Nonlinear Dynamics and the Problem of Polymer Fracture

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Synopsis

The results of the experimental and molecular-dynamics study of the process of mechanical degradation of polymer chain, testifying to the essential role of nonthermal channels of dissipation of elastic energy accumulated during deformation, have been discussed. High-energy molecular products of mechanical degradation, which are able to induce a chain branching process leading to "explosive" formation of submicrocracks, have been discovered. It has been noted that a considerable part of polymer chain energy is concentrated in localized excitations of a soliton type, which play the determining role at all the stages of mechanical degradation under consideration.

Deformation and fracture of polymers as well as of other solids are accompanied by complex and little-studied physicochemical processes. One may assume that, at the stage going immediately after the first act of macromolecule breaking, the elastic energy stored in the macromolecule during its stretching dissipates in the following way:

—It leads to electronic excitation and ionization and is carried away by electrons, photons, and ions.
—It is spent on the fragmentation of chains and transforms into translational, rotatory, and vibratory energy of molecular products of mechanical degradation.
—It transforms into heat including infrared (IR) radiation.

Ultimately, the energy of molecular products of mechanical degradation, electrons, ions, and photons also transforms into heat. This may lead to additional IR radiation, thermal degradation, and plastic flow.

Theoretical interpretation of mechanical degradation is based on a model of thermal fluctuations,[1] which takes into account only thermal processes. These characteristic times of elastic energy thermalization are practically assumed to be small so that direct influence of nonthermal effects on mechanical degradation can be neglected. Both experimental data and the results of computer simulation of mechanical degradation of polymer chain by the method of molecular dynamics are discussed in terms of thermal fluctuations.[2] At the present time the consistent molecular theory of mechanical degradation has not been available.

Two principal questions arise in connection with the development of such a theory. Speaking about thermal fluctuations in solids, one usually bears in mind phonons, which are determined in a harmonic approximation and

weakly interact due to anharmonicity. Can one apply such an approximation to high-excited macromolecules?

The second even more important question relates to the clarification of the potential role of nonthermal channels of transformation of elastic energy, stored during deformation, after the first breaking. This question is closely connected with the determination of characteristic times of thermalization. Besides theoretical considerations, the putting of such a question is also due to considerable difference in the composition of molecular products of mechanical and thermal degradation observed during experiments[3] as well as to the emission of electrons,[4-6] ions, and photons[7] during mechanical fracture of polymers.

The important information concerning the above-mentioned questions could be given by complex investigation of the process of mechanical degradation, and first of all by the study of energies of primary molecular products. The analysis of this channel of accumulated energy transformation is extremely important since it allows one to correlate the corresponding experimental data with the results of computer simulation of mechanical degradation. The simulation may be carried out by molecular dynamics method (MD)—the only available theoretical method of studying nonaveraged characteristics of molecular processes after the first act of breaking.

To carry out the experimental study, the method of registrating molecular products, directly escaping from the main propagating crack, and of determining the kinetic energy of their translation was developed.[8] The mechanical degradation of linear polymer PMMA, network epoxy polymer DGER–mPhDA, and composite material (ebonite) was studied.

It was found that a considerable part of the primary molecular products has very high energies of translation (0.2–0.7 eV) corresponding to translation temperature of the order of thousands of degrees. High values of kinetic energy of molecular products of mechanical degradation clearly testify to their nonthermal origin and are explained by the fact that, during polymer chain breaking, a considerable part of the accumulated elastic energy transforms into the kinetic energy of detachable fragments translation.

To clarify the detailed mechanism of high-energy products formation during mechanical degradation and to analyze the factors, which cannot yet be studied experimentally, molecular dynamics investigation was carried out. The model system considered was a one-dimensional chain of carbon atoms ($m = 2 \times 10^{-23}$ g), modeling a tie molecule in an amorphous layer of a semicrystalline polymer.[9-12] The interaction between neighboring atoms was described by the Morse potential with parameters characteristic for the C — C bond in polyethylene. The number of atoms was assumed to be 50 and 100. The chain was subjected to stretching with constant velocity varying from 1/10 to 1/50 of the sound velocity corresponding harmonic system. The initial velocities of atoms were given in accordance with Maxwell distribution; the process of deformation was preceded by the relaxation of the system to thermodynamical equilibrium. The following conclusions, relating to different stages on stretching process and subsequent mechanical degradation, have been obtained as the result of the studies.

At the stage of stretching, preceding the first breaking, the considerable part of vibratory energy of a macromolecule is concentrated in the form of localized excitations of a soliton type.

The existence of stable elementary excitations of the soliton type in the atom chain with fixed ends where interaction is described by the Morse potential is analytically shown by Collins[13] and numerically in Ref. 14. Rolfe, Rice, and Dancz[14] have not only proved that solitons may exist in one-dimensional chains with different interaction potentials (of Morse and Lehnard–Jones type 6–12 and 6–32), but they have also found that reflections of solitons from free and fixed ends and soliton–soliton interactions for all these potentials are similar to soliton behavior in the Toda chain.[15]

The previous MD analysis of thermal oscillations in one-dimensional chain of atoms, where interaction is described by the Morse potential, carried out by Zhukov[16] showed that two types of lattice excitations coexist in a thermalized chain: phonons and solitons, the solitons being high energy carriers. Several tens of percent of the total energy of the thermalized chain are carried by solitons and this ration increases with temperature. Instantaneous velocity values of the atoms in the middle part of a 500 atom chain are shown in Figure 1. At the initial moment of time (a) only a small region in the middle of the chain—20 atoms (from the 250th up to 270th)—is "heated" while the rest of the chain remains a "cold" zone. The migration of energy from the "hot" zone into the "cold" one is realized both by phonons and solitons. Since the velocity of solitons is supersonic, they leave the "hot" zone outstripping the phonons. Figures 1(b) and (c) show instantaneous values of velocities of the atoms after 2000 and 4000 time steps, respectively; vertical arrows indicate solitons that left the "hot" zone.

Let us call such low-energy solitons ($E_{sol} \simeq kT$) "thermal solitons." The experiments carried out by us showed that solitons also exist in stretched chains at all deformations. The evolution of velocities of all the atoms of a 50 atom chain during stretching up to its breaking is shown in Figure 2. At the initial moment of time the temperature of the chain is 300 K and the velocity of the upper atom is equal to $0.1V_s$ (V_s is the sonic speed). A heavily drawn incline indicates the loading wave front. Thus, to the left of this line one can see the thermal oscillations which take place in an unloaded chain, while, to the right of the line, those which take place in the already stretched chain. It is clear that thermal solitons (shaded) exist both in unloaded and stretched chain. That is why traditional (purely phononic) concepts of thermal motions in stretched polymer chains are not sufficient.

The formation of high-energy (~ 1 eV) excitations of a soliton type after chain breakdown and interactions between solitons of different energies with a stretched bond were described in Refs. 17 and 18. Moreover, the dependence of mass spectrum of fragments, which are the products of mechanical degradation, on the length of the chain and the degree of its stretching were studied in Ref. 17.

Further studies enabled us to obtain the elaborate picture of the process of high-energy (~ 1 eV) soliton formation at different stages of mechanical degradation. Figure 3 shows the evolution of kinetic energies of all the atoms of the chain stretched at the rate of $0.1V_s$. The numbers of the atoms of the chain and the scale of kinetic energy (with scale value 1 eV) are plotted on the left and right ordinate axes, respectively; the scale of time (in time units) is plotted on the abscissa axis. The locations of breakdowns are indicated by asterisks. As usual, the fixed end of the chain is at the bottom, while the end moving at a constant velocity is at the top.
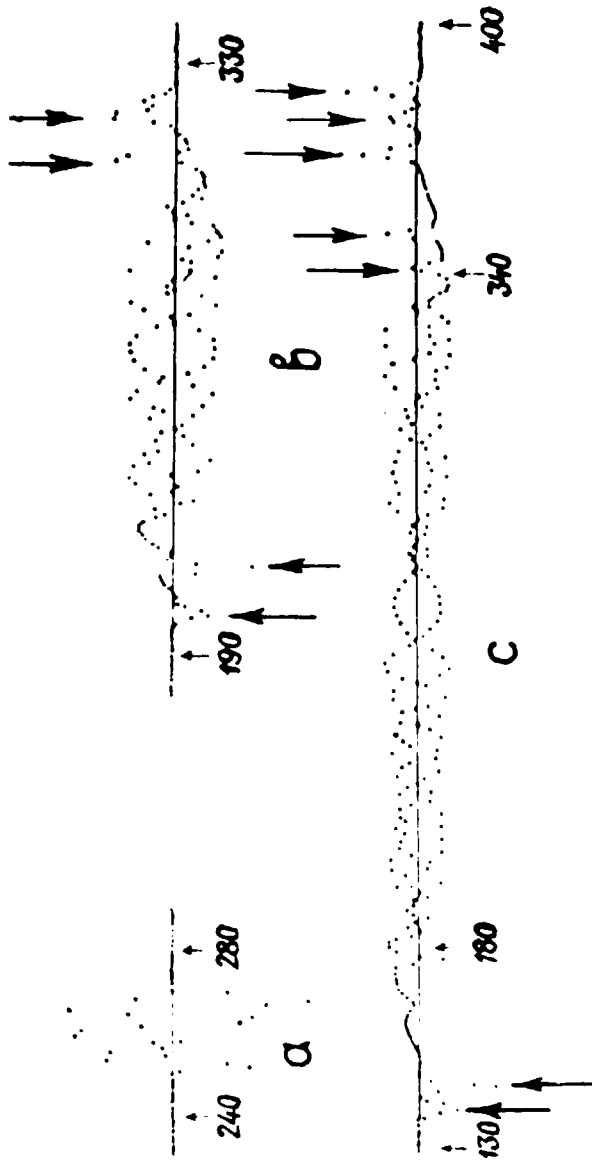
Fig. 1. Instantaneous values of the velocities of 500-atom chain atoms: (a) initial moment of time (zero); only 20 atoms in the middle of the chain (from the 250th to the 270th) are "hot," while the rest of the chain is "cold," that is, the velocities of the rest of atoms are zero; (b) distribution of atoms velocities along the chain after 2000 time steps; (c) after 4000 time steps. The run-out solitons are marked with arrows.
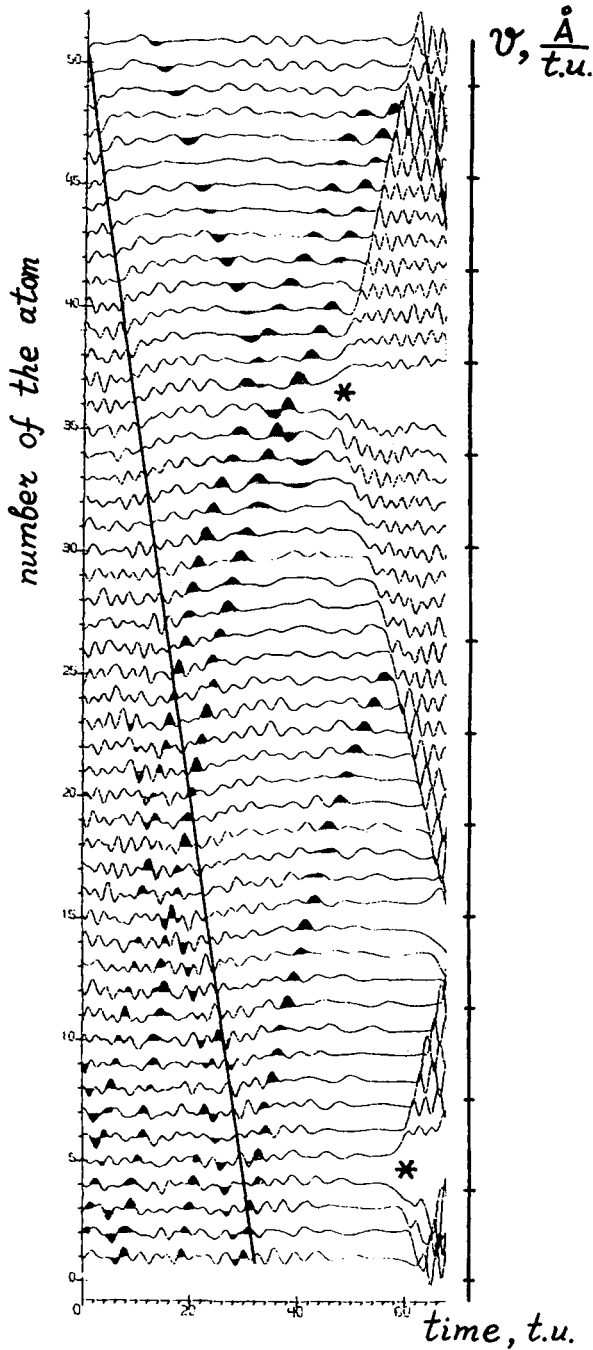
Fig. 2.   Time variation of velocities of all the atoms of a 50-atom chain during its stretching (up to breakdown) and subsequent mechanical degradation. The numbers of atoms are plotted on the left and the velocity scale on the right ordinate axes (the scale value is 1 Å $(t.u.)^{-1}$); the abscissa is the time measured in time units (t.u.), 1 t.u. $= 10^{-14}$ s. At zero the chain temperature is 300 K. The stretching of a chain is realized by the movement of the top atom at constant velocity $0.1 \cdot V_s$, where V_s is the sonic speed. The front of the rarefaction wave is marked with a heavily drawn incline line and thermal solitons are shaded. The locations of breakdowns are marked with asterisks (*).
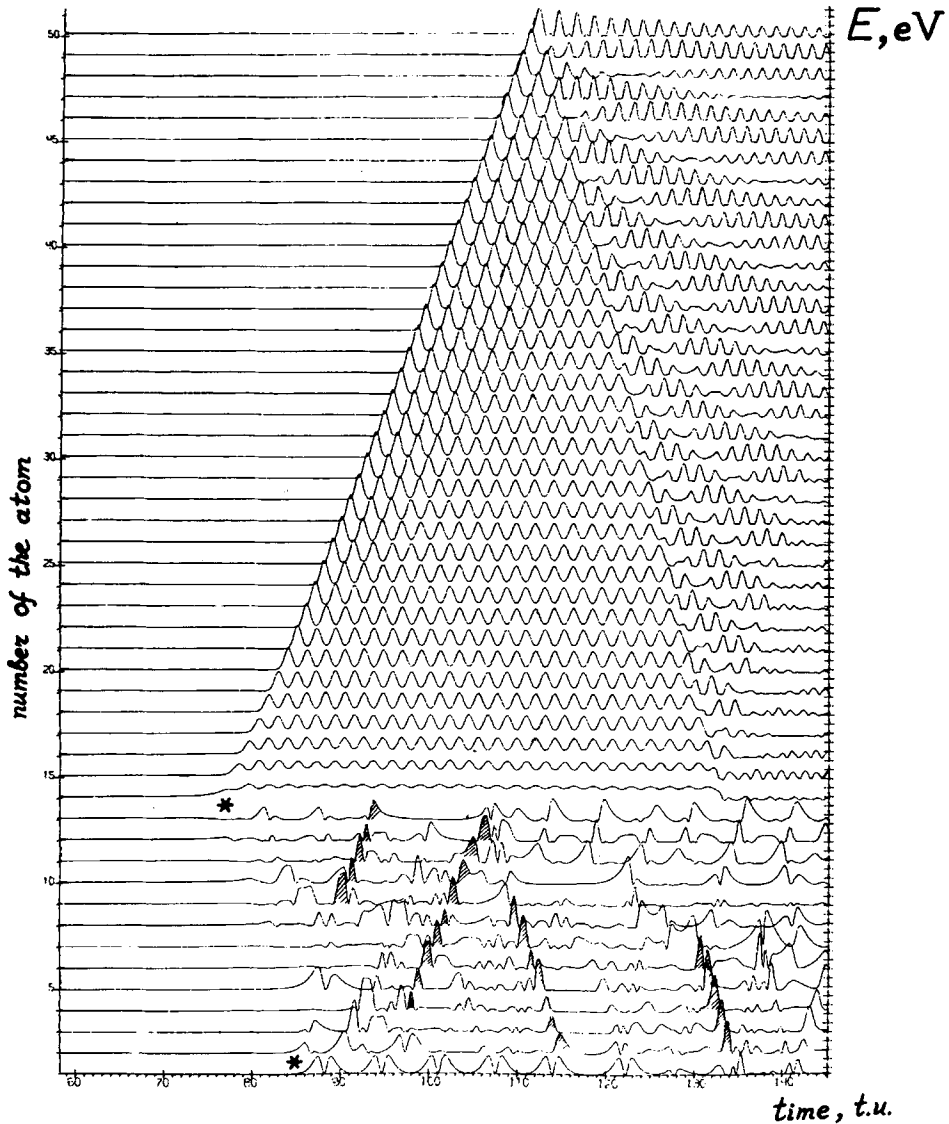
Fig. 3.   Time variation of kinetic energies of all the atoms of a 50-atom chain during its stretching up to breakdown and subsequent mechanical degradation. The numbers of atoms are plotted on the left and the kinetic energy - on the right ordinate axes (the scale value is 1 eV); an abscissa is the time measured in time units (t.u.), 1 t.u. = 10^{-14} s. At zero the chain temperature is zero. The stretching of the chain is realized by the movement of the top atom at constant velocity 0.1 V_s. The locations of breakdowns are marked with asterisks (*).

After the second chain breakdown (86 time units) there appear in fragment 1-13 localized irregular high-energy (more than 3 eV) waves of a soliton type, while regular succession of primary solitons originates in fragment 14-50. These solitons move from the location of the first breakdown towards the upper end of the chain at constant velocity. After reaching the upper end of the chain, the solitons are reflected and move towards the stream of primary solitons.
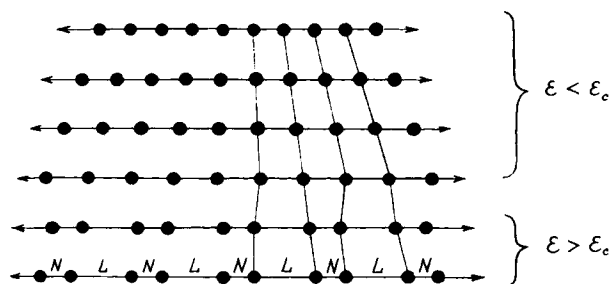
Fig. 4. Structural transition in a Morse chain during its stretching, leading to breakdowns in accordance with the mechanism of the first type.

Thus, at the stage of the polymer chain fragmentation (up to 10^{-11} s after first breakdown) the elastic energy, accumulated during stretching, does not practically transform into the energy of chaotic thermal motions but is mainly converted into the energy of ordered localized excitations of a soliton type.

As a result of the comparative analysis of all the breakdowns observed, one can single out three typical mechanisms of breakdowns.

The mechanism of the first type, typical only for primary breakdowns, is connected with the structural transition in the most stretched part of the chain (Fig. 4). The abrupt transition of the chain atoms into new equilibrium positions takes place in the zone of the stretched chain where deformation exceeds the critical value of $\epsilon_c = 0.224$. In this case the structure of the chain changes in such a way that, instead of the succession of evenly stretched bonds, one can observe the succession of alternating long (L) and normal (N) bonds ...LNLNLNL.... The length of L-bond is $l_L \simeq r_0 + 2\epsilon_c r_0 = (1 + 2\epsilon_c)r_0$ and the length of N-bond is $l_N \simeq r_0$. This structural transition is due to the change in the form of the effective potential for each internal atom of the chain after deformation reaches the critical value ϵ_c; that is, the potential will have two wells instead of one (Fig. 5). During further stretching of the chain, there occur primary breakdowns in L-bonds.

The mechanism of the second type is typical only for the fragments with very high density of energy (~ 1 eV per bond). Such fragments are formed at the initial stage of mechanical degradation. This mechanism is due to the appearance of a soliton packet containing several solitons moving in one direction to the free end of the chain or a large fragment. The following law has been discovered: The packet containing n solitons tears away the fragment containing n atoms.

In the vicinity of the developing breakdown, one can observe correlated movement of the atoms in opposite direction from the location of a future breakdown. Such correlated motion of atoms is caused by the movement of soliton packets in opposite directions. Figure 6 shows the breakdown of a three-atom fragment due to the exit of a three-soliton packet to the free end of the chain. All the solitons of the packet are numbered; the location of the breakdown is indicated by an asterisk (*). The correlated motion of atoms takes place on both sides of the breakdown (arrows indicate the directions of the velocities of atoms).
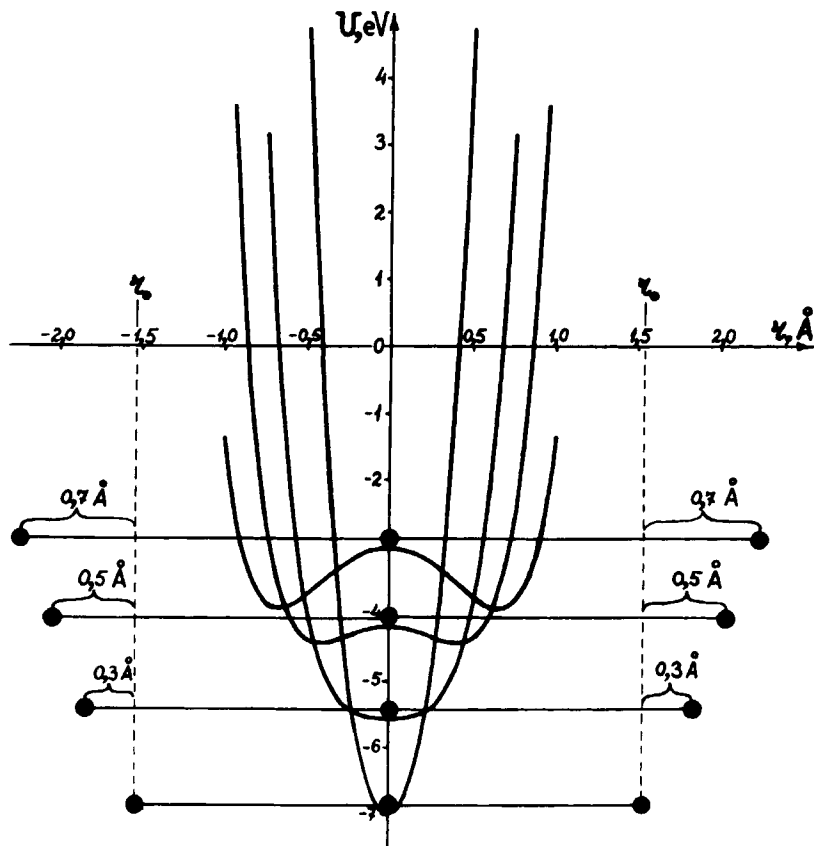
Fig. 5. Evolution of the effective potential for each internal atom of Morse chain during its stretching.

The mechanism of the third type is typical for primary and secondary breakdowns at the late stages of mechanical degradation, when the density of vibratory energy is no longer large ($\sim$ 0.1 eV per bond). The breakdowns of this type are caused by the penetration of a soliton into the stretching zone of the chain, or, to be more exact, into the zone, where the following conditions are valid: the degree of stretching exceeds the critical value ($\epsilon > \epsilon_c$); the degree of stretching increases ($d\epsilon/dt > 0$). Figure 7 shows a secondary breakdown at the late stage of mechanical degradation. A soliton is indicated by "s." When the soliton reaches the shaded zone where $\epsilon > \epsilon_c$ and $d\epsilon/dt > 0$; it initiates a breakdown which is indicated by an asterisk (∗).

In the investigated range of times after the first act of breaking (10^{-14}–10^{-11} s), the fragmentation of polymer chain with the formation of high-energy molecular fragments takes place. The translation energies of such fragments reach 1–2 eV (Table I), which agrees with the above-given experimental data.[8] Since each of high-energy products is able to impart excitation to neighboring taut tie molecules and to induce their breaking, the branching of the process of mechanical degradation becomes possible. Such a branched chain mechanism of fracture may explain the explosive character of submicrocracks formation.
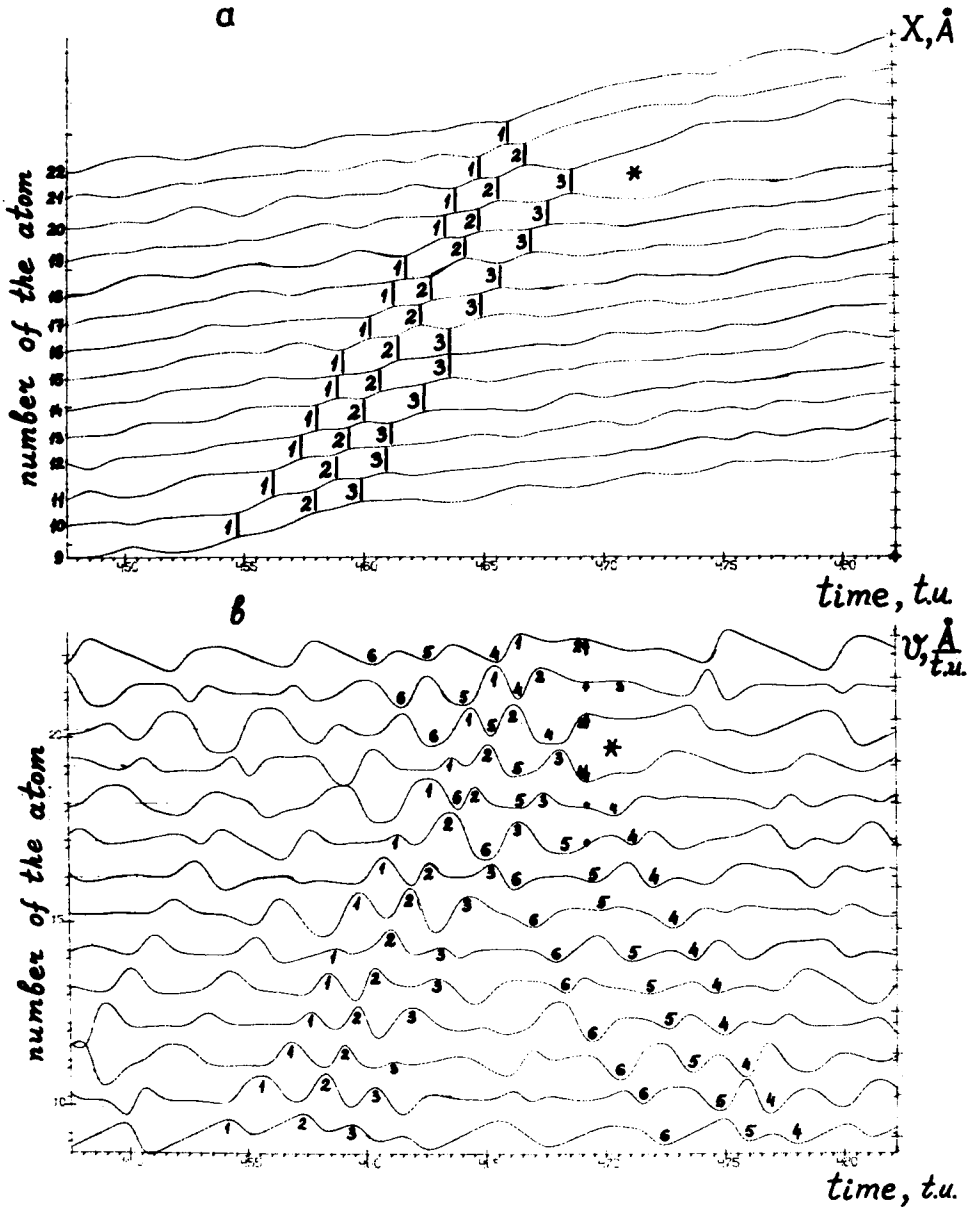
Fig. 6.   Breakdown of a high-energy intermediate product 9-22 of mechanical degradation of a 100-atom chain in accordance with the mechanism of the second type. (a) Trajectories of atoms in fragment 9-22. The numbers of atoms are plotted on the left and the length scale on the right ordinate axes (the scale value is 1 Å); the abscissa is the time measured in time units (t.u.); 1 t.u. $= 10^{-14}$ s. The location of breakdown is marked with an asterisk ($*$). The removal of a three-atom fragment 20-22 is due to the appearance of a three-soliton packet at the free end of the fragment. The solitons are marked with "numerated" vertical dashes, which connect the trajectories of atoms at the moment of their impact. (b) Time variation of velocities of atoms in fragment 9-22. The numbers of atoms are plotted on the left and the velocity scale on the right ordinate axes. The scale value is 1 Å $\cdot$ (t.u.)$^{-1}$; the abscissa is the time measured in time units (t.u.); 1 t.u. $= 10^{-14}$ s. The solitons of the soliton packet, which causes the removal of the fragment 20-22, are numerated (1, 2, 3). Solitons moving in opposite directions are also numerated (4, 5, 6). The movement of soliton packets in opposite directions induces the correlated motion of atoms (direction of their velocities are indicated by vertical arrows) in opposite directions from the location of breakdown, which is marked with an asterisk ($*$).
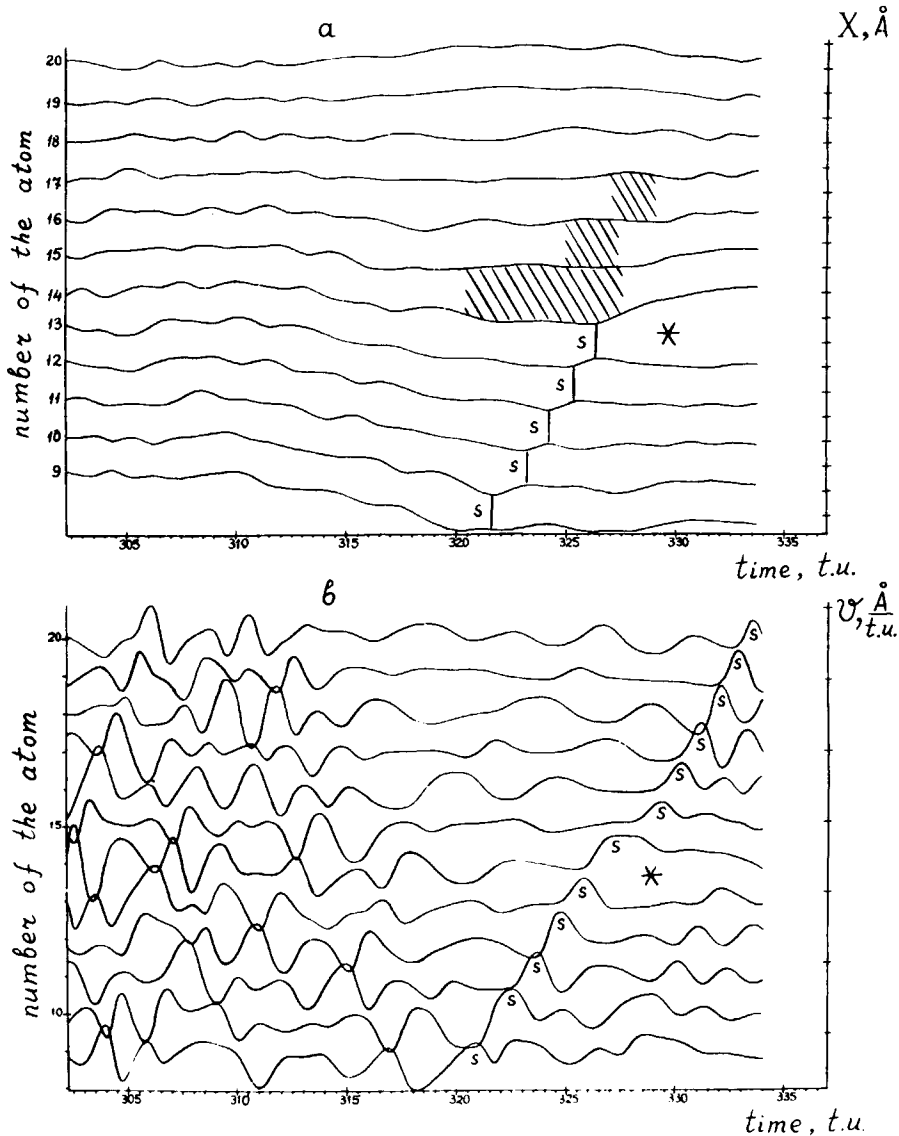
Fig. 7.   Chain breakdown according to the third-type mechanism. (a) Trajectories of atoms in the chain. The numbers of atoms are plotted on the left and the length scale (the scale value is 1 Å) on the right ordinate axes; the abscissa is the time measured in time units (t.u.), 1 t.u. = 10^{-14} s. The region of the chain being stretched ($\epsilon > 0$) and for which the value of bonds stretch exceeds the critical one ($\epsilon > \epsilon_c$) is shaded. The soliton, initiating the breakdown, is marked by "s" and is represented as vertical dashes, connecting trajectories of atoms at the moments of their impact. The location of breakdown is marked with an asterisk (∗). (b) Time variation of velocities of atoms. The numbers of atoms are plotted on the left and the velocity scale on the right ordinate axes (the scale value is 1 Å · (t.u.)$^{-1}$, the abscissa axis is the time measured in time units (t.u.). The soliton, initiating the breakdown, is marked with "s." The location of breakdown is marked with an asterisk (∗).

TABLE I
Information on Molecular Products of Mechanical Degradation of Chains at 0 K

Number of atoms in the chain	Rate stretching[a]	Initial position of fragment in the chain	The moment of the product formation [t.u. (1 t.u. = 10^{-14} s)]	Number of atoms in the product, n	E_{trans} (eV)	E_{vibr} eV	$E_{vibr}/(n-1)$ (eV/bond)
50	$0.1 \cdot V_s$	2–13	93.977	12	0.001	17.364	1.58
		11–13	119.25	3	0.764	2.024	1.01
		8–10	136.971	3	0.001	3.261	1.63
50	$0.05 \cdot V_s$	43–48	148.881	6	0.516	5.20	1.04
		43–46	201.026	4	0.656	1.438	0.48
		47–48	201.026	2	0.028	0.096	0.096
100	$0.1 \cdot V_s$	10–27	157.741	18	0.016	21.40	1.26
		5–27	180.691	23	0.040	20.97	0.95
		5–22	182.579	18	0.312	13.52	0.80
		23–27	182.579	5	2.22	1.07	0.27
		15–22	217.149	8	0.295	7.49	1.07
		19–22	307.930	4	0.295	2.20	0.73

[a] $V_s = 2.3$ Å (t.u.)$^{-1}$.

Besides that, the direct effect of solitons may lead (due to intensive compression) to the formation of double C — C bonds and the "discarding" of side groups.

To what extent are the conclusions general? Unfortunately, the detailed information on the process, occurring during other kinds of fracture, has not been available. Here are the recent results of molecular-dynamics calculations of shock loading of solids.[19] It has been shown that shock fronts can impart to internal molecular motion large amounts of energy (1–2 eV) over dramatically short times ($10^{-12} + 10^{-13}$ s). As a consequence, for a considerable period of time after shock front transit, and internal molecular energy in a small region is almost 2 orders of magnitude larger than the thermal energy of the environment. Thus, molecules may rapidly be excited to the point of dissociation. However, for such dissociation to occur, it is necessary for molecules to be free to escape from their environment (if this is not the case, the energy will easily dissipate) and the products of dissociation to move quite a distance apart. That is why the important role is played by free surfaces, submicrocracks, and microscopic voids.

More detailed mathematical experiments, dealing with 1-dimensional systems, have shown that the front of shock wave falls apart into the succession of coming solitons, while concentrate the whole energy of the shock wave. In this case in the studied range of times, thermalization does not occur.[20]

Theoretical study,[21] dealing with another consequence of mechanical deformation due to stretching or high pressure and shearing, i.e., the change in the ionizing potential (IP) of molecules, allows clarification of the inherent relationship between fracture mechanisms under different conditions of loading. In this study the first of the above-mentioned channels of degradation of accumulated elastic energy is considered. It has been previously shown (with polyethylene as an example)[22] that during stretching of a C — C bond, the IP of a macromolecule can markedly decrease. This result was used by the authors[23] for the explanation of charged particles (electrons and ions) emission[4-6] observed during polymer fracture. It was assumed that not only the stretching of chemical bonds, but also the deformation of valence angles, which can occur under the conditions of considerable stretching or compression, would favour the ionization of macromolecules. The estimations showed that there was only one possibility for polymer to overcome high-energy barrier hindering ionization, i.e., the decrease of IP of the molecule itself due to its deformation. Since it is difficult to experimentally verify this possibility, the methods of quantum chemistry were used to establish the relationship between IP of a molecule and deformation value. Figure 8 shows that IP can considerably decrease (by several eV) during the deformation of valence angles by tens of degrees.[21]

Finally, let us consider the problems of multiquantum dissociation of polyatomic molecules, which has recently drawn much attention due to the appearance of a new picosecond technique of exciting molecules by photons as well as of meaning the kinetics of their dissociation from high-excited states, which provides detailed information on high-excited states of molecules.[24] The high-excited states are characterized by considerable deviations from equilibrium geometry. That is why one cannot use the traditional description of a dissociation process in terms of normal modes as well as of the process of
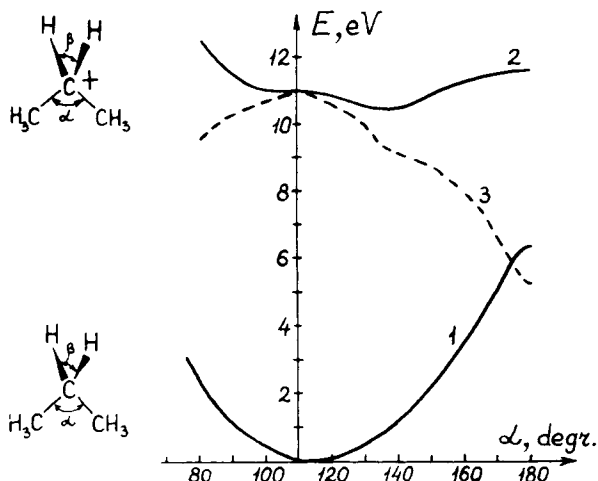
Fig. 8.   Decrease in the ionization potential of a propane molecule (as a low-molecular weight homolog of polyethylene) during deformation of valence angles. Theoretical calculation by the quantum-mechanical method MNDO.[21] Variation of energy of propane molecule (1) and its cation radical (2) during simultaneous variation of valence angles α and β ($\alpha = \beta$). Curve (3) [the difference between curves (2) and (1)] shows the dependence of ionization potential of a propane molecule on the value of valence angles α and β.

mechanical degradation. Thus, the channels of monomolecular decomposition are determined by dynamic factors, but not the statistical (thermal) ones. In this case the specific role is played by local high-anharmonic mode of a soliton type, observed in polymer chains.

So physicochemical and numerical experiments clearly show that the statistical approach to a number of problems, concerning mechanical degradation and dissociation is insufficient.

After classical works of Maxwell, Boltzmann, and Gibbs, the statistical approach prevailed in macroscopic physics and theoretical chemistry forcing back dynamics which is the basis of statistics. Chemical thermodynamics and kinetics and, particularly, the kinetic concept of mechanical degradation, as well as the whole mechanochemistry, were explained under the framework of statistical physics. The statistical approach as applied to Arrhenius kinetics suggest the preservation of equilibrium energy distributions and the possibility of introducing temperature as a parameter of Maxwell–Boltzmann or Gibbs distribution. In this case both activation energy and preexponential coefficient in the equation for velocity constants

$$k = A(T)\exp(-E_a/RT)$$

have statistical, that is, average meaning. Nonequilibrium chemical kinetics[25] does not consider thermal equilibrium, but it also deals with average values.

It has become clear that in a number of cases, dynamic effects but not the statistical ones, play the leading role. In this connection there appears the necessity in the new interrelation between dynamics and chemical kinetics. However, one does not speak about the elementary dynamics (elastic collisions, harmonic fluctuations), which formed the basis of statistics, but the

dynamics of high-anharmonic systems, which has been recently intensively developed and acquired fundamental meaning due to such new universal concepts as soliton and localized nonlinear mode.

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