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# Debye temperatures and nanostructuring of polyurethane auxetics

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Based on experimental values of longitudinal and transverse ultrasonic wave propagation velocities and surface Rayleigh wave velocities were calculated phonon energies and Debye limiting frequencies and temperatures were determined of metal-filled polyurethane auxetics samples. Modeling the structural formations of such systems and obtaining the value of the lattice and Grüneisen acoustic parameter made it possible to find the root-mean-square displacement of the atomic groups of the macromolecule, as well as the limits of forced elasticity, shear deformation, and deformation of the interstructural bond. The relationship between Debye frequencies (temperatures) and Poisson's ratio, Grüneisen parameter, was established. A quantum-mechanical approach to the movement of electrons, atomic groups of macromolecules, thermal and sound phonons made it possible to estimate the size of nanoformations in the composition. The theoretical values of Poisson's ratio obtained based on models of polymer auxetics and processes of propagation of ultrasonic waves in such systems are analyzed.

**Keywords:** polymer auxetic, longitudinal, transverse and surface waves, propagation velocity, Poisson's ratio, temperatures and Debye frequencies, root mean square deviation, nanostructuredness.

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## Introduction

The creation of new structural materials requires the search for unconventional experimental and theoretical approaches. This is due to the fact that such materials must have intellectual properties that are programmed in the process of their creation and are able to change depending on external conditions. The work [1] summarizes the regularities of the realization of physical phenomena and phase-structural transformations that develop during the exploitation of intellectual materials of different physical nature, composition, and functional application, which ensure the formation of their physical-mechanical and operational properties. A classification scheme of physicochemical phenomena is proposed, covering phase and structural transformations on which the formation of the properties of intellectual materials (metallic and non-metallic, solid and liquid) during their operation is based. The class of such materials includes heterogeneous polyurethanes and their compositions. Polyurethanes are synthesized mainly from petroleum raw materials, but green chemistry of polyurethanes has also been proposed, which leads to the improvement of the environmental situation in the world [2]. Methods of obtaining polyurethane compositions by adjusting the content of components and structure make it possible to adjust the physical and mechanical properties [3]. An important aspect in the creation of intelligent polymer systems is their ability to exhibit auxetic properties, which determines the prospect of their use from the biomedical to the aerospace industry [4]. The auxetic properties of polyurethane materials are revealed under the influence of external dynamic mechanical fields (compression test with a high rate of deformation at a constant velocity) [5]. An important issue in the study of such materials is the modeling of their structure and properties [6].

The Debye temperature is a parameter used in models of structural organization of materials and prediction of thermophysical and mechanical properties [7–9]. In [10], the temperature and Debye frequency were used to estimate the Grüneisen parameter of auxetic fullerite. For polymeric materials, this parameter was used to calculate the frequency spectrum of the structural elements of macromolecules [11, 12], the contribution of the macrolattice of the filler to the mechanical and thermophysical properties [13], and the modeling of thermal energy transfer processes [14].

The purpose of this work is to determine the Debye temperatures and frequencies of auxetic polyurethane compositions and use them to estimate structural parameters.

## I. Research materials and methods

The object of the study was thermoplastic polyurethane (TPU) synthesized based on 4,4-diphenylmethane diisocyanate, 1,4-butanediol and polyoxytetramethylene glycol with MM = 1500. Highly dispersed powders of iron (Fe), molybdenum (Mo), tungsten (W) were selected as fillers, the particle sizes were 0.3–1.0 µm. The compositions were obtained by direct mixing in the T-mode. The volume concentration of the filler for TPU systems corresponded to the critical concentration in the system and, respectively, for Mo, Fe, W equal to 48, 43 and 52 %.

The density $\rho$ of polymer composite materials was determined by the method of hydrostatic weighing, the error of the method does not exceed 0.3 %. Determination of the speed of propagation of longitudinal $\upsilon_l$ and transverse wave $\upsilon_t$ of ultrasound waves at a frequency of $\omega$ = 1.884 MHz was carried out using a method based on the comparison of the results of direct measurements of the propagation time of a probing pulse through an immersion liquid in the absence of a sample ($\tau$) between the emitter and the signal receiver ($\tau_l,\ \tau_t$) [15].

The value of $\upsilon_l$ was determined by the ratio:

$$\upsilon_l = \frac{\upsilon_{i.liq.} d_0}{d_0 - \Delta\tau_l \upsilon_{i.liq.}}, \tag{1}$$

where $\upsilon_{i.liq.}$ – velocity of propagation of the ultrasound wave in the immersion liquid; $d_0$ – thickness of a sample of material with parallel surfaces, $\Delta\tau_l$ – the difference between the time of passage of the probing pulse in the absence of a sample and in the presence of a sample ($\Delta\tau_l = \tau - \tau_l$).

The value of $\upsilon_t$ calculated according to the ratio:

$$\upsilon_t = \frac{\upsilon_{i.liq.}}{\sqrt{sin^2(\theta_{cr.}) + \left(cos(\theta_{cr.}) - \frac{\upsilon_{i.liq.}\Delta\tau_i}{d_0}\right)^2}}, \tag{2}$$

where $\Delta\tau_t$ – the difference between the time of passage of the probing pulse in the absence of a sample and in the presence of a sample, placed at an angle $\theta_{cr.}$ to the direction of fall wave.

With known values of $\upsilon_l$, $\upsilon_t$ Poisson's ratio ($\nu$) of polymer auxetic is calculated according to the relation:

$$\nu = \frac{2 - \left(\frac{\upsilon_l}{\upsilon_t}\right)^2}{2\left(1 - \left(\frac{\upsilon_l}{\upsilon_t}\right)^2\right)}, \tag{3}$$

weighted average value of ultrasound speed in TPU systems:

$$\bar{\upsilon} = \left(\frac{3\upsilon_l^3 \upsilon_t^3}{\upsilon_t^3 + 2\upsilon_l^3}\right)^{\frac{1}{3}}. \tag{4}$$

In addition to volumetric ultrasonic waves, Rayleigh ($R$) surface waves can also propagate in materials, which cause features of interaction with atoms and structural elements of macromolecules located in the surface layer [16–18]. Poisson's ratio, which characterizes the viscoelastic properties of the medium, is an important parameter in the processes of propagation, absorption, and scattering of surface acoustic waves (SAW).

The equation that relates the propagation speeds of the three types of waves is Rayleigh equation [19]:

$$\left(2 - \left(\frac{\upsilon}{\upsilon_t}\right)^2\right)^2 = 4\left(2 - \left(\frac{\upsilon}{\upsilon_l}\right)^2\right)^{\frac{1}{2}}\left(2 - \left(\frac{\upsilon}{\upsilon_t}\right)^2\right)^{\frac{1}{2}}, \tag{5}$$

where $\upsilon = \upsilon_R$ – Rayleigh SAW velocity.

Equation (5) can be represented in polynomial form [20]:

$$\eta^6 - 8\eta^4 + 8(3 - 2\xi^2)\eta^2 - 16(1 - \xi^2) = 0, \tag{6}$$

where: $\eta = \frac{\upsilon_R}{\upsilon_t}$; $\xi = \frac{\upsilon_t}{\upsilon_l}$.

In the range of negative values of $\nu$ the determinant of the reduced cubic equation (6) with respect to $\eta^2$ is negative, and therefore the equation has three real roots. For the value $\eta$ in the range $0 < \eta < 1$ we obtain the following analytical solution [21]:

$$\frac{\upsilon_R}{\upsilon_t} = \frac{4}{3}\left(\sqrt{2(6\xi^2 - 1)^3}\, cos\left(\frac{1}{3}\left(arc\ cos\left(\frac{45\xi^2 - 17}{2\sqrt{2(6\xi^2 - 1)^3}}\right) + 2\pi\right)\right) + 2\right), \tag{7}$$

where $\xi^2 = \frac{2\nu - 1}{2\nu - 2}$.

The results of determining the density speed of propagation of ultrasound waves, Poisson's ratio of TPU systems is presented in the Table. 1.

**Table 1.**

Density, velocity of propagation of acoustic waves and Poisson's ratio of TPU systems

| Material | $\rho$, kg/m$^3$ | $\upsilon_l$, m/s | $\upsilon_t$, m/s | $\upsilon_R$, m/s | $\bar{\upsilon}$, m/s | $\nu$ |
|---|---|---|---|---|---|---|
| TPU | 1107 | 1635 | 1415 | 991 | 1475 | – 0.99 |
| TPU+W | 9888 | 1775 | 1370 | 1084 | 1464 | – 0.24 |
| TPU+Fe | 3642 | 1750 | 1395 | 1039 | 1481 | – 0.37 |
| TPU+Mo | 4603 | 1755 | 1405 | 995 | 1490 | – 0.39 |

## II. Results and their discussion.

Taking into account the local fluctuations of structural elements of macromolecules, the spectral density ($\rho(\omega)$) of the state is given by the sum of three independent components: longitudinal, two transverse and surface waves. Such waves have different maximum oscillation frequencies, which are determined from the $3N$ normalization condition (the polymer consists of $N$ structural elements):

$$\rho(\omega) = \rho_l(\omega) + 2\rho_t(\omega) + \rho_R(\omega), \tag{8}$$

where $\rho_l(\omega) = \frac{V-V^*}{2\pi^2\upsilon_l^3}\omega^2$; $\rho_t(\omega) = \frac{V-V^*}{2\pi^2\upsilon_t^3}\omega^2$; $\rho_R(\omega) = \frac{V^*}{2\pi^2\upsilon_R^3}\omega^2$, $V$ – body volume, $V^*$ – the volume in which Rayleigh surface waves propagate.

Using this approach, the Debye frequency for oscillation of the structural elements of macromolecules of TPU systems caused by intra- and intermolecular interactions was found as [16]:

$$\omega_D^l = \left(\frac{6\pi^2 N}{V_M}\right)^{\frac{1}{3}}\upsilon_l; \qquad \omega_D^t = \left(\frac{6\pi^2 N}{V_M}\right)^{\frac{1}{3}}\upsilon_t,$$
$$\omega_D^R = \left(\frac{6\pi^2 N}{V_M}\right)^{\frac{1}{3}}\upsilon_R, \qquad \omega_D^{max} = \left(\frac{18\pi^2 N}{V_M}\right)^{\frac{1}{3}}\bar{\upsilon}, \tag{9}$$

where $N$ – the number of structural elements of a macromolecule in one mole, $V_M$ – molar volume.

The values of $\omega_D^l$, $\omega_D^t$ $\omega_D^R$ and $\omega_D^{max}$ make it possible to determine the characteristic temperatures:

$$\theta_D^l = \frac{\hbar\omega_D^l}{k}; \ \ \theta_D^t = \frac{\hbar\omega_D^t}{k} \ \ \theta_D^R = \frac{\hbar\omega_D^R}{k}; \ \ \theta_D^{max} = \frac{\hbar\omega_D^{max}}{k}, \tag{10}$$

where $k = 1{,}38\cdot10^{-23}$ J/K.

From the analysis presented in the Table 2 of the data for TPU systems, it follows that the values of the oscillation frequencies of the structural elements of macromolecules caused by the propagation of longitudinal and transverse disturbances are close to and exceed the corresponding frequencies in the surface layers. This indicates that bulk interstructural interactions are “stiffer” than surface interactions. The value of the maximum limiting Debye frequency exceeds $\omega_D^l$, $\omega_D^t$, $\omega_D^R$.

The Debye spectrum of vibrations of structural elements of macromolecules corresponds to the infrared range. The corresponding Debye temperatures for the studied TPU systems range from 55 K to 121 K. The type of filler in TPU systems does not significantly affect the value of the Debye temperatures. Comparison of values $\theta_D^l$ ($\omega_D^l$) for TPU systems and filled linear polymers [11–14] indicates that the spectrum of longitudinal oscillations is stiffer for structural elements of polyvinyl chloride and poly(vinyl butyral) macromolecules. For transverse oscillations, the values of $\theta_D^t$ ($\omega_D^t$) are close.

Debye temperatures (frequencies) make it possible to estimate interstructural anharmonicity during the propagation of excitations along the TPU macromolecule. In order to evaluate the interstructural anharmonicity in the implementation of intramolecular and intermolecular interactions, the ratio of the root mean square displacement of the structural element to the square of the mean interstructural distance was determined.

In the range of temperatures $T > \theta_D$, when moving to integration by frequency for intramolecular interactions, we obtained:

$$\frac{\bar{x}^2}{r_1^2} = \frac{3kT\omega_D^l}{2\pi^2\rho\upsilon_l^3 r_1^2}, \tag{11}$$

and for intermolecular interactions:

$$\frac{\bar{y}^2}{r_2^2} = \frac{3kT\omega_D^t}{2\pi^2\rho\upsilon_t^3 r_2^2}, \tag{12}$$

where $r_1$ i $r_2$ – respectively, the equilibrium distances between the structural elements of the macromolecule.

For the maximum Debye frequency and when surface effects are detected, such values were determined by ratios:

$$\frac{\bar{x}_R{}^2}{r_1^2} = \frac{3kT\omega_D^R}{2\pi^2\rho\upsilon_R^3 r_1^2}, \qquad \frac{\bar{x}_{max}{}^2}{r_1^2} = \frac{3kT\omega_D^{max}}{2\pi^2\rho\bar{\upsilon}^3 r_1^2} \tag{13}$$

Values were found from relations (10)–(12) $\bar{x}$, $\bar{y}$, $\bar{x}_R$, $\bar{x}_{max}$:

$$\bar{x} = \sqrt{\frac{3kT\omega_D^l}{2\pi^2\rho\upsilon_l^3}}; \quad \bar{y} = \sqrt{\frac{3kT\omega_D^t}{2\pi^2\rho\upsilon_t^3}}; \tag{14}$$

$$\bar{x}_R = \sqrt{\frac{3kT\omega_D^R}{2\pi^2\rho\upsilon_R^3}}, \quad \bar{x}_{max} = \sqrt{\frac{3kT\omega_D^{max}}{2\pi^2\rho\bar{\upsilon}^3}}. \tag{15}$$

The relative strain between structural bonds in a macromolecule can be estimated by Poisson's ratio [22]:

$$\frac{\Delta r^2}{r^2} = \left(\frac{2-3\nu}{9(1+\nu)}\right)^2; \quad \Delta r = r\left(\frac{2-3\nu}{9(1+\nu)}\right) \tag{16}$$

The analysis of the obtained values of these structural parameters (Table 3) shows that both for intra- and intermolecular interaction, taking into account anharmonic effects, the force constants of the third and

**Table 2.**

Frequencies and Debye temperatures of TPU systems

| Material | $\omega_D^l \cdot 10^{-13}$, Hz | $\omega_D^t \cdot 10^{-13}$, Hz | $\omega_D^R \cdot 10^{-13}$, Hz | $\omega_D^{max} \cdot 10^{-13}$, Hz | $\theta_D^l$, K | $\theta_D^t$, K | $\theta_D^R$, K | $\theta_D^{max}$, K |
|---|---|---|---|---|---|---|---|---|
| TPU | 1.198 | 1.037 | 0.726 | 1.560 | 91.8 | 79.5 | 55.6 | 119.5 |
| TPU+W | 1.301 | 1.004 | 0.795 | 1.548 | 99.6 | 76.9 | 60.9 | 118.6 |
| TPU+Fe | 1.283 | 1.023 | 0.762 | 1.566 | 98.3 | 78.3 | 58.4 | 120.0 |
| TPU+Mo | 1.286 | 1.030 | 0.729 | 1.576 | 98.6 | 78.9 | 55.9 | 120.7 |

**Table 3.**

Displacement of structural elements of the molecular grid of TPU systems

| Material | $\bar{x}$, Å | $\bar{y}$, Å | $\bar{x}_R$, Å | $\bar{x}_{max}$, Å | $\frac{\bar{x}^2}{r_1^2}$ | $\frac{\bar{y}^2}{r_2^2}$ | $\frac{\bar{x}_R^2}{r_1^2}$ | $\frac{\bar{x}_{max}^2}{r_1^2}$ | $\Delta r$, Å | $\frac{\Delta r^2}{r^2}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| TPU | 0.39 | 0.79 | 1.09 | 0.52 | 0.064 | 0.206 | 0.501 | 0.114 | 85.04 | 55.2 |
| TPU+W | 0.21 | 0.29 | 0.20 | 0.17 | 0.019 | 0.027 | 0.017 | 0.012 | 0.61 | 0.160 |
| TPU+Fe | 0.35 | 0.45 | 0.34 | 0.29 | 0.053 | 0.065 | 0.049 | 0.035 | 0.84 | 0.303 |
| TPU+Mo | 0.32 | 0.39 | 0.31 | 0.25 | 0.042 | 0.050 | 0.041 | 0.026 | 0.89 | 0.333 |

fourth orders play a significant role:

$$f = \frac{\left(\omega_D^l\right)^2 M}{4}; \qquad \chi = \frac{\left(\omega_D^t\right)^2 M}{4};$$
$$f_{max} = \frac{\left(\omega_D^{max}\right)^2 M}{4}; \qquad f_R = \frac{\left(\omega_D^R\right)^2 M}{4}. \tag{17}$$

The anharmonicity of the thermal vibrations of the quasi-lattice, interatomic (intermolecular) bonds, and the nonlinearity of the intermolecular interaction forces can be estimated on the basis of the Grüneisen parameter.

According to the identity of the potential of interatomic and intermolecular interaction for heterogeneous polymer systems, the Poisson's ratio is related to the Grüneisen parameter by the relation:

$$\gamma_L = \frac{1+\nu}{1-2\nu}. \tag{18}$$

In the propagation of acoustic waves, the processes of nonlinearity are characterized by the Grüneisen ac

$$\gamma_A = \frac{3(1+\nu)}{2(2-3\nu)}. \tag{18*}$$

The analysis of the obtained values of these structural parameters (Table 3) shows that both for intra- and intermolecular interaction, taking into account anharmonic effects, the force constants of the third and fourth orders play a significant role:

$$q = \frac{\gamma_L f}{r_1};\ q' = \frac{\gamma_L \chi}{r_2};\ q_{max} = \frac{\gamma_L f_{max}}{r};\ q_R = \frac{\gamma_L f_R}{r}, \tag{19}$$

$$h = \frac{(m_1+m_2+1)^2 - 36(m_1 m_2 - 2)}{36 r_1^2} f;$$
$$h' = \frac{(m_1+m_2+1)^2 - 36(m_1 m_2 - 2)}{36 r_1^2} \chi. \tag{20}$$

where $m_1$, $m_2$ – power exponents in the Lennard-Jones potential, $m_1 = 12$, $m_2 = 6$; $r_1$, $r_2$ – equilibrium distances during intramolecular and intermolecular interactions;

It is known that the elementary act of forced-elastic deformation of glassy polymers can occur only in the presence of fluctuating microvoids of sufficient size. Therefore, the ratio of the volume of the minimum hole $V_h$ to the molecular volume can be considered as forced-elastic deformation under comprehensive compression or tension. The free volume theory gives the same result as the phonon theory of forced-elastic deformation of glassy polymers. According to this theory, the critical strain corresponding $\varepsilon_f$, to forced elasticity is inversely proportional to the Grüneisen parameter

$$\varepsilon_f = \frac{1}{2\gamma_L}, \tag{21}$$

critical shear deformation in which the stability of the system is lost:

$$\varepsilon_{sh} = \frac{1}{3\gamma_L}, \tag{22}$$

and the maximum limit of deformation of the interstructural connection:

$$\varepsilon_d = \frac{1}{6\gamma_L}, \tag{23}$$

Using the Grüneisen acoustic parameter, these characteristics were determined as:

$$\varepsilon_{f.A} = \frac{1}{10}\left(\frac{9}{2\gamma_A} - 1\right); \qquad \varepsilon_{sh.A} = \frac{1}{5}\left(\frac{3}{2\gamma_A} - \frac{1}{3}\right);$$
$$\varepsilon_{d.A} = \frac{1}{10}\left(\frac{3}{2\gamma_A} - \frac{1}{3}\right). \tag{24}$$

Potential energy is defined as:

$$U_P = \frac{fx^2}{2} - \frac{qx^3}{3} + \frac{hx^4}{4}. \tag{25}$$

The calculations of these parameters (Table 4) prove that auxetic TPU systems are highly elastic and can undergo significant deformations.

Given that the heterogeneous polymer system at $\varphi \geq \varphi_{cr.}$ is a set of macrolattices [6, 15], we choose one of them with period $L$ in the composition and consider the

**Table 4.**

Grüneisen parameter and force constants of the third and fourth orders of TPU

| Material | TPU | TPU+W | TPU+Fe | TPU+Mo |
|---|---|---|---|---|
| $\gamma_L$ | 0.003 | 0.51 | 0.36 | 0.34 |
| $\gamma_A$ | 0.002 | 0.42 | 0.31 | 0.28 |
| $f$, N/m | 5.96 | 7.02 | 6.83 | 6.86 |
| $\chi$, N/m | 4.46 | 4.18 | 4.34 | 4.40 |
| $f_R$, N/m | ∞ | 2.62 | 2.41 | 2.21 |
| $f_{max}$, N/m | 10.06 | 9.94 | 10.17 | 10.31 |
| $q \cdot 10^{-10}$, N/m$^2$ | 0.01 | 2.32 | 1.60 | 1.51 |
| $q' \cdot 10^{-10}$, N/m$^2$ | 0.008 | 1.38 | 1.01 | 0.97 |
| $q_R \cdot 10^{-10}$, N/m$^2$ | ∞ | 0.87 | 0.56 | 0.49 |
| $q_{max} \cdot 10^{-10}$, N/m$^2$ | 0.02 | 3.29 | 2.38 | 2.28 |
| $h \cdot 10^{-20}$, N/m$^3$ | 148.94 | 175.43 | 170.68 | 171.43 |
| $h' \cdot 10^{-20}$, N/m$^3$ | – 85.32 | – 79.96 | – 83.02 | – 84.17 |
| $h_R \cdot 10^{-20}$, N/m$^3$ | ∞ | – 65.47 | – 60.23 | – 55.23 |
| $h_{max} \cdot 10^{-20}$, N/m$^3$ | – 251.40 | – 248.40 | – 254.15 | – 257.65 |

**Table 5.**

Potential energy, forced elasticity, critical shear strain and maximum strain limit of interstructural connection of TPU systems

| Material | TPU | TPU+W | TPU+Fe | TPU+Mo |
|---|---|---|---|---|
| $U_{P\ lon.} \cdot 10^{21}$, J | 4.53 | 1.53 | 4.13 | 3.48 |
| $U_{P\ tran.} \cdot 10^{21}$, J | 13.90 | 0.92 | 3.90 | 3.05 |
| $U_{P\ R} \cdot 10^{21}$, J | $\frac{\infty}{0}$ | 0.35 | 1.07 | 0.91 |
| $U_{P\ max}\ 10^{21}$, J | 13.58 | 1.38 | 4.23 | 3.11 |
| $\varepsilon_f$ | 166.667 | 0.980 | 1.387 | 1.471 |
| $\varepsilon_{f.\ A}$ | 224.9 | 0.971 | 1.352 | 1.507 |
| $\varepsilon_{sh}$ | 111.112 | 0.654 | 0.924 | 0.980 |
| $\varepsilon_{sh.\ A}$ | 149.94 | 0.654 | 0.908 | 1.011 |
| $\varepsilon_d$ | 55.556 | 0.327 | 0.462 | 0.490 |
| $\varepsilon_{d.\ A}$ | 74.97 | 0.327 | 0.454 | 0.506 |

total force acting on it.

We define the total force as the sum of only those forces acting on this volume from the parts of the body surrounding it. Since these forces act on the macrolattice through its surface, in addition to the forces of interatomic interaction, surface forces $F_n$ can act on the particles of the body in the direction of the $z$ axis. If stress is applied in the direction of the normal to the surface $G$, then the average value of the surface force per atom of the outer layer will be $F_1 = \frac{G}{n_0}$, where $n_0$ – the number of cross links in the TPU grid. We consider the case of deformation of the composition, which is accompanied by a change in volume without a change in the shape of the body. Under the assumption that the wavelength is much longer than the distance between two neighboring atoms of the system, the deformation process of elastic oscillations in systems with $\nu < 0$ propagates in the form of an expanding ellipsoid of rotation [24]. With this simulation, Poisson's ratio can be expressed in terms of Debye temperatures (frequencies):

$$\nu = -\frac{v_t}{v_l}\left(\frac{\omega_D^t}{\omega_D^l}\right)^2. \qquad (26)$$

Since TPU systems at the molecular level are considered as mesh structures with intra- and intermolecular bonds, according to their models [24, 25], the Poisson's ratio is equal to:

$$\nu = -\frac{1}{n_0}\frac{\bar{y}}{\bar{x}}\frac{r_1}{r_2}; \qquad \nu = -\frac{1}{n_0}\frac{r_1}{r_2}\sqrt{\frac{\omega_D^t v_l^3}{\omega_D^l v_t^3}}. \qquad (27)$$

As follows from the results presented in Fig. 1–4, the number of transverse bonds that are subjected to a deformation effect during the propagation of an ultrasonic wave is different, in particular, for the original TPU it is equal to 1, TPU+Mo 2–3, TPU+Fe, TPU+W 3–4.

If the concept of Debye momentum is introduced for particles and quasi-particles that are able to move in the structure formation of TPU systems [26], then their sizes can be estimated. For the longitudinal direction (axis $Ox$) according to relations (9)–(10) we obtain:

$$\hbar\omega_D^l = k\theta_D^l = \frac{p_x^2}{2m} = \frac{h^2}{2mL_l^2};$$

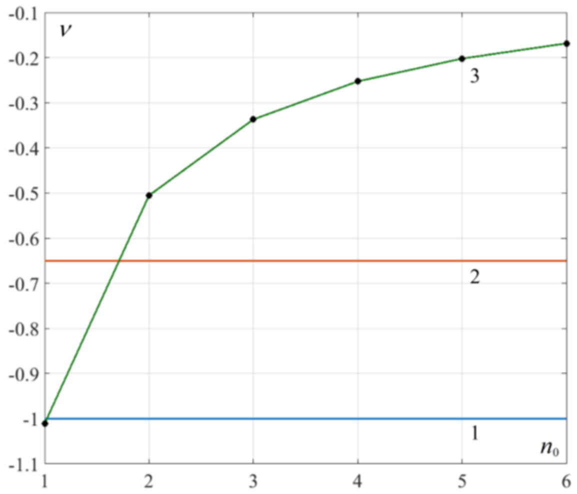

**Fig. 1.** Dependence $\nu$ on $n_0$ for TPU:
1 – experiment; 2 – according to the ratio (26);
3 – according to the ratio (27).

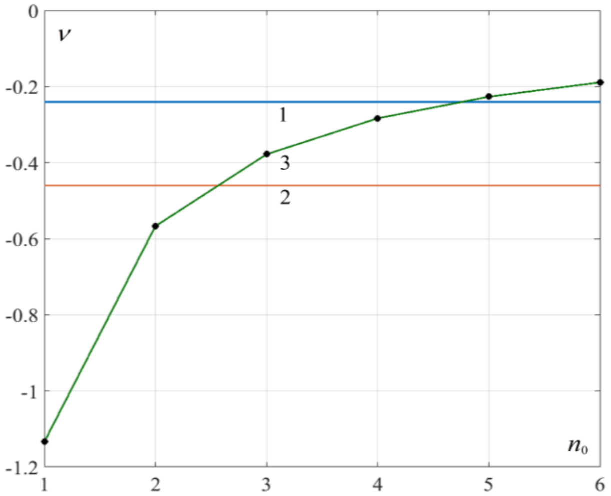

**Fig. 2.** Dependence $\nu$ on $n_0$ for TPU+W:
1 – experiment; 2 – according to the ratio (26);
3 – according to the ratio (27).

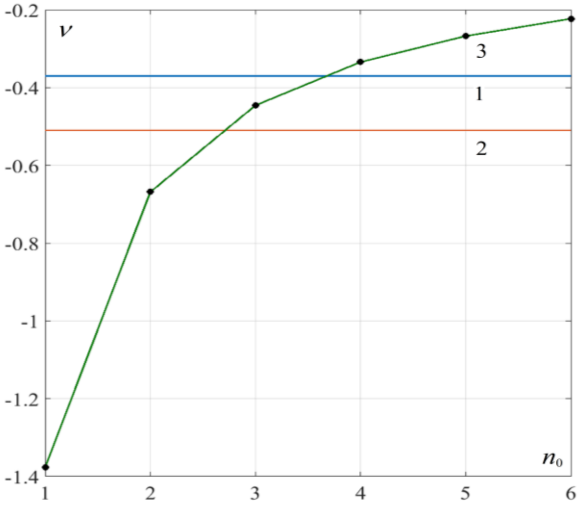

**Fig. 3.** Dependence $\nu$ on $n_0$ for TPU+Fe:
1 – experiment; 2 – according to the ratio (26);
3 – according to the ratio (27).

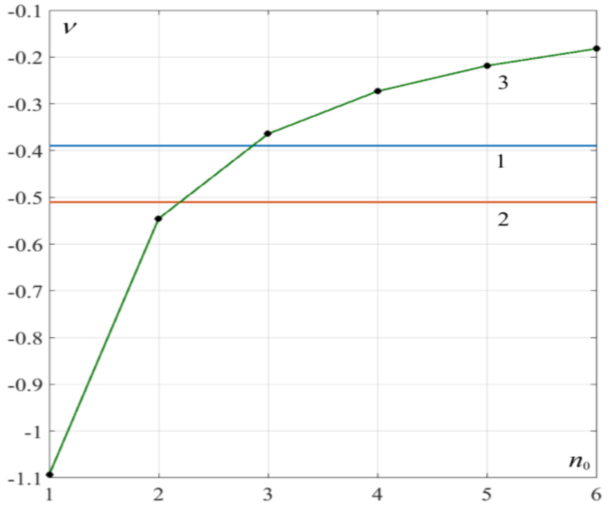

**Fig. 4.** Dependence $\nu$ on $n_0$ for TPU+Mo:
1 – experiment; 2 – according to the ratio (26);
3 – according to the ratio (27).

$$L_l = h\sqrt{\frac{1}{2mk}}(\theta_D^l)^{-\frac{1}{2}};\ L_l = \sqrt{\frac{\pi h}{m}}(\omega_D^l)^{-\frac{1}{2}}. \qquad (28)$$

and in the transverse (axis *Oy*):

$$\hbar\omega_D^t = k\theta_D^t = \frac{2p_y^2}{2m} = \frac{2h^2}{2mL_t^2};$$

$$L_t = h\sqrt{\frac{1}{mk}}(\theta_D^t)^{-\frac{1}{2}}; \qquad L_t = \sqrt{\frac{2\pi h}{m}}(\omega_D^t)^{-\frac{1}{2}}. \qquad (29)$$

In the case of surface effects, the sizes of structural formations were determined as:

$$\hbar\omega_D^R = k\theta_D^R = \frac{2p^2}{2m} = \frac{2h^2}{2mL_R^2};$$

$$L_R = h\sqrt{\frac{1}{mk}}(\theta_D^R)^{-\frac{1}{2}}; \qquad L_R = \sqrt{\frac{2\pi h}{m}}(\omega_D^R)^{-\frac{1}{2}}. \qquad (30)$$

Limiting the frequency spectrum by values $\omega_D^{max}$ makes it possible to estimate the linear dimensions of volume structures:

$$\hbar\omega_D^{max} = k\theta_D^{max} = \frac{3p^2}{2m} = \frac{3h^2}{2mL_{max}^2};$$

$$L_{max} = h\sqrt{\frac{3}{2mk}}(\theta_D^{max})^{-\frac{1}{2}};\ L_{max} = \sqrt{\frac{3\pi h}{m}}(\omega_D^{max})^{-\frac{1}{2}}. \qquad (31)$$

Calculation $L_{l1}$, $L_{t1}$, $L_{R1}$, $L_{max1}$, for an electron ($m_1 = 9.31\cdot10^{-31}$ kg) indicate that their values (Table 6) are close to the linear dimensions of the structural formations of TPU systems obtained on the basis of fractal approaches [27].

In the case of participation in processes of energy or momentum transfer of atomic groups of ($m_2 = 1.66\cdot10^{-25}$ kg) values $L_{l2}$, $L_{t2}$, $L_{R2}$, $L_{max2}$ correlate with the corresponding parameters characterizing the deviation of the structural elements of the TPU macromolecule during the propagation of ultrasonic or thermal waves (Table 3). For sound ($m_3 = 9.12\cdot10^{-35}$ kg) and thermal ($m_4 = 1.81\cdot10^{-37}$ kg), the corresponding values of the sizes of structural formations indicate their ability to move along the force bonds of the structural elements

**Table 6.**

Sizes of particles and quasi-particles that are able to move in the structure formation of TPU

| Material | TPU | TPU+W | TPU+Fe | TPU+Mo |
|---|---|---|---|---|
| $L_{l1}$, nm | 13.8 | 13.3 | 13.4 | 13.3 |
| $L_{l2}$, nm | 0.032 | 0.031 | 0.031 | 0.031 |
| $L_{l3}$, nm | 1320 | 1266 | 1275 | 1273 |
| $L_{l4}$, nm | 29499 | 28307 | 28505 | 28472 |
| $L_{t1}$, nm | 14.9 | 15.1 | 15,0 | 14,9 |
| $L_{t2}$, nm | 0.035 | 0.035 | 0.035 | 0.035 |
| $L_{t3}$, nm | 1418 | 1441 | 1428 | 1423 |
| $L_{t4}$, nm | 31706 | 32231 | 31922 | 31814 |
| $L_{R1}$, nm | 12.1 | 12.2 | 12.1 | 12.1 |
| $L_{R2}$, nm | 0.028 | 0.029 | 0.028 | 0.028 |
| $L_{R3}$, nm | 1156 | 1161 | 1154 | 1150 |
| $L_{R4}$, nm | 25851 | 25951 | 25801 | 25719 |
| $L_{max1}$, nm | 17.8 | 17.0 | 17.3 | 17.7 |
| $L_{max2}$, nm | 0.042 | 0.039 | 0.041 | 0.042 |
| $L_{max3}$, nm | 16915 | 16194 | 16541 | 16912 |
| $L_{max4}$, nm | 37894 | 36212 | 26988 | 37841 |

of macromolecules to significant distances, which significantly exceed the linear dimensions of nanostructured regions (ordered and disordered) in TPU systems [6, 27].

## Conclusions

The use of the Debye temperature (frequency) parameter to predict the processes of structure formation and energy transfer in metal-filled polymer systems allows predicting the manifestations of auxetic behavior during the propagation of ultrasonic waves (provided $\theta_D^l = \theta_D^t$, or $\omega_D^l = \omega_D^t$). Harmonic and anharmonic effects for the structural elements of TPU macromolecules were analyzed based on the values of Debye temperatures (frequencies). Since the displacement of the structural elements of macromolecules has the order of the interstructural distance, the components of the interaction energy in its decomposition are of the same order per one structural element. With anharmonic effects of higher orders, the influence of intermolecular interactions becomes noticeable. The parameters characterizing the critical deformations of interstructural connections, forced elasticity, shear for TPU systems are significantly different from the corresponding values for systems based on linear amorphous polymers. The values of Debye temperatures make it possible to analyze the structure of auxetic polymer compositions.

Due to Debye temperatures (frequencies), Poisson's ratio can be expressed using relations (3), (7) and (9):

$$\nu = \frac{2-\left(\frac{\omega_D^l}{\omega_D^t}\right)^2}{2\left(1-\left(\frac{\omega_D^l}{\omega_D^t}\right)^2\right)} = \frac{2-\left(\frac{\theta_D^l}{\theta_D^t}\right)^2}{2\left(1-\left(\frac{\theta_D^l}{\theta_D^t}\right)^2\right)}$$

and Grüneisen parameters by expressions (18), (18$^*$):

$$\gamma_L = \frac{3}{2}\left(\frac{\omega_D^l}{\omega_D^t}\right)^2 - 2 = \frac{3}{2}\left(\frac{\theta_D^l}{\theta_D^t}\right)^2 - 2;$$

$$\gamma_A = \frac{3}{2}\frac{3\left(\frac{\omega_D^l}{\omega_D^t}\right)^2-4}{\left(\frac{\omega_D^l}{\omega_D^t}\right)^2+2} = \frac{3}{2}\frac{3\left(\frac{\theta_D^l}{\theta_D^t}\right)^2-4}{\left(\frac{\theta_D^l}{\theta_D^t}\right)^2+2}.$$

The obtained relations for Poisson's ratio and Grüneisen parameters due to the Debye temperature make it possible to determine these parameters not only by the results of mechanical measurements, but also by thermophysical, infrared spectroscopy, X-ray structural analysis (Debye temperatures are determined).

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# Температури Дебая та наноструктурованість поліуретанових ауксетиків

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За експериментальними значеннями швидкостей поширення поздовжніх, поперечних та поверхневих ультразвукових хвиль розраховані енергії фононів та визначені обмежуючі частоти і температури Дебая у зразках металонаповнених поліуретанових ауксетиків. Моделювання структуроутворень таких систем та отримані значення решіткового, акустичного параметру Грюнайзена дозволило знайти середньоквадратичне зміщення атомних груп молекулярної сітки, а також межі вимушеної еластичності, деформації зсуву та деформації міжструктурного зв'язку. Встановлено взаємозв'язок між частотами (температурами) Дебая та коефіцієнтом Пуассона, параметром Грюнайзена. Квантово-механічний підхід до переміщення електронів, атомних груп молекулярної сітки, теплових та звукових фононів дозволив оцінити розмірі наноутворень у композиція. Аналізуються теоретичні значення коефіцієнта Пуассона, отримані на основі моделей полімерних ауксетиків та процесів поширення різного типу ультразвукових хвиль в таких системах.

**Ключові слова*:*** полімерний ауксетик, поздовжня, поперечна та поверхнева хвилі, швидкість поширення, коефіцієнт Пуассона, температури та частоти Дебая, середньоквадратичне відхилення, наноструктурованість.