NONLINEARITY EFFECT OF HIGHLY ELASTIC DEFORMATION OF AN AMORPHOUS POLYMER

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The analysis of the kinetics of the tensile deformation of *amorphous polyimide* samples with a constant rate of $7 \cdot 10^{-5} < \dot{\varepsilon} < 6 \cdot 10^{-3}$ s^{-1} at constant values of the temperature T in the warm state ($T = 293$ K) and under the conditions of moderate ($T = 77$ K) and deep ($T = 4.2$ K) cooling begun in [1] was continued. The three-stage deformation diagrams were registered in [1] and are shown schematically in Fig. 1, here $\varepsilon = \dot{\varepsilon} t$ is the relative deformation, σ is the deforming stress. The initial stages of linear elasticity $\sigma_{\mathrm{I}} = M_e \varepsilon$ with Young's modulus $M_e = M_e(T)$ were recorded within $\varepsilon < 0.1$. The next relaxation stage σ_{II} was interpreted in [1, 2] as a consequence of the thermomechanical activation of specific *elaston excitations* on molecular chains in an amorphous polymer, i.e., elementary acts of highly elastic deformation under the action of effective stress $\sigma^* = \sigma - \sigma_i(\varepsilon; T)$ (Fig. 2). Here, σ_i is the entropy component of internal stresses caused by changes in conformational entropy during the straightening of molecular chains. The stage of highly elastic deformation σ_{III} is also determined by the kinetics of elaston excitations, it always has an extended linear component $\sigma_{\mathrm{III}} = \sigma_{fe} + M_{he} \varepsilon$ with the modulus of entropy elasticity $M_{he} = M_{he}(T)$ and the conditional limit of elasticity σ_{fe}. But when the part of the samples were deformed in a warm state of $T = 293$ K, a significant deviation from the linear law was found within the strength limit of polymer $\varepsilon < \varepsilon_r$.
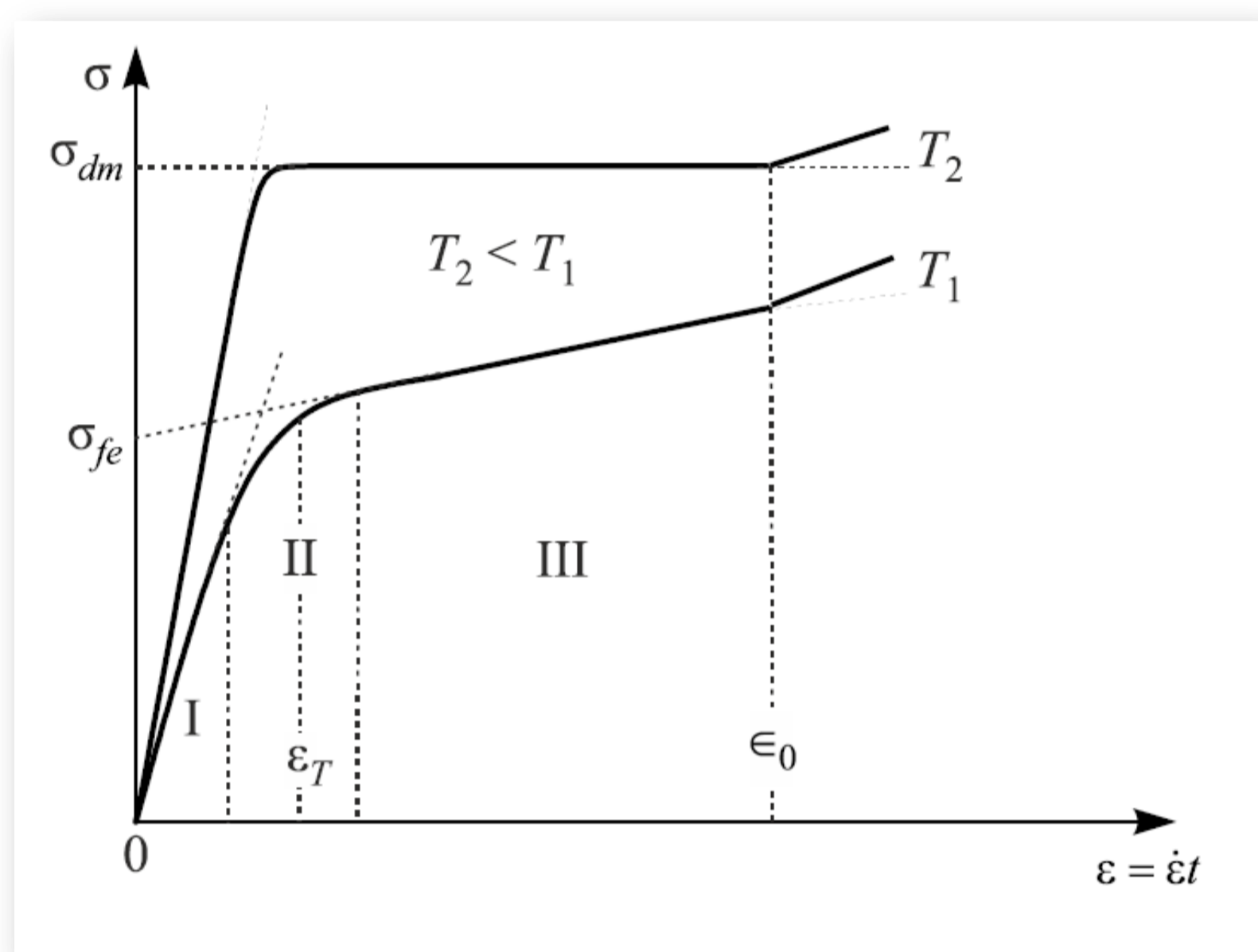

Fig. 1. General view of the deformation diagram and its transformation at polymer cooling. The lower curve T_1 and σ_{fe} is the deformation state of a warm or moderately cooled polymer; the upper curve T_2 and σ_{dm} is the limiting state of low-temperature deformation melting.
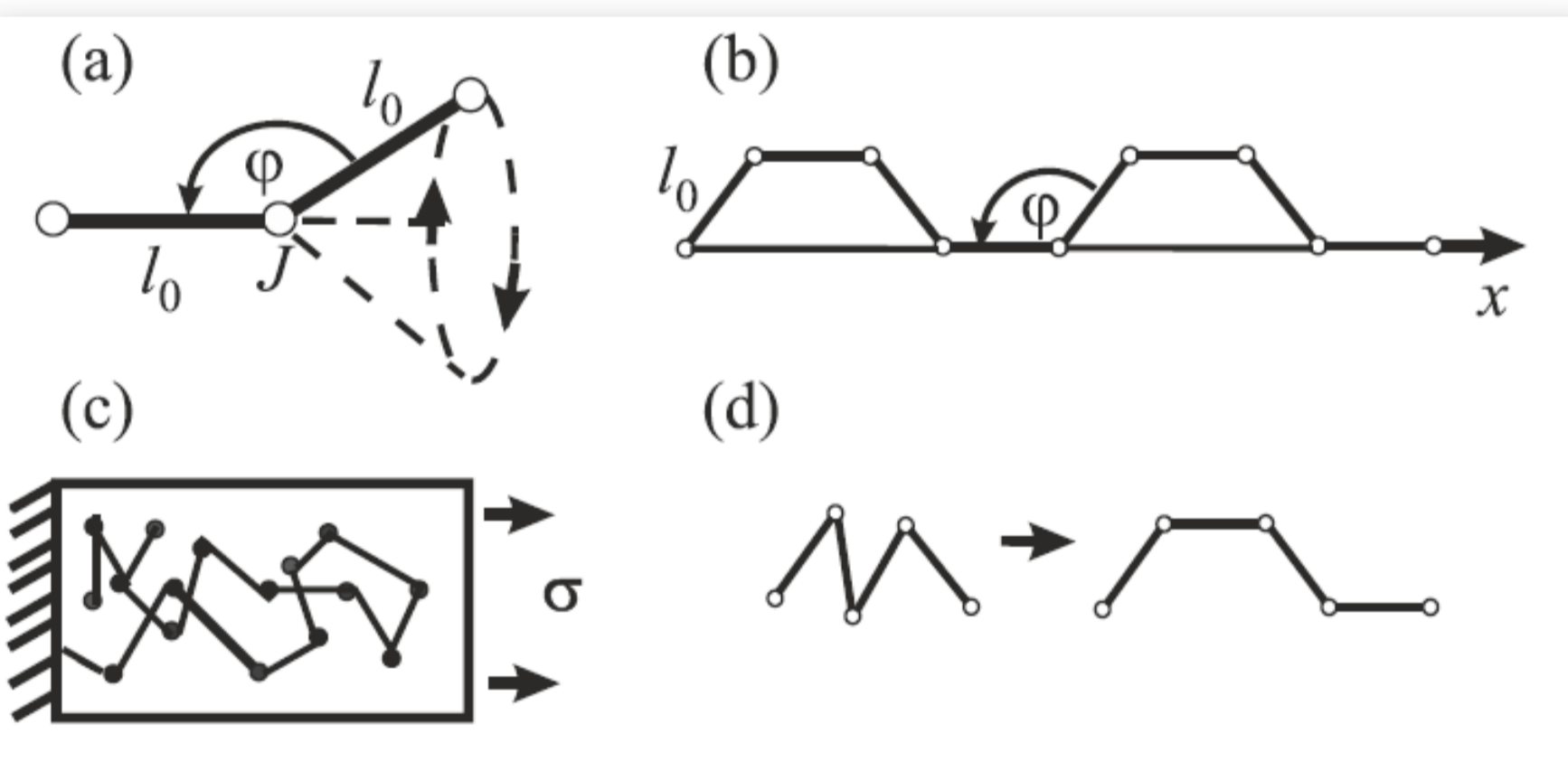

Fig. 2. Mechanical model (rods – joints) of the monomer structure of a molecular chain, a fragment of a molecular coil (sample) and an elementary act of highly elastic deformation: limited rotation of adjacent monomer units (a), molecular chain straightened along the x axis (b), conformations of molecular chains in a polymer sample (c), mechanical activation of the molecular segment (elaston excitation) (d), l_0 is monomer unit (rod), J is simple covalent bond (joint), φ is bond angle.

The nonlinearity of the stage σ_{III} is interpreted as a consequence of the nonlinear dependence of on deformation with the second-order elastic modulus $\mu_{he} = \mu_{he}(T)$:

$$\sigma_i(\varepsilon; T) = M_{he}\varepsilon + \mu_{he}\varepsilon^2. \tag{1}$$

This assumption transforms the four-parameter nonlinear deformation equation [2] into a more complex five-parameter nonlinear equation, in which the kinetics of elaston activation is complicated by the consideration of nonlinearity (1):

$$\frac{d}{d\varepsilon}\sigma = M_e - (M_e - M_{he})\,\beta\,\mathrm{sh}\left[\frac{\sigma - M_{he}\varepsilon - \mu_{he}\varepsilon^2}{(M_e - M_{he})\varepsilon_T\sqrt{1+\beta^2}}\right]. \tag{2}$$

Parameters of this equation are three isothermal coefficients of elasticity $M_e(T)$, $M_{he}(T)$, $\mu_{he}(T)$ and two kinetic coefficients β, ε_T. Its solution with the initial condition is described by the formula:

$$\sigma(\varepsilon; T, \dot{\varepsilon}) = (M_e - M_{he})\,\varepsilon_T\,\sqrt{1+\beta^2}\,\ln\left[\frac{\sqrt{1+\beta^2}+\beta+1+\left(\sqrt{1+\beta^2}-\beta-1\right)\delta(\varepsilon)}{\sqrt{1+\beta^2}+\beta-1+\left(\sqrt{1+\beta^2}-\beta+1\right)\delta(\varepsilon)}\right] +$$
$$+ 2\mu_{he}\varepsilon_T^2[1-\delta(\varepsilon)] + (M_{he}-2\mu_{he}\varepsilon_T)\,\varepsilon + \mu_{he}\varepsilon^2. \tag{3}$$

The exponential function $\delta(\varepsilon) = \exp(-\varepsilon/\varepsilon_T)$ determines the shape of the deformation diagram within the relaxation stage σ_{II}.

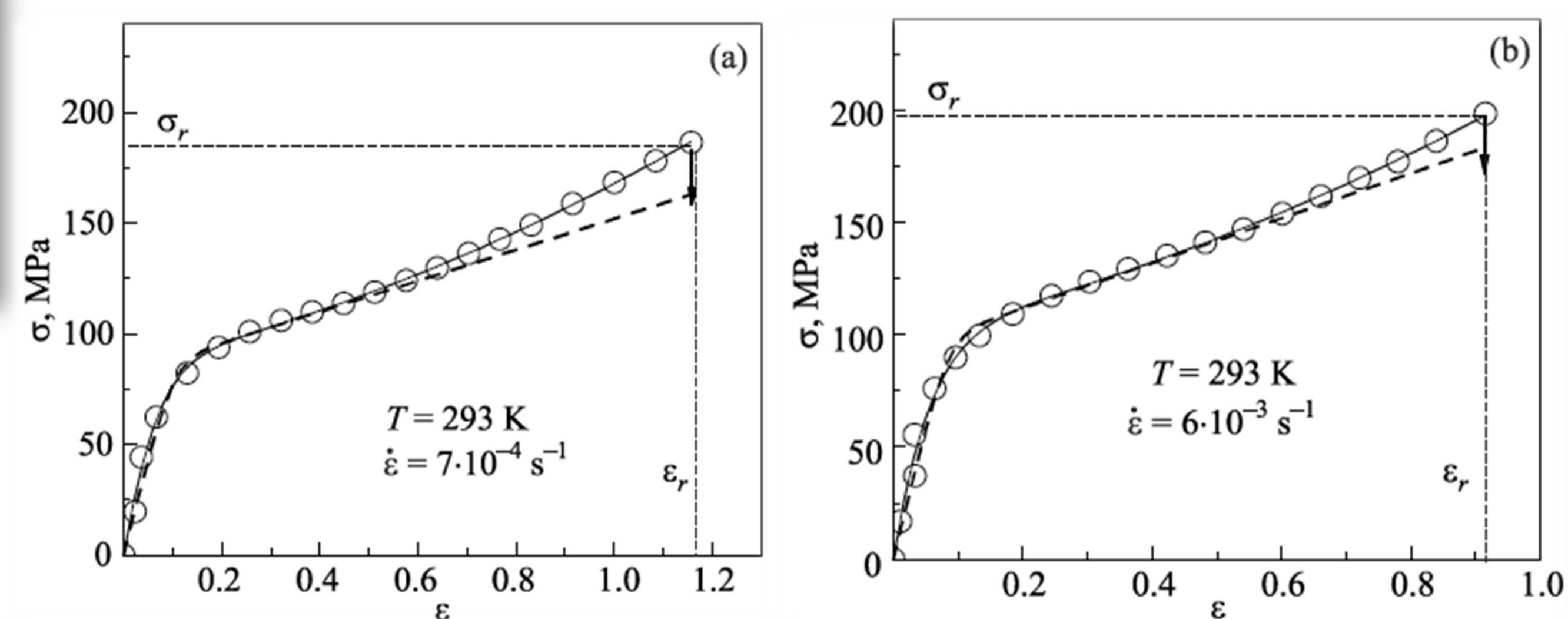Fig. 3. The deformation diagrams of two samples of amorphous polyimide at $T = 293$ K and two values of the deformation rate recorded in the experiments [1]: ○ – experimental points. Their analytical approximations are also shown: by the function $\sigma(\varepsilon)$ – formula (3), solid line; by the function $\sigma(\varepsilon)$ without taking into account nonlinearity, dash line.

Table. Optimal values of rheological characteristics of polyimide samples obtained as a result of analytical approximation of their tensile test diagrams by the function (3).

$\dot{\varepsilon}$, s^{-1}	β	ε_T	M_e, MPa	M_{he}, MPa	μ_{he}, MPa	σ_{he}, MPa	$\sigma(\varepsilon_r; T, \dot{\varepsilon})$, MPa
$7 \cdot 10^{-4}$	0.6	0.05	1413	52	34	92	187
$6 \cdot 10^{-3}$	1.2	0.05	1745	65	51	100	198

[1] V. D. Natsik, H. V. Rusakova, S. V. Lubenets, V. A. Lototskaya, and L. F. Yakovenko, Fiz. Nizk. Temp. 49 569 (2023) [Low Temp. Phys. 49, 521 (2023)], https://doi.org/10.1063/10.0017812.
[2] V. D. Natsik, H. V. Rusakova, Low Temp. Phys. 49, 228 (2023). http://dx.doi.org/10.1063/10.0016875.