G.M. Bartenev and Yu.V. Zelenev, Dokl.Akad.Nauk SSSR, 154, 661 (1964).
200. G.P. Mikhailov and V.N. Kirilina, Zhur.Tekh.Fiz., 8, 1723 (1937).
201. E.I. Chuikin, Zhur.Tekh.Fiz., 25, 595 (1955).
202. Y. Ishida, H. Ito, and M. Takayanagi, J.Polymer Sci., B3, 87 (1965).
203. H.G. Kilian, H. Linz, F.H. Muller, and H. Ringsdort, Kolloid.Z., 202, 108 (1965).
204. J. Koppelman, Kolloid Z., 189, 1 (1963).
205. W. Zeil, Angew.Chem., 8, 271 (1962).
206. B.L. Funt and T. Sutherland, Canad.J.Chem., 30, 940 (1952); T. Sutherland and B.L. Funt, J.Polymer Sci., 11, 177 (1953).
207. P.P. Kobeko, "Amorfnye Veshchestva" (Amorphous Substances), Izd.Akad.Nauk SSSR, 1952.
208. M. Matsuo, G. Ishida, K. Gamafuni, M. Tokayanagi, and F. Irie, Kolloid Z., 201, 89 (1965).
209. A.H. Willbourn, Trans.Faraday Soc., 54, 717 (1958).

210. W. Pechhold, S. Blasenbrey, and S. Woerner, Kolloid Z., 189, 14 (1963).
211. G. P. Mikhailov, T. I. Borisova, and D. A. Dmitrichenko, Zhur. Tekh. Fiz., 26, 1924 (1956).
212. K. A. Andriyanov and G. E. Golubkov, Zhur. Tekh. Fiz., 26, 1963 (1956).
213. P. F. Veselovskii, Izv. Tomsk. Politekh. Inst., 91, 399 (1956).
214. G. P. Mikhailov, Zhur. Tekh. Fiz., 21, 11 (1951).
215. G. P. Mikhailov and T. I. Borisova, Zhur. Tekh. Fiz., 23, 2160 (1953).
216. G. P. Mikhailov, A. I. Lobanov, and B. I. Sanin, Zhur. Tekh. Fiz., 24, 1553 (1954).
217. G. P. Mikhailov, S. P. Kabin, and B. I. Sanin, Zhur. Tekh. Fiz., 25, 590 (1955).
218. L. V. Hoeroyd, B. A. Mrowca, and E. Guth, Phys. Rev., 79, 1026 (1950).
219. E. R. Andrew, "Nuclear Magnetic Resonance" (Translated into Russian), Inostr. Lit., Moscow, 1957.
220. W. P. Slichter, Symposium, "Fizika Polimerov" (The Physics of Polymers) (Translated into Russian), Inostr. Lit., Moscow, 1960, p. 171.
221. W. Low, "Paramagnetic Resonance in Solids" (Translated into Russian), Inostr. Lit., Moscow, 1962.
222. I. Ya. Slonim, Uspekhi Khim., 31, 609 (1962) [Russ. Chem. Rev., 308 (1962)].
223. J. G. Powles, Arch. Sci. (Geneva), 9, 182 (1956).
224. N. L. Alpert, Phys. Rev., 72, 637 (1947).
225. N. Fuschillo and J. A. Sauer, J. Appl. Phys., 28, 1073 (1957).
226. R. C. Rempel, H. E. Waver, R. H. Sands, and R. L. Miller, J. Appl. Phys., 28, 1082 (1957).
227. M. J. Herring and J. A. S. Smith, J. Chem. Soc., 273 (1900).
228. K. H. Illers and R. Kosfeld, Makromol. Chem., 42, 44 (1960).
229. A. E. Woodward and J. A. Sauer, J. Polymer Sci., C3, No. 8, 137 (1965).
230. C. W. Deely, D. E. Kline, J. A. Sauer, and A. E. Woodward, J. Polymer Sci., 28, 109 (1958).
231. A. Odajima, J. Sohma, and M. Koike, J. Phys. Soc. Japan, 12, 272 (1957).
232. N. Fuschillo and J. A. Sauer, Bull. Amer. Phys. Soc., 4, 187 (1959).
233. R. H. Wiley and G. M. Brauer, J. Polymer Sci., 3, 544 (1948).
234. W. Knappe and A. Schulz, Kunststoffe, 41, 321 (1951).
235. S. Alford and M. Dole, J. Amer. Chem. Soc., 77, 4774 (1955).
236. V. S. Postnikov (Editor), "Relaksatsionnye Yavleniya v Metallakh i Splavakh, Trudy 3-i Vsesoyuznoi Konferentsii" (Relaxation Phenomena in Metals and Alloys, Proceedings of the Third All-Union Conference), Metallurgizdat, 1963.
237. R. M. Fuoss, J. Amer. Chem. Soc., 63, 369 (1941).
238. L. Bohn, Rheol. Acta, 3, 212 (1964).

Voronezh Polytechnic Institute