Journal of Thermal Analysis, Vol. 38 (1992) 1047-1060

PHONONS IN SOLID POLYMERS

Yu. F. Zabashta

SHEVCHENKO STATE UNIVERSITY, KIEV, THE UKRAINE

On the basis of a qualitative theory the phonon spectrum is obtained. Two- and three phonon interactions are examined. The theoretical results are applied for the analysis of the experimental data: for heat conduction, dielectric relaxation, heat capacity.

Keywords: dielectric relaxation, heat capacity, heat conduction, phonons, pholymers

Introduction

This article addresses the problem of thermal vibrations in solid polymers.

It is known that in this case the model of force constants – the ensemble of material points connected by elastic bonds – is applied. According to this model the particle displacement $U(\vec{x},t)$ is written as

$$\vec{U}(\vec{x},t) = \sum_j \vec{w}_j(\vec{x})\cdot\exp(i\,\omega_j\,t), \tag{1}$$

where $\vec{x}$ is the radius-vector, which determines the equilibrium position of the particle; t is time, ω_j is the natural frequency.

The function $\vec{w}_j(\vec{x})\cdot\exp(i\omega_j t)$ is called either a normal oscillation or an elementary oscillation excitation.

The term 'phonon' was applied at first to determine the normal oscillations in the ideal lattice, where these excitations have the form

$$\vec{w}(\vec{x}) \sim \exp(i\vec{k}\vec{x}), \tag{2}$$

where $\vec{k}$ is the wave vector.

Some authors [1] keep this name only for these excitations, which have the form (2). Others [2] understand this term in a broad sense and apply this notion for the vibration quantum $\hbar\omega_j$ independently of the form of excitation. In this case some important features of phonon formalism hold, for example, a notion about the representative particle number.

It is simple to prove it: the Hamilton operator $\hat{H}$ of any system of material points connected by elastic bonds have the form

$$\hat{H} = \hbar\Omega : (\hat{A}^{+}\hat{A} + 1/2), \tag{3}$$

where $\Omega \equiv \{\omega_j \delta_{jx}\}$ is the matrix of natural frequencies, $\hat{A}^{+} \equiv \{\hat{a}_j^{+}\}$, $\hat{A} \equiv \{\hat{a}_j\}$ are the $3N$–dimensional vectors, N – the number of particles in the system, $\hat{a}_j^{+}$ and $\hat{a}_j$ are the creation and annihilation operators to which the introduction of the representative particle numbers is connected. In this article the term 'phonon' is applied in a broad sense.

Phonon localization and phonon spectrum

It is known that the main peculiarity of solid polymers is their 'terrible' disorder. There is not the least chance to calculate strictly the frequencies and the forms of the normal oscillations. Therefore, the author applies the methods of the qualitative theory [3].

In the work [4] the thermal oscillations in amorphous polymers are considered. The segment length L is chosen with the characteristic structure scale. Let κ^{-1} be the characteristic displacement scale (i.e., the wave length for the flat wave). Let us call phonons of a large scale and of a middle scale those phonons that satisfy the conditions, resp.

$$\kappa L << 1 \tag{4}$$

$$\kappa L \leq 1 \tag{5}$$

Conditions (4), (5) allow to present the amorphous polymer as the random heterogeneous continuum. In this continuum the oscillations are dissipated and because of the dissipation they are extinguished. Let us define the extinction length by l. The value of l depends on frequency. Because of the extinction the phonon is localized in the region with size l. Therefore, the phonons are divided into localized and unlocalized ones, that satisfy the conditions

$$l < z \tag{6}$$

$$l > z \tag{7}$$

where z is the size of the system.

Due to the localization the excitation is distributed over the totality of spherical (average) packages disposed at a distance l (approximately) one after another. Such package contains [4]

$$\mu \sim (L\,\omega/v)^2$$

of the oscillations states (v is the acoustic velocity). Since the number of packages $\sim (\frac{z}{l})^3$, the total number of the oscillation states $\sim \mu\,(\frac{z}{l})^3$.

If we introduce the condition

$$n\,l = z \tag{8}$$

where n is the integer, we get the frequency spectrum

$$g(\omega) \sim (\frac{z\,\omega}{v})^2 \cdot z^2\, l^{-1} \cdot \frac{\mathrm{d}l^{-1}}{\mathrm{d}\omega} \tag{9}$$

The dependence $l(\omega)$ is known only for the oscillation of a large scale: it is the Rayleigh dissipation, when $l(\omega) \sim \omega^{-4}$. Let us determine the general form of the function $l(\omega)$.

The law of energy conservation suggests

$$\lim_{\omega\to\infty} l^{-1}(\omega) = \mathrm{const} \tag{10}$$

The sole linear size of the model is L. Therefore

$$\lim_{\omega\to\infty} l^{-1}(\omega) \sim L^{-1} \tag{11}$$

Using conditions (10) and (11), we get

$$\lim_{\omega\to\infty} \frac{\mathrm{d}l^{-1}}{\mathrm{d}\omega} = 0 \tag{12}$$

The function $l(\omega)$ is even. Therefore

$$\frac{\mathrm{d}l^{-1}}{\mathrm{d}\omega}(0) = 0 \tag{13}$$

Since $l(\omega) > 0$ according to Eqs (12) and (13) the function $\mathrm{d}l^{-1}/\mathrm{d}\omega$ has the maximum near the frequency $\Omega_a \sim v/L$. In accordance with formula (9), the spectrum $g(\omega)$ should have the maximum near this frequency.

The structure-crystalline polymers can be characterized by two linear scales: L_K is the size of the separate crystallite and L is the segment length (for the amorphous regions). The spectrum $g(\omega)$ of these polymers should have two maxima: near the frequencies $\Omega_a \sim v/L$ and $\Omega_k \sim v/L_k$ accordingly.

Phonon heat capacity

It is known that for the temperature $T < T_g$ (T_g is the glass transition temperature) the heat capacity C is given by

$$C = K_B \int g(\omega) E\left(\frac{\hbar\omega}{K_B T}\right) d\omega, \tag{14}$$

where K_B is the Boltzmann's constant. $\hbar = h/2\pi$. h is the Plank's constant,

$$E\left(\frac{\hbar\omega}{K_B T}\right) = \left(\frac{\hbar\omega}{K_B T}\right)^2 \cdot \frac{\exp(-\hbar\omega/K_B T)}{[1+\exp(-\hbar\omega/K_B T)]^2}$$

is the Einstein's function.

Due to the term, $\exp(-\frac{\hbar\omega}{K_B T})$ in formula (14), the spectrum $g(\omega)$ in formula (14) is limited to the oscillation of the large and middle scales.

Let us determine the spectrum $g(\omega)$ from the dependence $C(T)$ approximately. Let us differentiate (14)

$$\frac{dc}{dT} = K_b \int g(\omega) \cdot \frac{\partial E}{\partial T} d\omega. \tag{15}$$

Function $E(z)$ has the appearance of the gently sloping step with the inflection point at $z \approx 3$. This allows to write

$$\frac{\partial E}{\partial T} = \delta\left(\frac{\hbar\omega}{K_B T} - 3\right)\frac{\hbar\omega}{K_B T^2} \tag{16}$$

$$g\left(\frac{3K_B T}{\hbar}\right) = \frac{\hbar}{3K_B^2} \cdot \frac{dc}{dT}(T) \tag{17}$$

The calculated (from the experimental [5] dependences $C(T)$) (Figs 1, 2) spectra $g(\omega)$ are shown in Figs 3, 4. It is clear that the spectrum $g(\omega)$ of the amorphous polymers has one maximum (Fig. 3) and spectrum $g(\omega)$ of amorphous-crystalline polymers has two maxima (Fig. 4). The values of the experimental function $g(\omega)$ conform to the theory [4].

Two-phonon interactions

It is known that the elementary act of the dissipation on a defect can be considered as a two-phonon process: the phonon of frequency ω' is destroyed (the falling wave) and the phonon of frequency ω is born (the dissipating wave). The equality of the frequencies means a conservation of energy at the collision of two phonons: $\hbar\omega = \hbar\omega'$. Speaking strictly, this equation is valid only in the thermody-

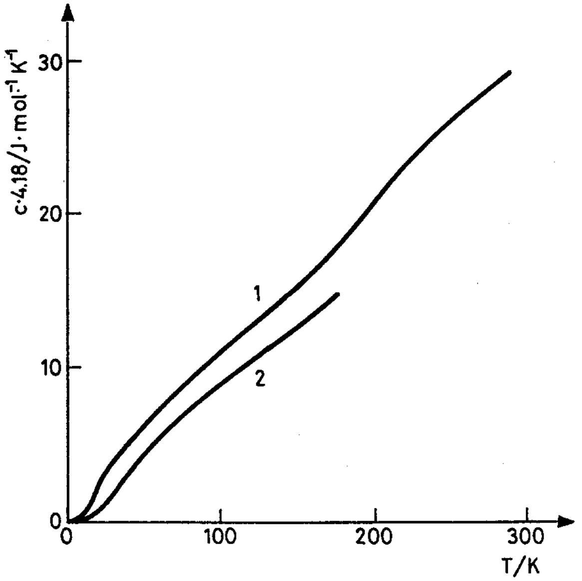

Fig. 1 The dependence of the heat capacity of amorphous polymers (1 — PS, 2 — PI) on the temperature

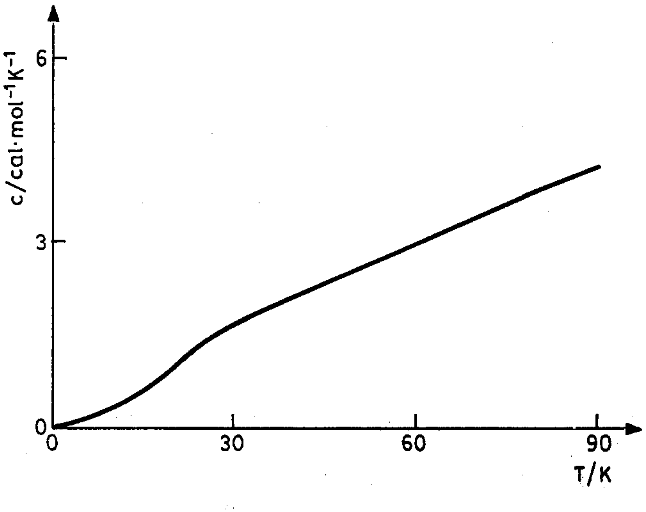

Fig. 2 The dependence of the heat capacity of an amorphous-crystalline polymer (PTFE) on the temperature

namic limit $z \rightarrow \infty$. In the case, where $z < \infty$, the condition of the conversation of energy is not strictly satisfied, namely

$$\omega - \omega' < \Delta\,\omega, \tag{18}$$

where $\Delta\,\omega$ is the indeterminacy of the frequency.

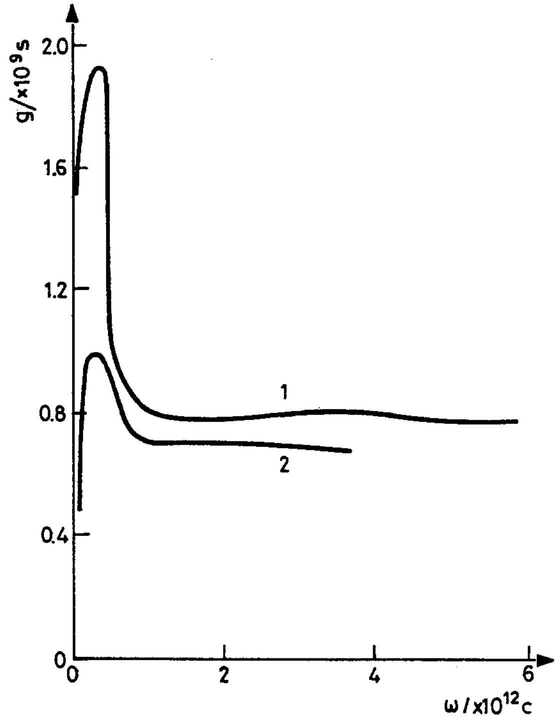

Fig. 3 The phonon spectra of amorphous polymers (1 — PS, 2 — PI)

If the phonon is delocalized, the region where the oscillation was excited is the whole system. For $\Delta\,\omega$ the value

$$\Delta\,\omega \sim \frac{v}{z}$$

is valid.

The frequencies of the delocalized phonons were changing with the portions $\delta\omega \sim \Delta\omega$. Therefore, formula (18) means in fact the equality $\omega = \omega'$: the interaction of the delocalized phonons on the defects is elastic.

For the localized phonons the indeterminacy of the frequency is

$$\Delta\omega' \sim \frac{v}{l} \tag{19}$$

The value of l is changing with the portions

$$\delta l \approx \frac{z}{n^2} \tag{20}$$

Since

$$\delta l = \frac{\mathrm{d}l}{\mathrm{d}\omega} \cdot \delta\omega' \tag{21}$$

from formulae (20) and (21) we get

$$\delta\omega' \sim \frac{z}{n^2} \cdot \frac{1}{\mathrm{d}l/\mathrm{d}\omega} . \tag{22}$$

Taking into account formula (8), we write (22) in the form

$$|\delta\,\omega'| \sim \frac{1}{z \cdot \mathrm{d}\Gamma^{-1}/\mathrm{d}\omega} . \tag{23}$$

It is seen that the function $\mathrm{d}\Gamma^{-1}/\mathrm{d}\omega$ increases for the frequencies $\omega < \Omega_a$ with increasing frequency and the function $l(\omega)$ decreases in this interval of frequencies. Therefore, starting from some frequency Ω_1 the inequality $\delta\omega' < \Delta\omega'$ applies, i.e., the two-phonon processes were permitted with the unequal frequencies.

Consequently, the dissipation of the heat wave on the defects can be inelastic for the definite conditions ($\omega \neq \omega'$. The energy $\hbar(\omega - \omega')$ is supplied to the region of the localization of size l.

Phonon mechanism of the heat conduction of amorphous polymers

By definition, the heat conduction occurs on the condition of the temperature gradient: the known correlation for the density of the heat flow energy has the form:

$$\vec{q} = \lambda \nabla T$$

where λ is the coefficient of the heat conduction.

According to the last formula, the infinitely small volume dx is at the temperature $T(\vec{x})$. Since the temperature is introduced for the state of equilibrium, this equilibrium is local and is characterized by the local temperature $T(\vec{x})$. Therefore, the mechanism of the heat conduction should explain how the local equilibrium is set up.

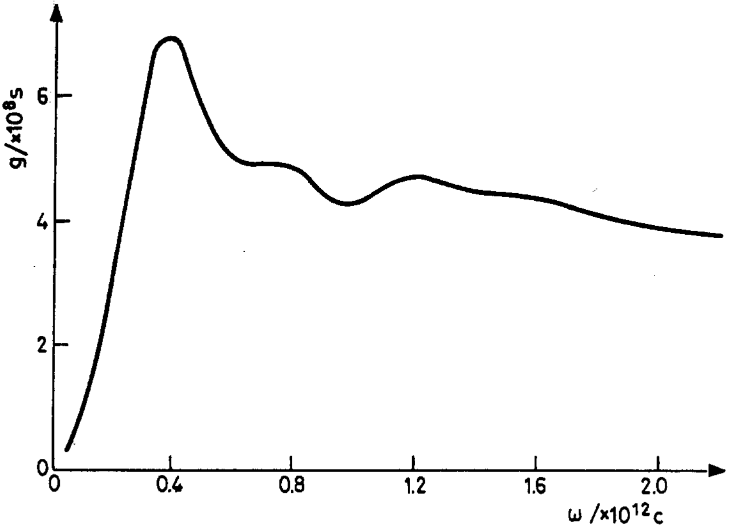

Fig. 4 The phonon spectrum of an amorphous-crystalline (PTFE) polymer

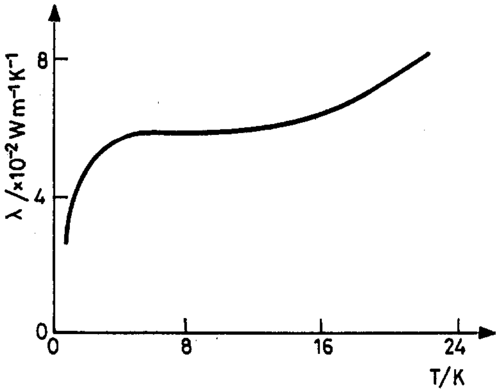

Fig. 5 The dependence of the heat conduction of an amorphous polymer (PMMA) on the temperature

It is supposed [6] that the heat conduction of amorphous polymers is limited by the dissipation of phonons on the defects and besides, that this dissipation is elastic. This means that the given phonon does not share its energy with other phonons. Hence, the elastic dissipation cannot lead to a local equilibrium and the notion of local temperature and temperature gradient loses sense. Therefore, the elastic dissipation of the phonons on the defects cannot be the mechanism of the heat conduction.

It is settled, that the localized phonons can be dissipated on the defects inelastically. In this the exchange of energy is realized for the volume d*x* with the environment, that leads to the establishment of the local temperature.

This allows to suppose a new mechanism of heat conduction, which is limited by inelastic dissipation of the localized phonons on the defects.

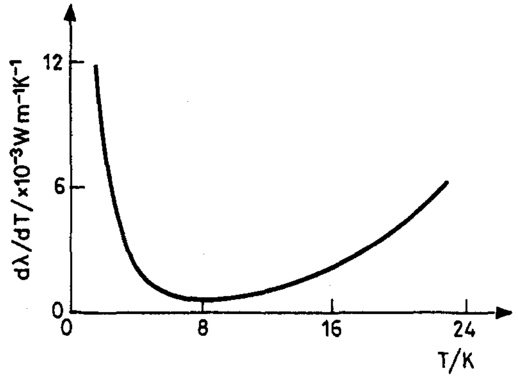

Fig. 6 The temperature derivative of the heat conduction of an amorphous polymer (PMMA)

According to [6, 7], the experimental dependence of heat conduction on the temperature has two outstanding peculiarities. The first one is the existence of the 'plateau' near the temperature about 10 K (Fig. 5) [8]. Secondly, starting from the temperature approximately several tens of K, the form of the dependence $\lambda(T)$ repeats the form of the dependence $C(T)$ in fact. Now, can the supposed mechanism explain these peculiarities?

The heat conduction is given by

$$\lambda \sim \int E \cdot \frac{\hbar\omega}{K_B T} \cdot v\, l(\omega) \cdot g(\omega)\, d\omega \tag{24}$$

Differentiating (24)

$$\frac{d\lambda}{dT} \sim \int \frac{\partial E}{\partial T} \cdot v\, l(\omega) \cdot g(\omega)\, d\omega$$

and substituting (16), we get

$$\frac{\mathrm{d}\lambda}{\mathrm{d}T} \sim \frac{3K_{\mathrm{B}}^{2}}{\hbar} \cdot v \cdot l\,(3K_{\mathrm{B}}T/\hbar) \cdot g\,(3K_{\mathrm{B}}T/\hbar) \tag{25}$$

The differentiation of the dependence shown in Fig. 5 gives the curve (Fig. 6), where the "plateau" is replaced by the 'pit'. It was shown [4], that the dependences $g(\omega)$ and $l(\omega)$ have the form of the curves shown in the Fig. 7. Multiplying these dependences, we receive the curve $\mathrm{d}\lambda/\mathrm{d}T$, that have the 'pit'. Hence, the first peculiarity was explained.

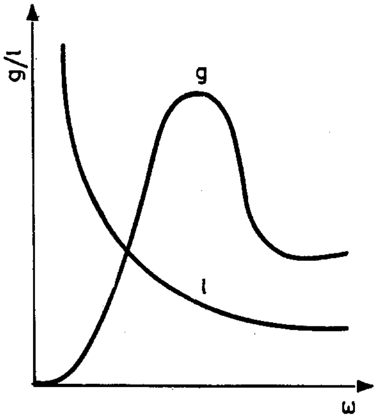

Fig. 7 The phonon spectrum and the extinction length of amorphous polymers

It is clear from Fig. 7 that if $\omega > \Omega_a$ of the size l is constant ($l \sim L$) and formula (25) acquires the appearance for the temperatures $3\,K_{\mathrm{B}}T/\hbar > \Omega_a$

$$\frac{\mathrm{d}\lambda}{\mathrm{d}T} \sim g\,(3K_{\mathrm{B}}T/\hbar) \tag{26}$$

Comparing formulae (17) and (26), we conclude that the values $\frac{\mathrm{d}\lambda}{\mathrm{d}T}$ and $\frac{\mathrm{d}C}{\mathrm{d}T}$ are proportional; the second peculiarity was explained too.

Three-phonon interactions

It is shown in [9, 10] for the amorphous-crystalline polymers that the phonons satisfying the condition

$$\overrightarrow{kL}_{\mathrm{K}} >> 1$$

(where $\vec{k}$ is the wave vector) are localized in the crystalline regions.

It is known [11] that by three-phonon collisions equation

$$\Delta\omega=0 \tag{27}$$

should be satisfied, where $\Delta\omega$ is

$$\Delta\omega \equiv \begin{cases} \omega-\omega'-\omega'' \\ \omega-\omega'+\omega'' \end{cases} \tag{28}$$

where ω, ω', ω'' are the frequencies of the phonons taking part in the collision.

For three-phonon normal processes, moreover, the equation

$$\Delta\vec{k}=0 \tag{29}$$

should be satisfied, where $\Delta\vec{k}$ is

$$\Delta\vec{k}=\vec{k}+\vec{k}'+\vec{k}'' \tag{30}$$

$\vec{k}, \vec{k}', \vec{k}''$ are the wave vectors of phonons taking part in the collisions.

Equations (27), (29) are valid for the delocalized phonons. For interactions with the participation of localized phonons Eqs (27) and (30) are not strictly satisfied [12], namely

$$\Delta\omega \sim \frac{C_g}{L_k} \tag{31}$$

$$\Delta K \sim \frac{1}{L_k} \tag{32}$$

where C_g is the envelope velocity of localized phonons. It is shown in [12], that

$$C_g \sim \Omega\cdot\frac{a^2}{L_k}$$

where Ω is the upper bound of phonon spectrum, a is the distance between the particle links. Condition (30) allows to write formula (34) in the form

$$\Delta\omega \sim \Omega\cdot\frac{a^2}{L_k^2} \tag{33}$$

Because of the availability of two kinds of phonons (localized and delocalized), three kinds of three-phonon processes are possible when the phonons of one kind (localized and delocalized) take part in the collision or the phonons of different kinds take part in the collision. Let us call those L-V, D- and LD-processes.

Since the localized phonons have the frequency $\sim\Omega$ [12], the indeterminacy of the frequency should be equal to Ω also. Condition (35) is not satisfied. Consequently the L-processes were forbidden. The D- processes are allowed because of formulae (28) and (29).

For LD-processes conditions (32) and (33) can be satisfied in fact for all values of ω'' and K'' of the delocalized phonons when one delocalized phonon and two localized phonons take part in the collision and, besides wave vectors K and K' of localized phonons are directed face to face.

Phonon relaxation

This relaxation process is the result of the fact that the average phonon number of the given kinds attains this equilibrium value. It is known [11] that the relaxation time of this process is determined by the formula

$$\tau^{-1} = \frac{\pi}{\hbar}\sum_{K'K''}\frac{|F|^2\cdot \mathrm{sh}\,(\hbar\,\omega/2K_BT)}{\mathrm{sh}\,(\hbar\,\omega'/2K_BT)\cdot \mathrm{sh}\,(\hbar\,\omega''/2K_BT)}\cdot f\,(\Delta\,\omega) \tag{34}$$

where F is the matrix element of the perturbation, $f\,(\Delta\,\omega)$ is the function of $\Delta\,\omega$.

The relaxation times of LD- and L-processes are calculated according to formula (34) in [12].

$$\tau_{LD}^{-1} \sim \frac{v}{a}\cdot\frac{K_BT}{m\,c^2}\cdot\left(\frac{g}{\rho\,v^2}\right)^2\cdot\left(\frac{L_k}{a}\right)^2\cdot(\chi\,a)^3 \tag{35}$$

$$\tau_{D}^{-1} \sim \frac{v}{a}\cdot\frac{K_BT}{m\,c^2}\cdot\left(\frac{g}{\rho\,v^2}\right)^2\cdot(\chi\,a)^4 \tag{36}$$

where m is the mass of the particle, g is the unharmonic constant, χ is the highest value of the wave number of the delocalized phonons, ρ is the density.

It is clear from formulae (35) and (36) that the relaxation time is inversely proportional to the temperature for three-phonon processes. Since the position of the maximum on the dielectric loss versus temperature plot is defined by the equation $\Omega_e\tau = 1$, where Ω_e is the frequency of the external field, the temperature of the maximum should be a linear function of the frequency for three-phonon processes. Such maximum was discovered for polyethylene at $T \sim 1$ K, $\Omega_e \sim 10^3\cdot s^{-1}$ [13] (Fig. 8). Calculating according to formulae (35) and (36), we receive $\tau_{LD}^{-1} \sim 10^3$ s^{-1}, $\tau_D^{-1} \sim 10^{-5}$ s^{-1} [12, 14]. Hence, the discovered maximum is caused by the LD-process.

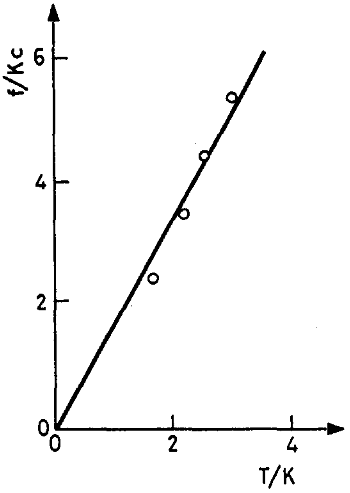

Fig. 8 The dependence between the temperature *T* and the frequency of the maximum of dielectric loss for polyethylene

Conclusion

In this article with the help of the methods of a qualitative theory the important fact of the phonon localization was established, and the qualities of the localized phonons were determined. On this basis the temperature dependences on heat capacity and heat conduction were written, the phonon relaxation was studied. Moreover, in [15] and [16] the dependence of the elastic modulus on temperature and the combinatoric scattering caused by the localized phonons were investigated.

It is clear from the enumerated examples that the study of the localized phonons allows to determine the mechanism of the thermal properties of solid polymers.

References

1 J. A. Reissland, The physics of phonons (Russian translation), Mir, Moscow 1975.
2 V. Z. Bontsh-Bruevitsh, The electron theory of disorder semiconductors (in Russian), Nauka, Moscow 1981.
3 A. B. Migdal, The qualitative methods in the quantum theory (in Russian), Nauka, Moscow 1975.
4 Yu. F. Zabashta, Vysokomol. Soed., 32A (1990).
5 B. Wunderlich and H. Baur, Heat capacities of linear high polymers (Russian translation), Mir, Moscow 1972.
6 V. S. Oskotsky and I. A. Smirnov, The defects in crystals and heat conduction (in Russian), Nauka, Moscow 1972.
7 Yu. K. Godovsky, The thermophysics of polymers (in Russian), Khimija, Moscow 1982.

8 W. J. Reese, J. Appl. Phys., 37 (1966) 3227.
9 Yu. F. Zabashta, Ukr. phys. J., 30 (1985) 112.
10 Yu. F. Zabashta, The composing polymer materials, 26 (1985) 19.
11 G. Leibfried, The lattice theory of the mechanical and thermal properties of crystals (in Russian translation), Physmatgiz, Moscow 1963.
12 Yu. F. Zabashta, Vysokomol. Soed., 32A (1990) 412.
13 O. Heybey and F. H. Müller, K-Z und Z für Polymer, 251 (1973) 383.
14 Yu. F. Zabashta, Vysokomol. Soed., 29B (1987) 209.
15 Yu. F. Zabashta, Vysokomol. Soed., 27A (1985) 1597.
16 Yu. F. Zabashta, Vysokomol. Soed., 32B (1990) 65.

Zusammenfassung — Ausgehend von einer qualitativen Theorie werden Phononenspektren erhalten. Zwei- und Dreiphononen-Wechselwirkungen werden untersucht. Theoretische Ergebnisse werden zur Analyse experimenteller Daten verwendet: Wärmeleitfähigkeit, dielektrische Relaxation, Wärmekapazität.