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Plastic Deformation of Glassy Polymethylene: Computer-Aided Molecular-Dynamic Simulation[1]

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Abstract—Molecular-dynamic simulation of low-temperature plastic deformation ($T_{\rm def}$ = 50 K, $T_{\rm def}/T_{\rm g} \le 0.3$) is studied for glassy polymethylene under the regime of active uniaxial compression and tension for a cell composed of 64 chains containing 100 $-\mathrm{CH_2}$ groups in each (as united atoms) and with periodic boundary conditions. Thirty-two such cells are created, and, in each cell, polymethylene chains in the statistical coil conformation are independently constructed. The cells are subjected to isothermal uniaxial compression at $T_{\rm def}$ = 50 K by ε = 30% and by ε = 70% under uniaxial tension. In the course of loading, a σ–ε diagram is recorded, while the mechanical work spent on deformation, the changes in the overall potential energy of the system, and the contributions from various potential interactions (noncovalent van der Waals bonds, chemical links, valence and torsional angles) are estimated. The results are averaged over all 32 cells. The relaxation of stored potential energy and residual strain after complete unloading of the deformed sample is studied. The relaxation of stored energy and residual strain is shown to be incomplete. Most of this energy and strain is stored in the sample at the deformation temperature for long period. The conformational composition of chains and the average density of polymer glass during loading are analyzed. Simulation results show that inelastic deformations commence not with the conformational unfolding of coils but with the nucleation of strain-bearing defects of a nonconformational nature. The main contribution to the energy of these defects is provided by van der Waals interactions. Strain-bearing defects are nucleated in a polymer glass during tension and compression primarily as short-scale positive volume fluctuations in the sample. During tension, the average density of the glass decreases; during compression, this parameter slightly increases to $\varepsilon \approx 8\%$ and then decreases. An initial increase in the density indicates that, during compression and at $\varepsilon < 8\%$, coils undergo compactization via an increase in chain packing. During compression, the concentration of *trans* conformers remains unchanged below $\varepsilon \approx 8\%$ and then decreases. During compression, it means that in a glass, coils do not increase their sizes at strains below $\varepsilon \approx 8\%$. During tensile drawing, coils remain unfolded below $\varepsilon \approx 35\%$; at higher strains, coils become enriched with *trans* conformers or unfold. At this stage, the concentration of *trans* conformers linearly increases. The development of a strain-induced excess volume (strain-bearing defects) entails an increase in the potential energy of the sample. Under the given conditions of deformation, nucleation of strain-bearing defects and an increase in their concentration are found to be the only processes occurring at the initial stage of loading of glassy polymethylene. The results of computer-aided simulation are compared with the experimental data reported in the literature.

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INTRODUCTION

Polymer physics as an independent scientific direction dates back to the interpretation of the basic phenomenon of entropic elasticity [1–3]. However, since then, the mechanism of deformation of chain macromolecular structures has remained a challenge for many academic studies [4–6] and for polymer materials science [7–10]. Nowadays, polymer science faces problems of the physics of deformation of glasses [11–15].

Against the background of articulate concepts on the plasticity of low-molecular-mass crystals [11, 16], the concept of inelastic deformation in disordered solids is far from perfect. Earlier ideas on the mechanism of plastic flow in glasses date back to the physics of flow of highly viscous low-molecular-mass liquids [17]. The analysis of the deformation of glasses at high temperatures not very far from glass-transition temperature $T_{\rm g}$ primarily supports the concepts concerning the liquidlike mechanism of this process. However, low-temperature deformation of glasses at $T \le (0.5–0.7)T_{\rm g}$ is different. At low $T_{\rm def}$, the deformation in various glasses shows many features that are characteristic

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of crystals (formation of shear bands and a yield tooth in σ–ε diagrams, the Bauschinger effect, etc.) [4–6, 14, 16, 18, 19]. This circumstance suggests that the concept of low-temperature plasticity in glasses should be supplemented with some crystal-like features [19, 20].

At present, the adopted standpoint is that, in macromolecular glasses, plasticity likewise proceeds via the mechanism of viscous flow of liquids [11, 13, 15]; however, this process is aggravated by the uncoiling of polymer coils [21, 22]. Coil unfolding (or uncoiling) under the action of external forces is the central process for the model of forced elasticity, which is widely used in the physics of glassy polymers [11–15, 21, 22]. According to this model of deformation, kinetic limitations are controlled by the ability of coils to undergo conformational transformations, which provide their unfolding. Macroplastic flow of a glassy sample (the stage of deformation after the yield region) is attained when conformational transitions proceed easily, as is the case in rubbers. In other words, this model assumes that, in macromolecular glasses, plastic deformation is similar to that in rubbers. Only the applied external stress is sufficiently high. A theoretical model of the plastic process has been constructed in [13].

However, this model has failed to explain many features of this process [4, 6, 10, 14, 18–20], including the above-mentioned crystal-like features of deformation [18, 19] and the deformation of glasses composed of rigid macromolecules, which are appreciably extended before deformation. Evidently, chains with low and medium rigidity can be unfolded and disentangled without any ruptures at high strains under all regimes of loading. However, in numerous publications devoted to the deformation of polymer glasses, neither experimental evidence nor theoretical speculations have been reported in favor of the assumption that unfolding is the limiting stage in the overall kinetics of deformation. This assumption has been adopted without any verification, and most scientists have simply accepted it at face value.

In the last 20 years, the results of experiments on the thermodynamics of plastic deformation, even for flexible-chain glassy polymers [18, 19, 23–27], showed that this process never commences with conformational coil unfolding. Immediately after transition to the post-Hookean regime of deformation (in glassy polymers, the Hookean regime is usually completed at $\varepsilon > 2$–2.5% at T_{room}), the potential energy of the samples increases; once this process is finished (the energy approaches the stationary limit), a well-pronounced yielding and macroscopic plastic flow commence.

Therefore, in a glass, plastic flow can arise only in a structurally excited state, when, in a material, the concentration of the above-mentioned strain-bearing defects with increased energy approaches a critical level. (This level is different for each polymer.) In a structurally intact state (defect-free state) of a glass, plastic flow is prohibited.

According to the model of plasticity with strain-bearing defects [23], such defects are the main carriers of inelastic strains (displacements) in a glassy material; later, the chain dimensions and conformational set are adjusted locally to the strain stored by the defect [18, 19, 23–27]. It appears that chain adjustment is accomplished through chain uncoiling. With no exceptions, all classical models of plastic deformation of glassy polymers fail to explain the experimentally observed energy accumulation; i.e., these models are inadequate and require further revision.

In the last 20 to 30 years, many studies have been devoted to the computer-aided simulation of plasticity in glassy polymers (see, for example, [28–37]). In most publications, the method of molecular dynamics has been used to study the conformational rearrangements in polymer chains and variations in the rates of such rearrangements under the action of an external force, the orientation of chain segments, the volume changes in elementary deformation events [31, 33–35, 37–39], and some other problems associated with chain behavior. However, in all the above-cited publications, growth in the potential energy of a polymer glass during its deformation has been neglected, while structures responsible for this growth have not been identified. This outcome is odd because, in this approach, all authors ignored the main process, which seems to be the central stage responsible for the macroscopic plasticity in glassy macromolecular materials [18, 19].

The objective of this study is to independently verify the mechanism of low-temperature plastic deformation in glassy polymers via the methods of computer-aided simulation when the key kinetic role belongs not to coil unfolding but to the nucleation and growth of strain-bearing defects in glasses under the action of external stress and when these defects are not associated with any conformational rearrangements in polymer chains. The results of molecular dynamic simulation of plastic deformation (uniaxial compression and tension) for an isotropic glassy system composed of 32 cells with 64 model polymethylene chains containing 100 $-CH_2$ groups (united atoms) in each cell are presented. In this study, the following main problems are revisited.

(i) How and for which processes is the work of external forces, W, spent during the deformation of a polymer glass? That is, which part of W is stored in the sample as internal energy ΔU and which part is dissipated as deformational heat Q? Which structural rearrangements are responsible for changes in the potential energy of polymer glasses during their deformation?

(ii) How does the relaxation of ΔU and the dimensions (strain) of a polymer glass during its unloading proceed?

(iii) Which potential intramolecular and intermolecular interactions are responsible for the accumulation of ΔU in a glassy sample during its loading?

(iv) How does the density of a polymer glass change during its deformation and subsequent unloading?

We can optimistically expect that the answers to the above-stated questions will offer better insight into the mechanisms of deformational processes in glasses composed of organic macromolecules.

MOLECULAR MODEL AND SIMULATION PROCEDURE

Into a calculation cubic cell with periodic boundary conditions, 64 polymethylene units containing 100-CH_2 groups (united atoms) each are placed. All 32 cells are constructed, and each cell includes 64 independent chains in the conformations of a random coil. All cells are deformed at 50 K in the regime of active uniaxial compressive and tensile deformation at a rate of 0.01 Å/ps ($\sim 10^{-2}$ with respect to the speed of sound). The results are averaged over all 32 cells.

Valence bonds and valence angles are given by the following harmonic potentials:

$$U(L) = K_L(L - L_0)^2 \quad \text{and} \quad U(\theta) = K_\theta(\theta - \theta_0)^2,$$

where L is the length of a covalent bond, $L_0 = 1.53$ Å, $K_L = 1047.5$ kJ kg^{-1} Å^{-2}, $\theta_0 = 113.0°$, and $K_\theta = 167.6$ kJ kg^{-1} rad^{-2}.

For chain torsion angles, the following potential is selected:

$$U(\varphi) = K_1[1 + \cos(3\varphi)] + K_2[1 + \cos(\varphi)],$$

where $K_1 = 6.7$ kJ kg^{-1} and $K_2 = 1.634$ kJ kg^{-1}. Nonvalence interactions are described by the Lennard-Jones potentials:

$$U(r) = \varepsilon_{LJ}[(R_{min}/r)^{12} - 2(R_{min}/r)^6],$$

where $\varepsilon_{LJ} = 0.503$ kJ kg^{-1} and $R_{min} = 4.2654$ Å.

For the numerical integration of the Newtonian equations of motion, the fast Verlet algorithm [40] with an integration step of 1 fs is used. Temperature in the system was maintained with a "collision" thermostat [41, 42] with the parameters $\lambda = 5.5$ ps^{-1} and $m_0 =$ 1 a.m. As a result, the increase in viscosity is low (below 1%). Pressure was set and maintained with a Berendsen barostat [43].

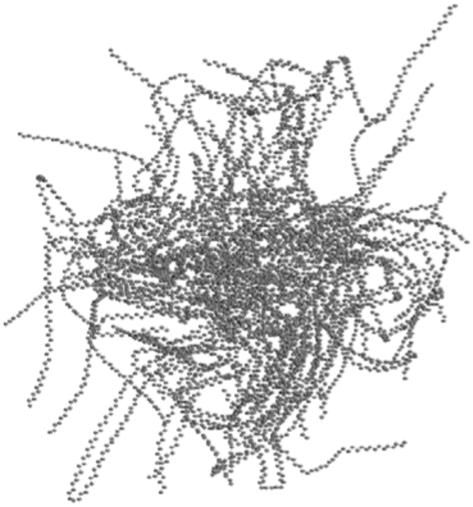
For the initial system, 32 cells are united into one cell; in this cell, molecular dynamic simulation at a temperature of 800 K and at constant volume is performed for 20 ps. Then, the dimensions of the calculation cell are decreased with a rate of 0.05 Å ps^{-1} until the density of the system achieves $\rho = 0.8$ g/cm^3. Then, the melt is cooled at a cooling rate of 0.1 K ps^{-1} to 250 K; later, at a constant temperature and a pressure of 1 atm, an additional molecular dynamic-simulation run is performed until the system reaches equilibrium.

The resultant melt of chains is cooled at a rate of 0.1 K ps^{-1} to 50 K at a constant pressure, and the melt is allowed to stay for 60 ps. Then, the system is subjected to active isothermal deformation via a change in the corresponding dimensions of the calculation cell. Once $\varepsilon = 30\%$ (compression) or $\approx 70\%$ (tension) is attained, a pressure of 1 atm is applied in all directions; then, this system is allowed to relax for 2 ns and, later, this system is heated to 250 K at a rate of 0.1 K ps^{-1}.

RESULTS OF SIMULATION

Structure of the Initial Computer Glass

The structure of one of the samples at 250 K is shown below.



This system does not show any high density fluctuations or voids. The atom-free volume is uniformly distributed in the calculation cell.

Density fluctuations are short-scale and can be revealed only by the detailed structural analysis of this system; such analysis is planned for future. In all 32 samples, there are no traces of crystallinity, even though the fraction of *trans* conformers is high: ≈0.925 (Fig. 1a). Figure 1b shows the length distribution histogram for the *trans* sequences. Since the relative number of individual *trans* conformers is high (28% at 250 K and 18.5% at 50 K), they are not shown in the figure. As follows from Fig. 1b, the fraction of *trans* sequences L_1 containing more than 10 methylene groups is low and cannot provide the existence of a crystallite of reasonable dimensions.

In addition, the calculations show that, during cooling, the dynamics of conformational transitions slows down. For example, within 50 ps at 250 K, the 400 $t \leftrightarrow g^{\pm}$ transition occurs; at temperatures of 100 K or lower, the number of such transitions approaches zero. In this case, the acceleration of transitions do not change the conformational composition of chains (Fig. 1a).

Figure 2 illustrates changes in density ρ of the computer sample during its cooling from 250 to 50 K. At 50 K, $\rho = 0.996$ g/cm^3, a value that agrees with the experimental data [44–48]. Volume thermal expansion coefficient β_v shows a jump at ≈165 K; in this

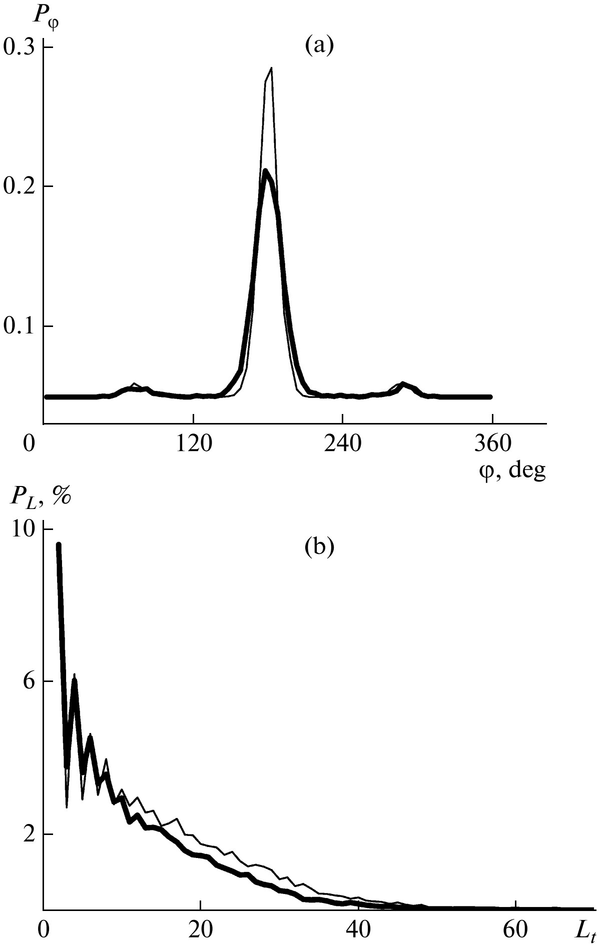


Fig. 1. Distributions P_L of (a) internal rotation angles in the test samples and (b) the *trans* sequences of different lengths L_t: (bold line) 250 K and (narrow line) 50 K.

study, this temperature is assumed to be glass-transition temperature T_g of the system.

Therefore, in our opinion, at 50 K, we have amorphous polymethylene in the glassy state at temperatures well below T_g. These samples were used in our further studies. Under the above conditions, deformation is a low-temperature process: $T/T_g \approx 0.3$. This result is important because, in glassy polymers, the mechanisms behind high-temperature and low-temperature deformation are known to be different [18, 19].

Mechanical Characteristics of Glasses and Thermodynamic Characteristics of the Deformation Process

Figure 3 presents the simulated stress–strain σ–ε diagrams for the polymer glass under active loading at 50 K for uniaxial compression (a) and tension (b). In addition, Fig. 3 shows deformation work W; the

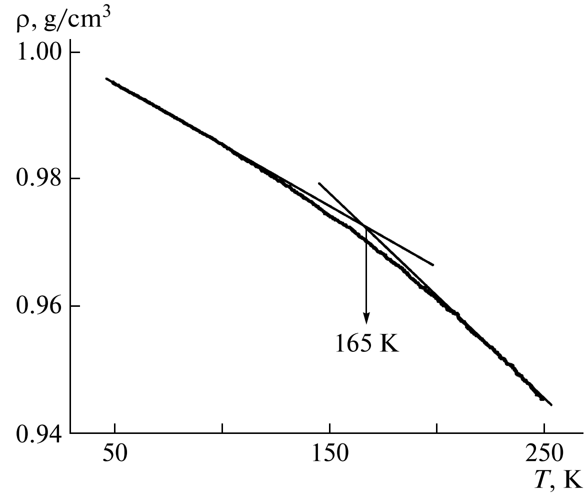


Fig. 2. Changes in density ρ of the computer sample during its cooling from 250 to 50 K at normal pressure.

heat of inelastic deformation, Q; and potential energy ΔU stored by the glass during loading.

The σ–ε diagrams and the dependences of W, Q, and ΔU on strain are similar to experimental ones [5, 6, 14, 21–27, 49]. Below $\varepsilon \approx 1.5$–2.5%, the sample shows an elastic (Hookean) response; in this case, the tensile elastic modulus is $E_t \approx 2.3$ GPa and the compressive modulus is $E_c \approx 2.6$ GPa. These values approach the known experimental values measured at T_{room} [5, 14, 23, 24, 49]. The diagrams illustrating compression and tension clearly show the yield tooth passing its maximum at a tensile strain of $\varepsilon_y \approx 12$–13%. During compression, the yield stress achieves ≈195 MPa; during tensile drawing, ≈150 MPa. Experimental data at T_{room}: for PMMA, $\sigma_y = 105$ MPa [4–6, 14, 49]; for epoxyamine crosslinked glassy polymer, $\sigma_y \approx 150$ MPa [50]; for polyamide, $\sigma_y = 200$ MPa [51]. In other studies on the simulation of deformation of glassy polymers [30, 33–35], similar values of σ_y were obtained.

New result obtained in our simulation experiments is an increase in potential energy ΔU of the system that commences at the early stages of loading and the tendency of this increase toward saturation. During tensile drawing, ΔU approaches its limit at $\varepsilon \approx 40$–50%. During compression, no saturation occurs; however, the rate of energy gain at $\varepsilon > 25\%$ markedly decreases. For glassy polymers, real deformation experiments show that ΔU approaches its limiting value at $\varepsilon \approx 30\%$ during compression and tension [18, 19, 23–27].

Experimental evidence on the energy gain for a polymer sample under deformation is interpreted under the assumptions that this increase is provided by the nucleation of new excited structural defects and that the sum of their local energies provides overall stored energy ΔU. Later, these states are referred to as

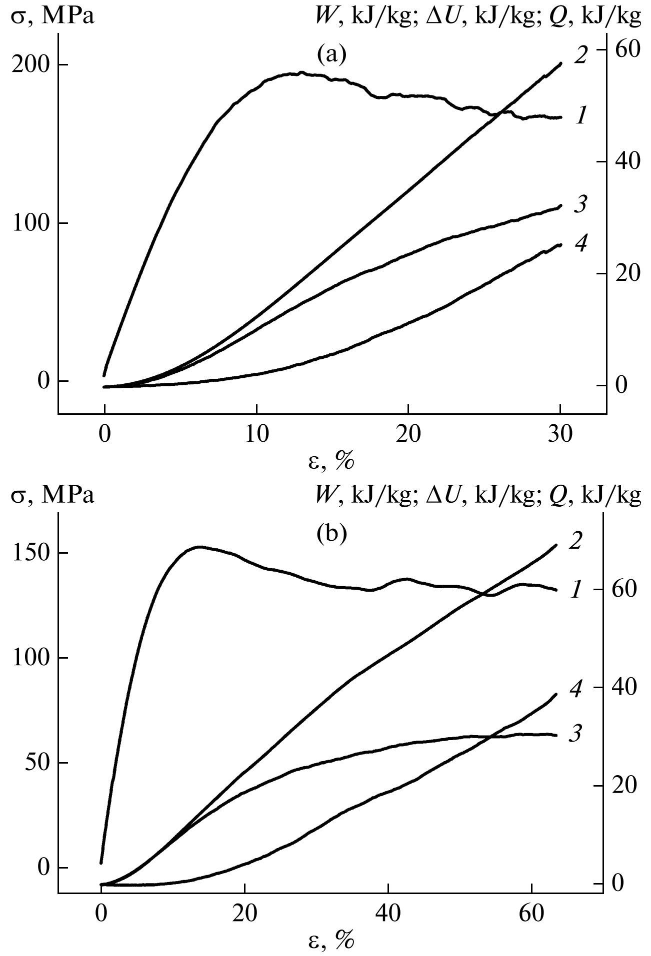


Fig. 3. (*1*) Mechanical and (*2–4*) thermodynamic characteristics of the deformation of the sample: (*2*) work W, (*3*) potential energy ΔU, and (*4*) heat of inelastic deformation Q of the computer sample during its deformation in the active mode under (a) uniaxial compression and (b) tension; $T = 50$ K.

excited strain-bearing defects with increased energy. Their structure will be discussed below.

From the viewpoint of structural concepts of the physics of crystals, a “defect” has no physical meaning in a disordered solid. The structure of a glass includes only topological (geometric) defects. The rules of translational symmetry do not apply to any atom (or atomic group) in a glass.

In this study, the term “strain-bearing defect” is related to the structure in some volume of a glassy bulk in which the coordinates of atoms are changed during loading with respect to the initial coordinates of the same atoms. A strain-bearing defect is an inelastic local structural rearrangement in a glass. This rearrangement is not a linear elastic, Hookean transformation. At low T_{def}, most structural defects are preserved in the deformed glass during its unloading, whereas elastic defects undergo a high rate of relaxation. Relaxation of strain-bearing defects during loading will be discussed below.

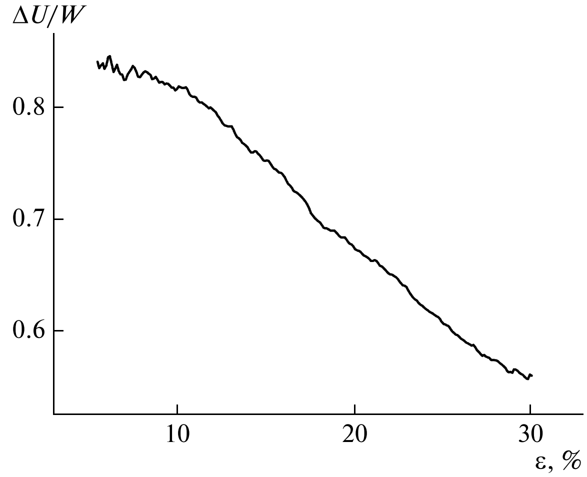


Fig. 4. Changes in $\Delta U/W$ during loading (uniaxial compression): $T = 50$ K, $\dot{\varepsilon} = 10^{-2}$ Å/ps.

Strain-bearing unelastic defects induced in a sample at the early stages of loading are short-scale. Hence, in the simulated glass, as was the case in the experiments, at the early stages of deformation when ΔU of the sample starts to grow, no microscopic structures, such as shear bands or crazes, are nucleated.

Important information concerning the limiting stage of the deformation process is provided by the ratio $\Delta U/W$, which is measured in the course of the deformation run [18, 19, 23–27]. Ratio $\Delta U/W$ plotted against ε is often used for the interpretation of the mechanism of deformation during plastic deformation of solids [18, 19, 23, 24, 27, 46]. Ratio $\Delta U/W$ shows which fraction of work W during loading is transformed into ΔU, i.e., which work is spent on the nucleation of strain-bearing defects. Figure 4 presents calculated values of $\Delta U/W$.

In the elastic region (at $\varepsilon < 2.5\%$), $\Delta U/W$ approaches unity. This tendency is expected because, for linear (Hookean) elasticity, no dissipative processes in solids occur and, during loading, all stored energy of elastic deformation Q_{el} is transformed into heat.

During loading of a solid, linear elasticity is followed by retarded elasticity. (In organic polymers, retarded elasticity (anelasticity) at T_{room} usually exists at values of ε varying from 2.5% to yield strain ε_y corresponding to the yield tooth at the maximum.) Then, the process passes to the regime of plasticity (after the yield point). The specificity of retarded elasticity can be formulated as follows: During unloading in the region of retarded elasticity, material transforms into the state with $\varepsilon_{res} = 0$; i.e., formally, its behavior is elastic. However, in the loading–unloading cycle, the σ–ε diagram shows a hysteresis loop, which is indicative

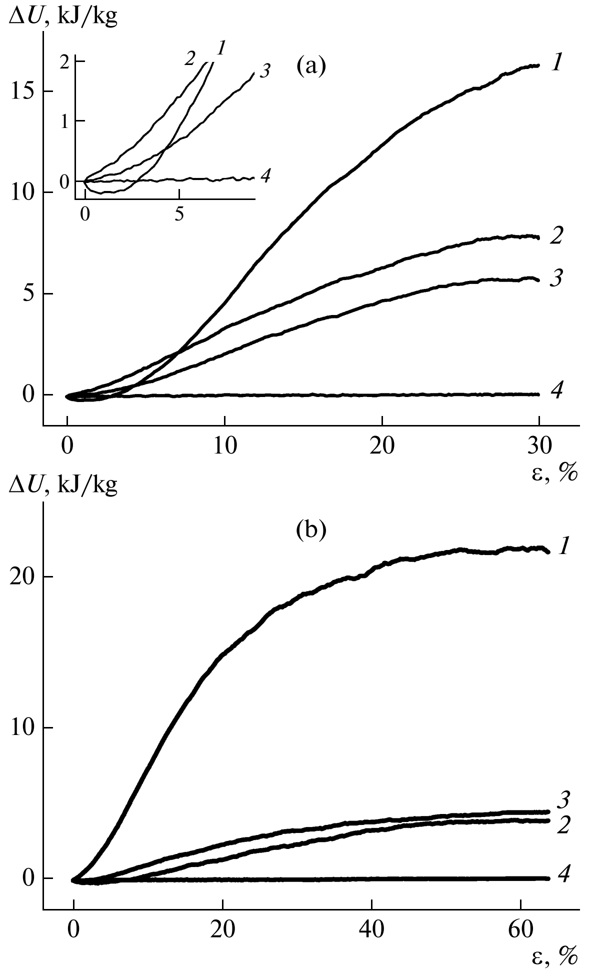


Fig. 5. Contribution from various interactions to potential energy ΔU of the system during (a) uniaxial compression and (b) tension at 50 K: (*1*) noncovalent interactions, (*2*) energy of internal rotation angles, (*3*) energy of valence angles, (*4*) energy of valence bonds. Insert: changes in the components of overall energy during compression by $\varepsilon < 7\%$.

of strain-energy dissipation, and relaxation of retarded elasticity proceeds at a slower rate than that of elastic relaxation [4, 6, 11, 16, 59]. This stress–strain behavior of solids is classified as retarded elasticity or anelastic behavior [6, 16, 45, 52].

In the post-Hookean region, $\Delta U/W$ should decrease because, owing to internal friction, dissipation of W in the course of deformation increases. The simulation results (Fig. 4) fairly agree with these speculations and with real experiments [18, 19, 23–27].

At the early stages of inelastic deformation (at $\varepsilon \geq 5\%$) of the computer sample, a conversion of ≈85% of spent mechanical work W to ΔU directly indicates that, in this interval of strains, another difficult process proceeds. All work of external force is fully consumed by this process, i.e., by the generation of excited strain-bearing defects, thereby providing an overall gain in the potential energy in a glassy material. Only ≈15% of work is dissipated as heat. This process is central for the kinetics of the nucleation of plasticity in glassy polymers, and it controls the kinetics of post-Hookean deformation of an organic polymer glass at least at the early stages of retarded elasticity.

Simulation experiments make it possible to separate all stored potential energy ΔU into individual components corresponding to the different types of intra- and intermolecular interactions. Figure 5 presents the results for compression and tensile drawing. In the case under study, the overall potential energy of the deformed glass includes four components: energy of intermolecular van der Waals interactions ΔU_{vw}, energy of opening of valence angles ΔU_{13}, energy of changes in dihedral angles ΔU_{14}, and energy of stretching of chemical bonds ΔU_{12}. As follows from Fig. 5, the maximum contribution to the stored energy ΔU is provided by noncovalent van der Waals interactions ΔU_{vw}. Their fraction achieves ≈71% during tensile drawing and ≈50% during compression. Energy of stretching of chemical bonds ΔU_{12} makes practically no contribution to ΔU. The contributions from ΔU_{13} and ΔU_{14} are nearly equal (≈12.5%) during tensile drawing; during compression, the contributions are ≈25% for ΔU_{13} and ≈18% for ΔU_{14}.

During compression, polymer glasses show another fascinating feature: Changes in ΔU_{vw} pass the minimum below $\varepsilon \leq 7\%$; only then does it increase. It seems that, during compression, in this interval of strains, compactization of coils (packing of chains in the sample) initially occurs and the energy of the sample decreases. In the course of loading during compression, this compactization is enhanced because, in this case of compression, the hydrostatic component of the stress tensor is positive. The data on changes in the density of the samples under uniaxial compression (see Fig. 9a) verify this assumption. However, note that overall energy ΔU of the system likewise increases in the interval where intermolecular interactions become weaker; i.e., overall energy ΔU is accumulated by the sample under compression even at low strains. The causes of this behavior of glassy polymethylene will be discussed below.

These results make it possible to draw the following conclusion: During loading, a gain in overall potential energy ΔU of a polymer glass is provided by the development of specific defects of a primarily intermolecular nature that are due to ΔU_{vw} interactions in the regime of retarded elasticity. Changes in ΔU_{vw} are mainly associated with the local increase in interchain distances.

Structure of Deformed Samples

Figure 6 presents the structure of initial and deformed samples (uniaxial compression by $\varepsilon = 30\%$ and tension by $\varepsilon = 70\%$). In the deformed sample, no macroscopic structural changes are observed. In particular, no micropores or cracks are formed. The

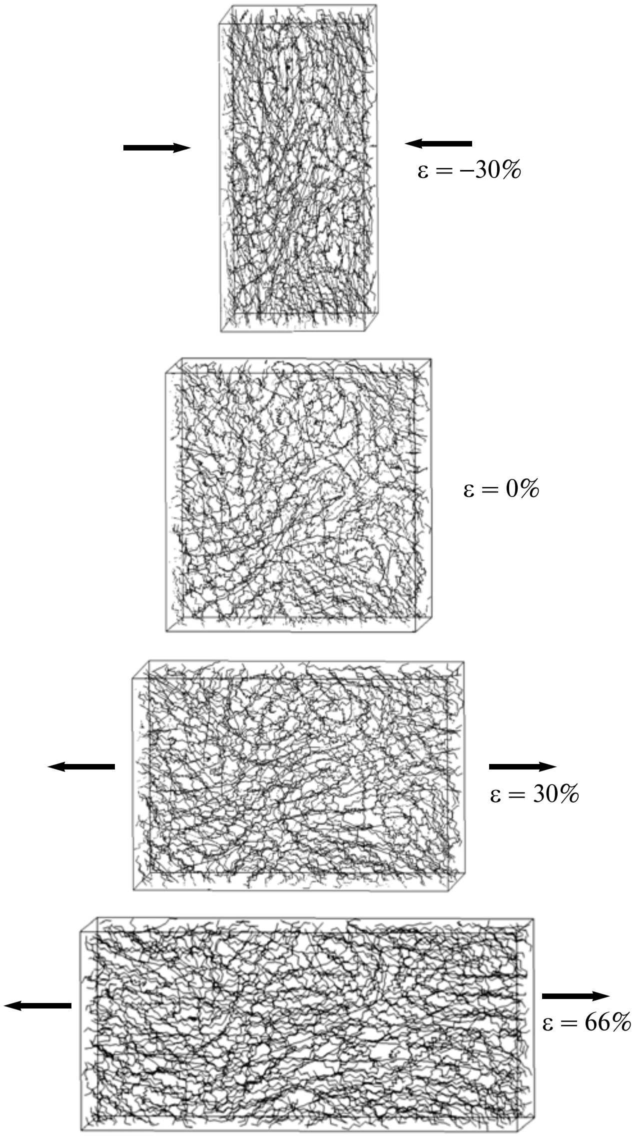


Fig. 6. Structure of the initial sample (ε = 0) after uniaxial compression (ε = 30%) and tension (ε = −30 and 66%): $T = 50$ K, $\dot{\varepsilon} = 10^{-2}$ Å/ps.

length distribution of *trans* sequences likewise remains practically unchanged (Fig. 7). Indeed, a certain orientation of chain fragments is observed, but its value is still low.

Of special interest are conformational changes in chains of the deformed sample. Figure 7 shows the distribution of internal rotation angles before (solid curve) and after (dashed curve) deformation. The initial distribution is slightly changed after deformation. During the deformation of a glassy polymer by ε ≈ 30–35% (compression), no changes in the conformational set of chains were observed in studies on the simulation of deformation of glassy PE [33, 34] and in experiments [53, 54].

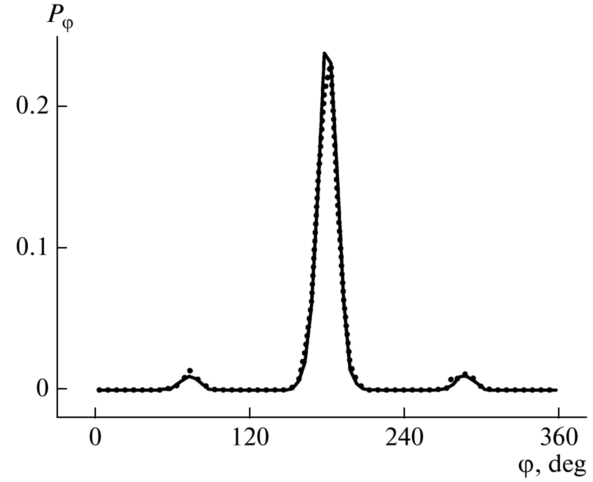


Fig. 7. Histogram of the distribution of internal rotation angles P_φ of the computer glass (solid line) before and (dotted line) after uniaxial compression (ε = 30%) at 50 K.

Figure 8 shows that, during compression by 30%, the fraction of *trans* conformers decreases (from 0.929 to 0.911) owing to an increase in the content of $g^{\pm}$ conformers. Therefore, in this region of compressive strains, chains are not extended but reduce their dimensions and become folded and compacted.

However, during compression, the fraction of *trans* conformers is constant below ε ≈ 7.8%. Since overall potential energy ΔU of the sample under deformation gradually increases, at ε ≤ 7% (Fig. 2), the observed invariability of the fraction of *trans* conformers in the system suggests the absence of any correlation between the potential energy of the sample and conformational rearrangements in chains at least at the above strains.

Another situation is observed during tensile drawing. In this case, the fraction of *trans* conformers remains unchanged at strains below ε ≈ 35% and amounts to about 0.928–0.929. Then, this fraction linearly increases with increasing strain up to ε ≈ 60% and reaches 0.934.

The behavior of glassy polymethylene during tensile drawing shows that chains and coils are unfolded, but this event occurs only after nucleation of strain-bearing defects (Fig. 3b). During tensile drawing, no compactization of chains and postpacking are observed; this result is expected. Such process is prevented by the negative component of the stress tensor [52].

Density Variations during Deformation of a Polymer Glass

Question concerning changes in the density of glassy polymers during their inelastic deformation is a subject of ongoing discussion in the literature [47, 55]. Over many years of studies, abundant experimental data on this problem have been accumulated [14, 47,

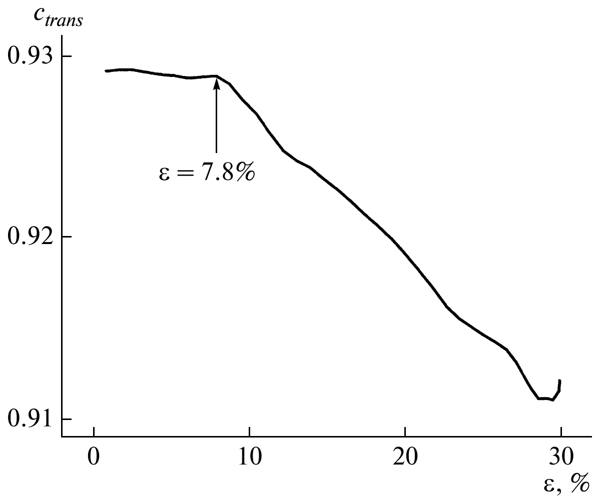


Fig. 8. Changes in the fraction of *trans* conformers during uniaxial compression: $T = 50$ K.

48, 55]. All experimental results can be briefly formulated in the following way: In most cases, the density of a sample deformed by moderate strains does not change; in some cases, it slightly increases or slightly decreases. This observation is related to experiments on compression, tensile drawing, and shearing.

Figure 9a presents the results of our simulation experiments on changes in the density of a glass during loading. During compression and tensile drawing, changes in density ρ are different. During tensile drawing, density decreases at the early stages of loading; at $\varepsilon = 30\%$, it achieves 0.960 g/cm^3, and at $\varepsilon \approx 45\%$, it reaches 0.956 g/cm^3. Hence, as a result of tensile drawing, the density of a deformed sample decreases by ≈3.8% with respect to that of the initial glass.

During compression, the density of a sample initially increases by ≈0.5% below $\varepsilon \approx 7\%$; then, it decreases by ≈1.6% at $\varepsilon = 30\%$. This initial increase is partially provided by the elastic response of the material at the early stages of loading. (The calculated Poisson coefficient is $\nu = 0.42$.) However, the elastic response of the sample can explain the above increase in ρ only partially, because this increase progresses well after the completion of the elastic response of the material; i.e., density increases even in the regime of retarded elasticity ($2.5\% < \varepsilon < 7\%$).

At strains $\varepsilon < \varepsilon_y \approx 12\%$, the central process is the development of inelastic strain-bearing defects, and this process is accompanied by the development of a new free volume in the material. As a result, densification is more efficient at low strains, and an increase in volume due to the nucleation of defects dominates at $\varepsilon > 7\%$.

The results on density variations are very important because, in our opinion, they reveal the correlation between the gain in the potential energy of the sample during loading of polymer glasses and the growth in free volume. In other words, in the case of low-temperature deformation of polymer glasses at $\varepsilon > \varepsilon_y$, the coefficient of chain packing decreases. However, it is problematic to suggest that, in the sample, chains are uniformly spaced. It is most likely that volume locally increases and that this process includes short chain fragments. Now, we proceed to the analysis of density fluctuation in a sample induced by deformation and we expect to clarify the physical pattern for the accumulation of excess volume in polymer glasses.

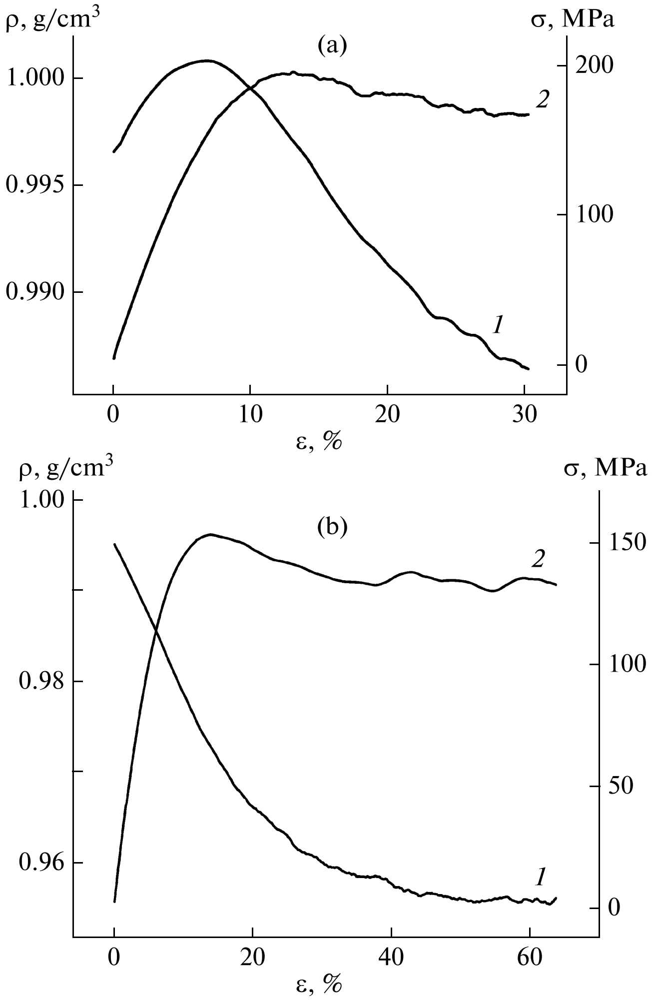


Fig. 9. (*1*) Density–strain ε and (*2*) σ–ε diagrams for polymethylene computer glass during (a) compression and (b) tension: $T = 50$ K, $\dot{\varepsilon} = 10^{-2}$ Å/ps.

During tensile drawing, ΔU (Fig. 3b) and density (Fig. 9b) approach their limiting values at practically equal strains: $\varepsilon \approx 45\%$. In our opinion, this result verifies the existing correlation between the volume variations in the deformed sample and the gain in ΔU. However, note that the recorded changes in density during tensile drawing and compression are low; this evidence may explain a slight increase in the energy of the glassy sample during loading. The maximum level of the accumulated energy in polymer glasses achieves only ≈10% with respect to the heat of fusion of a PE crystal.

Figure 10 shows the temperature dependence (50–250 K) of the density for two polymethylenes with different mechanical prehistories. Curve *1* demonstrates changes in $\rho(T)$ for an initial undeformed sample. Of course, the density of this sample decreases with temperature. Curve *2* illustrates the heating of the sample after its compression at 50 K (by $\varepsilon = 30\%$) and complete instantaneous unloading. After unloading, the sample preserves its residual strain, which is close to 30%. Curves *1* and *2* are appreciably different. This result is evident because the structure, density, and internal energy of the deformed sample are different from those of the initial sample. However, once $T > T_g$ is attained, the densities of both samples become equal. This evidence implies that, at $T > T_g$, polymers approach the same structure, independently of their prehistory below T_g.

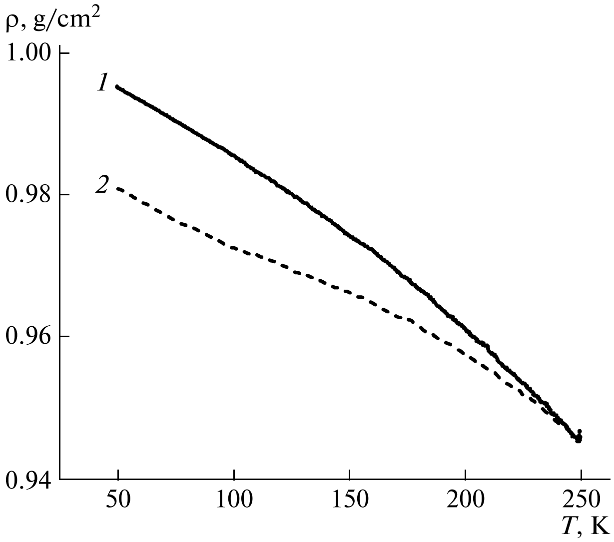


Fig. 10. Temperature-induced variations in the densities of (*1*) undeformed polymer glass and (*2*) polymer glass after compression at 50 K.

DISCUSSION AND COMPARISON WITH EXPERIMENTAL RESULTS

In the literature, abundant data on the mechanics and deformation thermodynamics of glassy polymers are available [4–6, 12–14, 18–27, 45, 47, 48, 55]. Thus, it is possible to compare simulation and experimental results in detail.

The character of changes in all thermodynamic parameters during deformation qualitatively agrees with the experimental results [23–27]. In addition, the quantitative thermodynamic characteristics of this process agree with the experimental data. For example, in the simulation, work W spent on the deformation below $\varepsilon = 30\%$ amounts to 58 kJ/kg during compression and 72 kJ/kg during tensile drawing ($\varepsilon = 64\%$); during compression at T_{room}, [23, 26, 51], the experiments yield 30–65 kJ/kg for various glassy polymers. The heat of deformation obtained in simulation experiments is ≈25 kJ/kg (compression by $\varepsilon = 30\%$), a value that agrees well with the experimental results at room temperature (23–32 kJ/kg for various polymers [23, 26, 51]). In simulation runs, stored energy ΔU is 32 kJ/kg during compression ($\varepsilon = 30\%$) and 24 kJ/kg during tensile drawing by the same tensile strain. Compression experiments at T_{room} give 20–30 kJ/kg for various polymers [23, 24, 26, 51].

Unfortunately, it is difficult to compare calculated and experimental results for $\Delta U/W$, because no experimental data at low T_{def} are available.

In our opinion, one of the key simulation results is an increase in ΔU once the post-Hookean deformation regime in the glass is attained; in this case, most of work W is spent on an increase in the potential energy of the glass. Similar measurements performed under the same loading conditions at T_{room} for crystals of metallic copper show [52, 56] that, in copper, no marked energy accumulation occurs. More than 95% of work W spent on the plastic deformation of copper is dissipated as heat even at the early stages of loading.

However, during the low-temperature ($T_{def} = 77$ K [46]) plastic deformation of crystalline metals, another scenario comes into play. At $\varepsilon < 1\%$, $\Delta U/W \approx$ 0.8–0.9; i.e., at low T_{def}, crystalline metals behave as polymer glasses.

At low ε, the deformation work of crystals is primarily consumed for the development of dislocations as the carriers of plasticity. Dislocations are defects in crystals whose energy of formation is high. Therefore, when dislocations are formed, the energy of the crystal increases. It is reasonable to assume that, as in the case of metallic crystals, the high level of energy stored in glasses during deformation is provided by the development of structural defects with increased energy. However, classical dislocations can arise and move only in crystal lattices and do not exist in glasses [6, 20].

The thermodynamics of deformation for crystals and glasses can differ appreciably at high strains. For example, in metals at $\varepsilon = 15\%$, $\Delta U/W \approx 0.1$ [46]; in polymer glasses, this ratio is 0.5–0.8 [23, 24, 26]. This simulation gives $\Delta U/W \approx 0.75$ during compression at $\varepsilon = 15\%$ and $\Delta U/W \approx 0.55$ at $\varepsilon = 30\%$ (Fig. 4). These values and experimental results [23–27] show that, in comparison to the plasticity of crystalline metals, the plastic deformation of polymer glasses at high strains proceeds via an appreciably different scenario.

During inelastic deformation of polymer glasses, a high level of stored energy indicates a central role of the nucleation of new defects (or initiation of macroscopic plastic deformation) for the deformation kinetics at strains above yield strain ε_y. This situation does not occur in metallic crystals, where initiation (nucle-

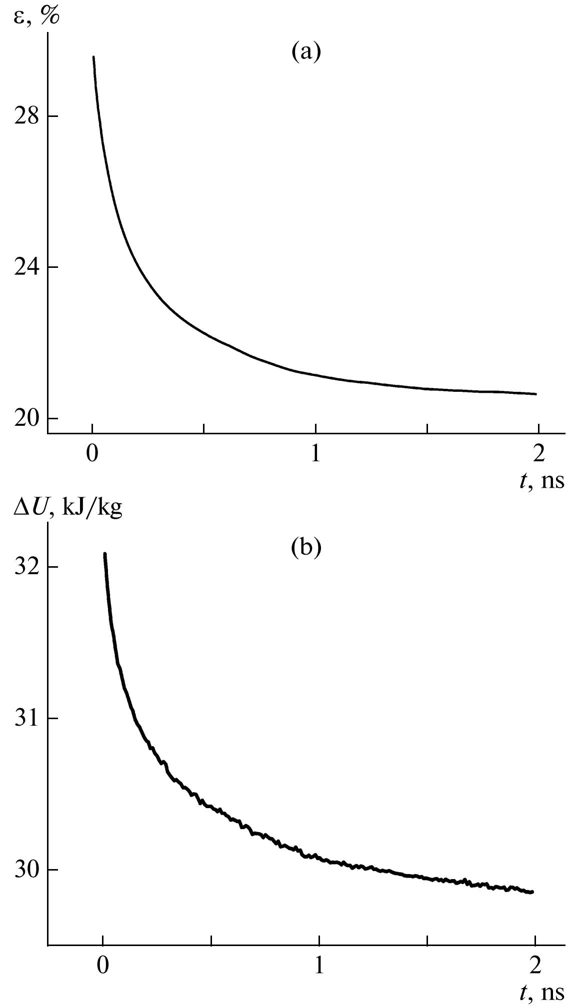


Fig. 11. Relaxation of ε and potential energy ΔU after instant unloading to $\sigma = 0$.

ation of dislocations) is often ceased once yield strain ε_y is attained.

Note that, during deformation of glassy polymers, work W is low, while at the yield point, it is approximately 15–20 kJ/kg, i.e., less than 10% with respect to the heat of fusion of PE crystals (293 kJ/kg [57]). The same ratio between deformation work W and heat of fusion ΔH_m is observed experimentally [6, 15, 22, 45, 47, 48, 57]. Therefore, transition of a solid polymer to the state of plastic flow requires less energy than the transition of the same polymer into a melt during heating.

There is an alternative standpoint that mechanically excited local strain-bearing defects in glasses have an elastic nature. However, the results on the isothermal relaxation of ΔU during unloading of the deformed sample disagree with this standpoint. Figure 11b shows the relaxation of potential energy ΔU stored by a glass at 50 K (compression by $\varepsilon = 30\%$) after instantaneous and complete unloading of the sample. Within 2 ns, relaxation of stored energy ΔU is seen to be incomplete (by only ≈30%). The remaining 70% of the stored energy is preserved in the deformed glass for long period. The experiments show that residual energy can be removed only by heating to temperatures well above T_{def} and T_g [22–27]. The relaxing part of ΔU is transformed into heat.

The fact that, after long-term relaxation in the unloaded state, the deformed sample retains a marked fraction of the stored energy indicates that the stored energy is primarily accumulated not by elastic (Hookean) structures but by local metastable states of the glass that are induced by deformation. Elastic states should rapidly vanish upon unloading. However, complete relaxation of strain-bearing defects and, hence, ΔU requires longer times and increased temperatures. This fact implies that excited states arise owing to either plastic [58] or anelastic local rearrangements [6] occurring in the material under the action of an external force [59].

Relaxation of residual strain-bearing defects requires overcoming of the activation barrier, which is associated with the rearrangement of the atomic structure of the nearest neighborhood. Defects with such characteristics have been found [18, 19, 27, 60–63] in simulation experiments on the shear deformation of atomic bicomponent organic glass. Localized shear transformations have been revealed and studied [58, 60–63] in the simulation of deformation in a metallic glass.

The metastable character of strain-bearing defects is also verified by the results shown in Fig. 11a, which shows isothermal (at 50 K) relaxation of strain ε. The sample deformed by $\varepsilon = 30\%$ quickly (≤0.5 ps) loses the elastic component of overall deformation; then, the inelastic component of residual deformation vanishes. Further relaxation and shape recovery of the sample substantially slow down. Within 2 ns, the relaxation rate of ε becomes almost zero. Only because of prolonged relaxation at 50 K does the sample lose ~9.5% of its overall strain. All residual strain is preserved in the sample over long periods. It can be removed from the sample only via heating above T_g. This behavior is typical of all glassy polymers that have been experimentally studied [22–24, 51].

CONCLUSIONS

Molecular-dynamic simulation of the inelastic deformation of a polymer glass composed of 64 polymethylene chains (model of united atoms) containing 100 $-\mathrm{CH}_2$ groups in each chain shows that the key deformation process is an increase in the potential energy of the sample that commences immediately after the completion of the linear elastic regime. The main contribution to this energy is provided by van der Waals interactions (50–70% of all stored energy ΔU). The contribution from intrachain rotations is low: 12.5% (tensile drawing) or 25% (compression) with respect to overall energy ΔU of the system. A similar contribution is provided by the energy of opening of valence angles of chains. During compression, no coil unfolding is observed, but this process comes into play during tensile drawing at $\varepsilon > 35\%$.

In other words, the stage corresponding to the development of strain-bearing defects, rather than the stage of chain unfolding, is central for the low-temperature plastic deformation of glassy polymers. In glasses, strain-bearing defects are anelastic mechanical states (retarded elasticity [59]); hence, they can persist over long period at unloading temperatures below T_g. The formation of strain-bearing defects is accompanied by the development of an excess volume in the sample. This process occurs during tensile drawing and compression.

Our results pose new challenging questions:

(i) What is the distribution of inelastic defects with respect to local energies and local volumes?

(ii) What is the mechanism of strain-induced heat release Q, which is likely related to the termination of strain-bearing defects [18, 19, 23]?

We hope that analysis of the structure of defects and the kinetics of their nucleation and termination will help solve the posed problems.

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REFERENCES

1. R. Ulman, in *Material Science and Technology*, Ed. by R. W. Cahn, P. Hansen, and E. J. Kramer (VCH, New York, 1993), Vol. 12, p. 358.
2. J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980).
3. A. Yu. Grosberg and A. R. Khokhlov, *Physics in Polymer World. “Kvant” Library, No. 74* (Nauka, Moscow, 1989) [in Russian].
4. *The Physics of Glassy Polymers*, Ed. by R. N. Haward and R. J. Young (Blackie, London, 1997).
5. *The Physics of Glassy Polymers*, Ed. by R. N. Haward (Applied Science, London, 1973).
6. J. Perez, *Physics and Mechanics of Amorphous Polymers* (A. A. Balkema, Rotterdam, 1998).
7. W. F. Chen and D. J. Han, *Plasticity for Structural Engineers* (Springer, New York, 1988).
8. I. Narisava, in *Strength of Polymer Materials*, Ed. by T. Ekobori (Khimiya, Moscow, 1987) [in Russian].
9. I. A. Hamley, *Introduction to Soft Matter* (Wiley, New York, 2003).
10. S. L. Rosen, *Fundamental Principles of Polymeric Materials* (Wiley, New York, 1989).
11. A. S. Krausz and H. Eyring, *Deformation Kinetics* (Wiley, New York, 1985).
12. Yu. S. Lazurkin and R. I. Fogel’son, Zh. Tekh. Fiz. **21**, 267 (1951).
13. R. E. Robertson, J. Chem. Phys. **44**, 3950 (1966).
14. P. B. Bowden, in *The Physics of Glassy Polymers*, Ed. by R. N. Haward (Applied Science, London, 1973), p. 279.
15. V. A. Kargin and G. L. Slonimskii, *Short Essays on Physical Chemistry of Polymers* (Khimiya, Moscow, 1967) [in Russian].
16. M. L. Bernshtein and V. A. Zaimovskii, *Mechanical Properties of Metals* (Metallurgiya, Moscow, 1979) [in Russian].
17. S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941; Inostrannaya Literatura, Moscow, 1948).
18. E. F. Oleinik, S. N. Rudnev, O. B. Salamatina, and M. I. Kotelyanskii, Polymer Science, Ser. A **50**, 773 (2008) [Vysokomol. Soedin., Ser. A **50**, 773 (2008)].
19. E. F. Oleinik, S. N. Rudnev, and O. B. Salamatina, Polymer Science, Ser. A **49**, 773 (2007) [Vysokomol. Soedin., Ser. A **49**, 2107 (2007)].
20. J. J. Gilman, in *Dislocation Dynamics*, Ed. by Rosenfeld (McGraw-Hill, New York, 1968), p. 3.
21. V. A. Kargin and G. L. Slonimsky, in *Encyclopedia of Polymer Science and Technology* (Wiley, New York, 1968), Vol. 8, p. 445.
22. V. A. Kargin, *Selected Works. Problems of Polymer Science* (Nauka, Moscow, 1986) [in Russian].
23. E. F. Oleinik, O. B. Salamatina, S. N. Rudnev, and S. V. Shenogin, Polymer Science, Ser. A **35**, 773 (1993) [Vysokomol. Soedin., Ser. A **35**, 1819 (1993)].
24. E. Oleinik, in *High Performance Polymers*, Ed. by E. Baer and S. Moet (Hanser, Munich, 1990), p. 60.
25. O. B. Salamatina, G. W. H. Hohne, S. N. Rudnev, and E. F. Oleinik, Thermochim. Acta **247**, 1 (1994).
26. E. F. Oleinik, O. B. Salamatina, S. N. Rudnev, and S. V. Shenogin, Polym. Adv. Technol. **6**, 1 (1995).
27. E. F. Oleinik, S. N. Rudnev, O. B. Salamatina, et al., E-Polymers, No. 029 (2006).
28. *Simulation Methods for Polymers*, Ed. by M. Kotelyanskii and D. N. Theodorou (Marcel Dekker, New York, 2004).
29. A. S. Argon, P. H. Mott, and U. W. Suter, Phys. Stat. Solidi B **172**, 193 (1992).
30. D. Brown and H. R. Clarke, Macromolecules **24**, 2075 (1991).
31. M. Hutnik, A. S. Argon, and U. W. Suter, Macromolecules **26**, 1097 (1993).
32. V. V. Bulatov and A. S. Argon, Phys. Rev. **46**, 5275 (1992).
33. F. M. Copaldi, M. C. Boyce, and G. C. Rutledge, Phys. Rev. Lett. **89**, 175505-1 (2002).
34. F. M. Copaldi, M. C. Boyce, and G. C. Rutledge, Polymer **45**, 887 (2004).
35. A. V. Lulin, B. Vorselaars, M. A. Mazo, et al., Europhys. Lett. **71**, 618 (2005).
36. C. Chui and M. C. Boyce, Macromolecules **32**, 3795 (1999).
37. M. D. Ediger and D. B. Adolf, Adv. Polym. Sci. **116**, 75 (1994).
38. A. A. Berlin, *Discussion in Conferences of Division of Polymers and Composites of Semenov Institute of Chemi-*

cal Physics, Russian Academy of Sciences, 2008, 2009 (Moscow, 2009).

39. E. A. Zubova, A. I. Musienko, N. K. Balabaev, et al., Dokl. Akad. Nauk **418**, 493 (2008).
40. M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).
41. A. S. Lemak and N. K. Balabaev, Mol. Simul. **15**, 223 (1995).
42. A. S. Lemak and N. K. Balabaev, J. Comput. Chem. **17**, 1685 (1996).
43. H. J. C. Berendsen, J. P. M. Postma, W. F. Gunsteren, et al., J. Chem. Phys. **81**, 3684 (1984).
44. B. Crist, C. J. Fisher, and P. R. Howard, Macromolecules **22**, 1709 (1989).
45. Yu. K. Godovsky, *Thermophysical Properties of Polymers* (Springer, Berlin, 1993).
46. V. A. Pavlov, *Physical Principles of Plastic Deformation of Metals* (Akad. Nauk SSSR, Moscow, 1962) [in Russian].
47. H. E. H. Meijer and L. E. Govaert, Prog. Polym. Sci. **30**, 915 (2005).
48. B. Crist, in *Materials Science and Technology* (VCH, New York, 1993), Vol. 12.
49. O. A. Hasan and M. C. Boyce, J. Polym. Sci., Part B: Polym. Phys. **31**, 185 (1993).
50. E. F. Oleinik, Adv. Polym. Sci. **80**, 50 (1986).
51. O. B. Salamatina, S. N. Rudnev, V. V. Voenny, and E. F. Oleinik, J. Therm. Anal. **38**, 1271 (1992).
52. Yu. N. Rabotnov, *Mechanics of Deformed Solid* (Nauka, Moscow, 1988) [in Russian].
53. M. Utz, A. S. Atallah, P. Robyr, et al., Macromolecules **32**, 6191 (1999).
54. Z. Xu, B. Jasse, and L. Monnerie, J. Polym. Sci., Part B: Polym. Phys. **27**, 355 (1989).
55. I. M. Ward, *Mechanical Properties of Solid Polymers* (Wiley, London, 1971).
56. S. V. Shenogin, G. W. H. Höhne, and E. F. Oleinik, Thermochim. Acta **391**, 13 (2002).
57. B. Wunderlich and C. M. Cormier, J. Polym. Sci., Part A **5**, 987 (1967).
58. A. S. Argon, in *Encyclopedia of Materials Science and Technology*, Ed. by R. W. Cahn, P. Hansen, and E. J. Kramer (VCH, Weinheim, 1993), Vol. 6, p. 461.
59. M. I. Kotelyanskii, Candidate's Dissertation in Mathematics and Physics (Moscow, 1996).
60. M. J. Kotelyanskii, M. A. Mazo, E. F. Oleinik, and A. G. Grivtsov, Phys. Status Solidi B **166**, 25 (1991).
61. A. S. Argon and L. T. Shi, Philos. Mag. A **46**, 275 (1982).
62. D. Deng, A. S. Argon, and S. Yip, Philos. Trans. R. Soc. London, A **329**, 575 (1989).