Topological solitons in spiral polymeric macromolecules:
A chain surrounded by immovable neighbors

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We present a numerical study of the existence and stability of topological solitons in helix polymeric macromolecules. It is shown on the example of polytetrafluoroethylene molecule that if taking into account deformations of valence bonds, torsion, and valence angles as well as interactions with neighbor chains, four types of localized defects can be revealed. One of them possesses a finite velocity spectrum in a subsonic region. Other defects are subjected to pinning and their mobility is manifested in thermally activated random jumps. Existence of four types of topological solitons is caused by chirality of the chain. We have shown the stability of solitons with respect to thermal vibrations of macromolecule. Accumulation of a solitonlike excitation near phase-transition temperature is observed. The appearance of localized oscillatory modes in the vicinity of topological solitons is predicted.

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I. INTRODUCTION

In the last decades the localized solitonlike excitations have attracted growing attention because of their role in different fields of physics. The defect structure of polymer crystals can be studied in terms of static topological solitons; their mobility determines a specific “solitonic contribution” to thermodynamics and kinetics of polymer crystals.

At the same time, when taking into account the realistic structure of crystal macromolecules, the theoretical analysis of soliton excitations deals with significant difficulties caused by nonlinearity of the equations of motion combined with that the system is multicomponent. That is why schematic models of polymer chains that are reduced to a one-component one, were used instead. The difficulties mentioned were successfully overcome when analyzing an isolated polymeric chain due to the application of a numerically variational method for finding solitonlike solutions. In Refs. 13–15 this method was used for the study of topological solitons in crystalline polyethylene (PE). In the framework of a realistic model, taking into account both intra- and intermolecular interactions, the three types of topological solitons have been revealed. These solitons correspond to local topological defects in PE crystal (tension or compression of a transzigzag chain on one lattice distance, tension, or compression on a halved-lattice distance accompanied by rotation of zigzag on 180°, pure rotation of zigzag on 360°). It was shown later that all results obtained for the chain surrounded by immovable neighbors are preserved when the mobility of all the chains in the crystal is taken into account. The reason is a relative weakness of intermolecular interaction with respect to intramolecular interactions.

However, for the majority of polymer crystals, the ground state of the chain is not a plane transzigzag but a three-dimensional helix. Therefore nonlinear dynamics of the crystal with helix chain are of great interest. Polytetrafluoroethylene (PTFE) is one of the simplest and important realizations of such a polymer. In the ground state a PTFE molecule has the form of a three-dimensional helix with symbol 1*13/6. The nonlinear dynamics of an isolated PTFE molecule has been studied in Refs. 18 and 19 where a new type of acoustic soliton, a solitary wave of torsion, has been revealed. The goal of this paper is a study of nonlinear dynamics of a helix macromolecule accounting for both intramolecular and intermolecular interactions in application to a PTFE crystal.

Taking into account the results obtained for PE crystals, which were mentioned above, and similar weakness of intermolecular interactions with respect to intramolecular ones for a PTFE crystal, we assume that the neighbors of the macromolecular chain considered are frozen. Despite predicting the existence and types of topological excitations from the topology of the chain surrounded by immovable neighbors, the questions concerning the shape of solitonlike excitations, their stability, and accumulation remain unsolved. In particular, as it was shown for PE crystals in Refs. 16 and 17, the accumulation of topological defects (even revealed in the approximation of immovable neighbors) can be considered as the first stage of phase transition in a polymer crystal. Because of the relative weakness of intermolecular interaction for a PTFE crystal, we study a temperature dependence of defects concentration in the same approximation.

II. MODEL

For temperature $T < 19^\circ$ C, the macromolecule of PTFE in the crystal has the helix form 13/6, i.e., there are 13 CF$_2$ groups on 6 its convolution. A crystalline lattice has periods $a = b = 5.59$ Å and $c = 16.88$ Å. The angular and longitudinal steps of the helix are $\Delta \phi = 12\pi/13 = 166.15^\circ$ and $\Delta z = c/13 = 1.298$ Å.

The helix radiuses with respect to carbon $\rho_C$ and fluoride $\rho_F$ atoms can be determined via values of valence bonds CC, CF, and valence angle FCF.
In the equilibrium state the radius vectors corresponding to the $n$th carbon atom will be, respectively:

\[
\mathbf{R}_c^n = \left[ \rho_c \cos(n \Delta \phi), \rho_c \sin(n \Delta \phi), n \Delta z \right],
\]

where \( \rho_c \) is the radius of helix.

The valence angle $\angle CCC$ in the equilibrium state has the value

\[
\theta_0 = \arccos\left( -\mathbf{e}_{n-1} \cdot \mathbf{e}_n / \rho_0^2 \right),
\]

where the vector \( \mathbf{e}_n = \mathbf{R}_{n+1} - \mathbf{R}_n \) determines direction of $n$th valence bond and \( \rho_0 = \rho_{CC} \) is the bond length in equilibrium. One can obtain after elementary transformations that

\[
\theta_0 = \pi - \arccos\left( 4 R_o^2 \sin^2(n \Delta \phi/2) \cos(n \Delta \phi + n \Delta z^2) / \rho_0^2 \right) = 116.30^\circ.
\]

The equilibrium value of the $n$th dihedral (torsional) angle can be written as follows:

\[
\eta_n = \arccos\left( \mathbf{v}_{n-1} \cdot \mathbf{v}_n / |\mathbf{v}_{n-1}| |\mathbf{v}_n| \right) = \eta_0
\]

\[
= \arccos\left( h^2 \frac{\cos \Delta \phi + \sin^2 \Delta \phi}{h^2 + \sin^2 \Delta \phi} \right),
\]

where \( \mathbf{v}_n = [\mathbf{e}_n, \mathbf{e}_{n+1}] \) is the vector product of vectors $\mathbf{e}_n, \mathbf{e}_{n+1}$, and $h = \Delta z / R_0$ is dimensionless longitudinal step of the helix. We use further the angle of rotation around the $n$th bond $\delta_n = \pi - \eta_n$, where $\eta_n$ is the $n$th dihedral angle. In equilibrium state
In accordance with Ref. 23, the energy $K_n$, where

$$\delta_0 = \pi - \eta_0 = 16.32^\circ.$$

Let $x_n, y_n, z_n$ be coordinates of the $n$th segment of the helix. We pass from the Cartesian coordinate system to the cylindrical one:

$$x_n = (R_0 + r_n) \cos(n \Delta \phi + \varphi_n),$$
$$y_n = (R_0 + r_n) \sin(n \Delta \phi + \varphi_n),$$
$$z_n = n \Delta z + h_n,$$

where $r_n, \varphi_n,$ and $h_n$ are radial, angular, and longitudinal displacements of the $n$th segment from its equilibrium state, respectively. Then the Hamiltonian of the chain has the form

$$H = \sum_n \left\{ \frac{1}{2} M \left[ r_n^2 + \varphi_n^2 (R_0 + r_n)^2 + h_n^2 \right] + V(\rho_n) + U(\theta_n) \right. + W(\delta_n) + S(r_n, u_n, v_n) \right\},$$

where the point denotes the derivation with respect to time $t$, and $\rho_n, \theta_n,$ and $\delta_n$ are the length of the $n$th valence bond, the $n$th valence angle and $n$th rotation angle, respectively.

The potential of the valence bond is

$$V(\rho_n) = D_0 \left[ 1 - \exp(-\alpha(\rho_n - \rho_0)) \right]^2,$$

where the length of $n$th bond is

$$\rho_n = [a_{n,1} + b_n^2]^{1/2}.$$

Here

$$a_{n,1} = d_n^2 + d_{n+1}^2 - 2d_n d_{n+1} c_{n,1},$$
$$b_n = \Delta z + h_{n+1} - h_n,$$
$$d_n = R_0 + r_n,$$
$$c_{n,1} = \cos(\Delta \phi + \varphi_{n+1} - \varphi_n).$$

In accordance with Ref. 22 the energy of valence bond, $D_0 = 334.72$ kJ/mol and parameter $\alpha = 1.91$ Å.

The deformation energy of the valence angle has the form

$$U(\theta_n) = \frac{1}{2} K_\theta \left[ \cos(\theta_n) - \cos(\theta_0) \right]^2,$$

where the value of $n$th valence angle is

$$\theta_n = \arccos\left(\frac{-a_{n,2} + b_{n-1} b_n}{\rho_{n-1} \rho_n}\right).$$

Here

$$a_{n,2} = d_n d_{n+1} c_{n-1,1} + d_n d_{n+1} c_{n,1} - d_n^2 - d_{n+1}^2 d_{n+1} c_{n,2},$$
$$c_{n,2} = \cos(2\Delta \phi + \varphi_{n+1} - \varphi_{n-1}).$$

In accordance with Ref. 23, the energy $K_\theta = 529$ kJ/mol.

The potential of internal rotation $W(\delta_n)$ characterizes a retardation of the rotation of chain segments around the $n$th valence bond. The value of the $n$th rotation angle is

$$\delta_n = \arccos\left[\frac{(b_n b_{n+1} a_{n,2} + b_{n-1} b_n a_{n+1,2} - b_n^2 a_{n,4}}{-b_{n-1} b_{n+1} a_{n,1} + a_{n,3} a_{n+1,3}}/\sqrt{b_n \beta_n + 1}\right],$$

where

$$\beta_n = a_{n,1} b_n^2 + a_n b_{n-1}^2 - 2a_{n,2} b_n - b_n^2 + a_{n,3},$$
$$a_{n,3} = d_{n-1} d_{n+1} s_{n-1,1} + d_n d_{n+1} s_{n,1} - d_{n-1} d_n + s_{n,2},$$
$$c_{n,3} = \cos(2\Delta \phi + \varphi_{n+2} - \varphi_{n-1}),$$

The form of the potential for a macromolecule PTFE is presented in Fig. 2. The PTFE has four rotary isomers on each bond C—C $W(\delta)$ for macromolecules PTFE. The curves 1, 2, and 3 correspond to potentials $W_1(\delta)$, $W_2(\delta)$, and $W_3(\delta)$, respectively.

The potential of rotation is characterized by the four energetic characteristics; by the height of the potential barriers between both trans conformations $\epsilon_0 = W(0)$ and between trans and gauche conformations $\epsilon_1 = W(\pi/3)$, by the level of a gauche-conformation energy $\epsilon_2 = W(2\pi/3)$, and the height of a barrier between gauche conformations $\epsilon_3 = W(\pi)$. According to Ref. 20,

$$\epsilon_0 = 1.674 \text{ kJ/mol}, \quad \epsilon_1 = 18.42 \text{ kJ/mol},$$
$$\epsilon_2 = 4.186 \text{ kJ/mol}, \quad \epsilon_3 = 23.02 \text{ kJ/mol}.$$

For the numerical modeling of the dynamics of a macromolecule PTFE it is convenient to present the potential of interaction by the formula.
where the one-parametric functions $Z_\alpha(\delta)$ and $Z_\beta(\delta)$ can be written as follows:

$$Z_\alpha(\delta) = \frac{(1 + \alpha) \sin^2(\delta/2)}{1 + \alpha \sin^2(\delta/2)},$$

$$Z_\beta(\delta) = \frac{(1 + \beta) \sin(3\delta/2)}{1 - \beta \sin(3\delta/2)}.$$

The parameter values $C_3 = 3.411$ (kJ/mol)$^{1/2}$, $C_4 = 2.681$ (kJ/mol)$^{1/2}$, $C_5 = 1.294$ (kJ/mol)$^{1/2}$, $\alpha = 14.6125$, and $\beta = 4.0028 \times 10^{-3}$ are determined from the following equations:

$$W_1(0) = C_3^2 = \epsilon_0,$$

$$W_1(\delta_0) = [C_1 Z_\alpha(\delta_0) + C_2 Z_\beta(\delta_0) - C_3]^2 = 0,$$

$$W_1(\pi/3) = \left[ \frac{1 + \alpha}{4 + \alpha} + \frac{1 + \beta}{1 - \beta} \right]^2 - C_3^2 = \epsilon_1,$$

$$W_1(2\pi/3) = \left[ \frac{3C_1}{4 + 3\alpha} - C_3 \right]^2 = \epsilon_2,$$

$$W_1(\pi) = (C_1 + C_2 - C_3)^2 = \epsilon_3.$$

The potential (9), at given values of parameters, is presented in Fig. 2 (curve 1). It has the absolute minimum at $\delta = \delta_0$ in $2\pi - \delta_0$.

Because we provide realistic energetic characteristics of torsion and other potentials, the key question is the role of elastic properties, i.e., the curvatures of potential wells. These curvatures have manifested themselves in dispersion curves. One can approach to realistic dispersion curves if decreasing the torsional potential (9) by ten times

$$W_2(\delta) = W_1(\delta)/10.$$ (10)

In such a case however, the energetic characteristics $\epsilon_0$, $\epsilon_1$, $\epsilon_2$, and $\epsilon_3$ become far enough from the values (8) (see Fig. 2, curve 2).

To decrease the torsional rigidity without a noticeable change of energetic characteristics, we use the potential

$$W_3(\delta) = f(\delta) W(\delta),$$

where the function

$$f(\delta) = \frac{1}{10} \left[ 36 \left( \frac{(1 + \gamma) \sin^2(\delta/2)}{1 + \gamma \sin^2(\delta/2)} - \frac{1}{2} \right)^2 + 1 \right]$$

and parameter $\gamma = 1/ \sin^2(\delta_0/2) - 2$. The potential (11) is presented in Fig. 2 (curve 3). As seen in this figure, $W_3(\delta_0) = W_1(\delta_0) = 0$, $W_3(0) = W_1(0) = \epsilon_0$, $W_3(\pi) = W_1(\pi) = \epsilon_3$, $W_3(2\pi/3) = W_1(2\pi/3) = \epsilon_2$, and $W_3(3\pi/3) = W_1(3\pi/3) = \epsilon_4$.

The interaction potential in this coordinate will be the two-dimensional periodic function $S(r, u \pm 1, v \pm 1) = S(r, u, v)$. The square $0 \leq u \leq 1$, $0 \leq v \leq 1$ corresponds to elementary cell of a discrete helix (Fig. 3). Actually, for $u = 1$, every $n$th segment of helix takes the place of the $(n - 1)$th segment and for $v = 1$, takes the place of the $(n + 1)$th segment. Therefore, it is enough to find numerically a form of the potential for the elementary cell only.

The interaction potential can be described analytically by finite double Fourier sum

$$u_n = (\varphi_n - h_n \Delta \phi/\Delta z)/2\pi,$$ (12)

$$v_n = u_n + h_n/\Delta z.$$ (13)
where transversal rigidity $K_r = 17.1$ N/m, the coefficient $b_{22} = -0.075878$ kJ/mol, and the values of other coefficients are given in Table I. The accuracy of this approximation is illustrated in Fig. 4. We see that the surface $E = S(0, u, v)$ coincides practically with the surface $E = S_0(0, u, v)$.

The level lines of the potential, which are shown in Fig. 5, demonstrate a ravine structure of the surface. The minima of the potential $(u, v) = (0, 0); (0, 1); (1, 0); (1, 1)$ correspond to the ground state of the chain. It is seen that the transformation of the chain from ground state $(0, 0)$ to the stable $(0, 1)$ required overcoming the smallest energy barrier $2.983$ kJ/mol. In this case the motion occurs via the bottom of a most deep ravine. Below, we show that such a transition corresponds to topological defect of the chain possessing solitonic dynamics.

### III. DISPERSION EQUATION

To deal with small amplitude vibrations of the chain, it is convenient to pass from the cylindrical coordinates $r_n, \varphi_n$, and $h_n$ to local ones

$$w_n = \begin{pmatrix} w_{n,1} \\ w_{n,2} \\ w_{n,3} \end{pmatrix} = \begin{pmatrix} \cos(n \Delta \phi) & \sin(n \Delta \phi) & 0 \\ -\sin(n \Delta \phi) & \cos(n \Delta \phi) & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} (R_0 + r_n) \cos(n \Delta \phi + \varphi_n) - R_0 \cos(n \Delta \phi) \\ (R_0 + r_n) \sin(n \Delta \phi + \varphi_n) - R_0 \sin(n \Delta \phi) \\ h_n \end{pmatrix}.$$
In the given coordinate frame, the Hamiltonian (7) has the form

$$H = \sum_n \left[ \frac{1}{2} M(w_n, \dot{w}_n) + V(w_n, w_{n+1}) + U(w_{n-1}, w_n, w_{n+1}) ight. \\
\left. + W(w_{n-1}, w_n, w_{n+1}, w_{n+2}) + S(w_n) \right], \quad (15)$$

The following equations of motion correspond to the Hamiltonian (15):

$$- M \ddot{w}_n = V_1(w_n, w_{n+1}) + V_2(w_{n-1}, w_n) \\
+ U_1(w_n, w_{n+1}, w_{n+2}) + U_2(w_{n-1}, w_n, w_{n+1}) \\
+ U_3(w_{n-2}, w_{n-1}, w_n) \\
+ W_1(w_n, w_{n+1}, w_{n+2}, w_{n+3}) \\
+ W_2(w_{n-1}, w_n, w_{n+1}, w_{n+2}) \\
+ W_3(w_{n-2}, w_{n-1}, w_n, w_{n+1}) \\
+ W_4(w_{n-3}, w_{n-2}, w_{n-1}, w_n) + S_1(w_n), \quad (16)$$

where the vectors

$$V_i(w_1, w_2) = \frac{\partial}{\partial w_i} V, \quad i = 1, 2,$$

$$U_i(w_1, w_2, w_3) = \frac{\partial}{\partial w_i} U, \quad i = 1, 2, 3,$$

$$W_i(w_1, w_2, w_3, w_4) = \frac{\partial}{\partial w_i} W, \quad i = 1, 2, 3, 4,$$

$$S_1(w) = \frac{\partial}{\partial w_1} S.$$

The linear approach to the nonlinear equations (16) takes the form

$$- M \ddot{w}_n = B_1 w_n + B_2 (w_{n-1} + w_{n+1}) + B_3 (w_{n-2} + w_{n+2}) \\
+ B_4 (w_{n-3} + w_{n+3}), \quad (17)$$

where the constants of the matrices are determined by the relations

$$B_1 = S_{11} + V_{11} + V_{22} + U_{11} + U_{22} + U_{33} + W_{11} + W_{22} + W_{33} + W_{44},$$

$$B_2 = V_{12} + U_{12} + U_{23} + W_{12} + W_{23} + W_{33} + W_{44},$$

$$B_3 = U_{13} + W_{13} + W_{24},$$

$$B_4 = W_{14}.$$

Here

$$S_{11} = \frac{\partial^2 S}{\partial w_1^2} (0),$$

FIG. 6. The frequency spectrum curves $\omega = \omega_q(q)$ [(b), curve 1], $\omega = \omega_q(q)$ [(b), curve 2], $\omega = \omega_o(q)$ [(a), curve 3] for the helix chain in the PTFE crystal with torsional potential $W_q(\delta)$ and for a chain with torsional potentials $W_q(\delta)$ and $W_o(\delta)$ [(d), curves 4 and 5; (c), curve 6]. Corresponding curves for an isolated chain are shown by dotted lines.

$$V_{ij} = \frac{\partial^2 V}{\partial w_i \partial w_j} (0, 0), \quad i, j = 1, 2,$$

$$U_{ij} = \frac{\partial^2 U}{\partial w_i \partial w_j} (0, 0, 0), \quad i, j = 1, 2, 3,$$

$$W_{ij} = \frac{\partial^2 W}{\partial w_i \partial w_j} (0, 0, 0, 0), \quad i, j = 1, 2, 3, 4.$$

Let us look for the solution of the linear system (17) in the form of the harmonic wave

$$w_n = A \exp[i(qn - \omega t)]. \quad (18)$$

After the substitution of expression (18) into the linear equation (17), we obtain the dispersion equation

$$|B_1 + 2 \cos(q) B_2 + 2 \cos(2q) B_3 + 2 \cos(3q) B_4 - \omega^2 E| = 0, \quad (19)$$

where $E$ is the unit matrix.

The dispersion equation (19) is an algebraic equation of the third order with respect to the variable $\omega^2$. The corresponding algebraic curve has three branches: two acoustic $\omega = \omega_a(q)$, $\omega = \omega'_a(q)$, and one optical $\omega = \omega_o(q)$ [$\omega_q(q) \approx \omega_a(q) \approx \omega'_a(q)$] $\omega_o(q) \approx \omega_e(q)$ $\omega_o(q) \approx \omega'_o(q)$.

The dispersion curves for all three torsion potentials (9), (10), and (11) are presented in Fig. 6. The lower curve $\omega = \omega_a(q)$ gives the dispersion law for acoustic phonons corresponding to torsional oscillations, and the median curve $\omega = \omega_o(q)$ to the dispersion law for acoustic phonons corresponding to longitudinal oscillations of the helix. The upper curve $\omega = \omega_e(q)$ corresponds to high-frequency optical phonons of the helix. If $q = 0$, the frequencies $\omega_a = 10.4 \text{ cm}^{-1}$, $\omega_o = 111.7 \text{ cm}^{-1}$, and $\omega_e = 519.9 \text{ cm}^{-1}$. For $q = \pi$, the frequencies $\omega_a = 76.2 \text{ cm}^{-1}$, $\omega_o = 111.9 \text{ cm}^{-1}$, and $\omega_e = 628.5 \text{ cm}^{-1}$.
When considering the potential (9), the longitudinal acoustic phonons have the frequency spectrum $111.7 \text{ cm}^{-1} \lesssim \omega_l \lesssim 253.2 \text{ cm}^{-1}$, the torsional phonons $- 10.4 \text{ cm}^{-1} \lesssim \omega_t \lesssim 194.2 \text{ cm}^{-1}$, and optic phonons $- 487.9 \text{ cm}^{-1} \lesssim \omega_o \lesssim 628.5 \text{ cm}^{-1}$. For isolated chain $[\mathcal{S}(w_0)=0]$ the acoustic branches for torsional and longitudinal oscillations are close. The frequencies $\omega_t$ and $\omega_l$ tend to zero if $q \to 0$ [Fig. 6(b)]. The velocity of long-wavelength longitudinal phonons

$$v_l = \Delta z \lim_{q \to 0} \frac{\omega_l(q)}{q} = 6978.6 \text{ m/s}$$

lightly exceeds the velocity of torsional phonons

$$v_t = \Delta z \lim_{q \to 0} \frac{\omega_t(q)}{q} = 5585.3 \text{ m/s}.$$

The ratio of the velocities is $s_t = v_t/v_l = 0.80035$.

For chain with torsional potentials (10) and (11), the acoustic branch of torsion oscillations lies significantly lower than the acoustic branch of longitudinal oscillations (a structure of dispersion curves in these cases corresponds well to known data$^{36}$), see Fig. 6(d). Here the velocity of torsional phonons, $v_t = 1768.5 \text{ m/s}$, is four times less than the velocity of the long-wavelength longitudinal phonons $v_l = 6972.4 \text{ m/s}$. The ratio of the velocities is $s_t = v_t/v_l = 0.25365$.

**IV. STATIONARY STATES OF TOPOLOGICAL DEFECTS**

Finding the stationary state of the topological defect (soliton) $\{r_n, \varphi_n, h_n\}_{n=1}^N$ of helix macromolecule PTFE, requires a numerical solution of the problem on conditional minimum:

$$P = \sum_{n=1}^N \{V(\rho_n) + U(\theta_n) + W(\delta_n) + S(r_n, u_n, v_n)\}$$

$$\rightarrow \min_{r_1, \varphi_1, h_1, \ldots, r_N, \varphi_N, h_N}$$

$$r_1 = 0, \quad \varphi_1 = \varphi_{-\infty}, \quad h_1 = h_{-\infty}, \quad (21)$$

$$r_N = 0, \quad \varphi_N = \varphi_{+\infty}, \quad h_N = h_{+\infty}. \quad (22)$$

The boundary conditions (21) and (22) for the problem (20) determine the type of topological defect. The number $N$ should be chosen sufficiently large in order to prevent the dependence of the soliton shape on $N$ (it is enough to accept $N = 500$).

Let us consider the localized topological defects of a helix chain. For this we rewrite the boundary conditions (21) and (22) in dimensionless helix coordinates (12) and (13):

$$r_1 = 0, \quad u_1 = 0.1, \quad v_1 = 0.1, \quad (23)$$

$$r_N = 0, \quad u_N = 0.1, \quad v_N = 0.1. \quad (24)$$

Every boundary condition, Eqs. (23) and (24), corresponds to one of the ground states of the chain. Then the solution of the problem on conditional minimum (20), (23), and (24) corresponds to topological defect describing the transition of the helix from the ground state (23) to the ground state (24). Let us define the topological charge of the defect as a two-dimensional vector $\mathbf{q} = (q_1, q_2)$, where $q_1 = u_N - u_1$, and $q_2 = v_N - v_1$. Thus, four types of elementary topological defects with topological charges $\mathbf{q} = \pm (1, 0), \pm (0, 1), \pm (1, 1), \pm (-1, 1)$ can exist in the helix chain.

Every stationary defect $\{r_n, u_n, v_n\}_{n=1}^N$ is characterized by the energy

$$E = \sum_{n=1}^N \{V(\rho_n) + U(\theta_n) + W(\delta_n) + S(r_n, u_n, v_n)\},$$

and the mean-square width (measured in the periods of the chain)

$$D = 2 \sum_{n=1}^N (n - n_c)^2 p_n,$$

determines the position of the soliton center $p_n = e_n/E$. The sequence

$$e_n = V(\rho_n) + U(\theta_n) + W(\delta_n) + Z(r_n, u_n, v_n)$$

gives a distribution of the energy along the chain.

Let us define the parameters that describe the amplitude of chain deformations in the region of soliton localization, i.e., of the maximal deformations of the valence bonds

$$\Delta p = \rho_n - \rho_0, \quad \text{where} \quad |\rho_n - \rho_0| = \max_{n=1,2,\ldots,N} |\rho_n - \rho_0|,$$

and the valence angle

$$\Delta \theta = \theta_n - \theta_0, \quad \text{where} \quad |\theta_n - \theta_0| = \max_{n=1,2,\ldots,N} |\theta_n - \theta_0|,$$

and the torsional angle

$$\Delta \delta = \delta_n - \delta_0, \quad \text{where} \quad |\delta_n - \delta_0| = \max_{n=1,2,\ldots,N} |\delta_n - \delta_0|.$$

Every topological defect is also characterized by local normal modes with frequencies $\omega_0 < \omega_1 < \ldots < \omega_N$, where the number of the modes $N_q < \infty$. If a topological defect is subjected to pinning, its propagation along the chain requires overcoming the Piersl potential barrier. The lowest eigenfrequency corresponds to oscillations of a defect’s center in the Piersl potential well. If the Piersl potential is absent, the defect can move as a free particle, with first eigenfrequency $\omega_0 = 0$. The next eigenfrequency $\omega_1$ corresponds to a change of width of the defect (the defect’s center being immovable). The eigenfrequencies $\omega_2, \omega_3, \ldots$ corresponds to more high overtones of the defect.

Let us consider the chain with torsional potential (9). The dependence of the energy $E$, width $D$, and maximal deformation $\Delta p$, $\Delta \theta$, $\Delta \delta$ on the topological charge $\mathbf{q} = (q_1, q_2)$, is presented in Table II; the dependence of the defect’s eigenfrequencies $\omega_0, \omega_1, \omega_2$ on the charge $\mathbf{q}$ is presented in Table III.
The distribution of deformations in the region of localization of topological defect with charge \( q = (1,0) \), is presented in Fig. 7. This defect is formed as a result of the rotation of the part of the chain on the angle \( 2\pi - \Delta \phi \) and shift along the axis \( z \) on \( -\Delta z \). As a result, this segment of the chain with number \( n \) occupies the place of the segment with number \( n - 1 \). We see in Fig. 7 that such a defect does not have a smooth profile with respect to radial \( r_n \) and angular \( \varphi_n \) components. Therefore it cannot propagate as a smooth solitary wave. It is also confirmed by the eigenfrequency of defect \( \omega_0 = 52 \text{ cm}^{-1} \) as strongly different from zero.

The defect with topological charge \( q = (0,1) \) (see Fig. 8) is formed as a result of the rotation of a part of the chain on the angle \( \Delta \phi \) and the shift along the \( z \) axis on \( \Delta z \). Due to this deformation, the segment with number \( n \) takes the place of the segment \( n + 1 \). This defect does not have a smooth profile with respect to components \( r_n \) and \( \varphi_n \) and eigenfrequency \( \omega_0 = 50 \text{ cm}^{-1} > 0 \). The defect with charge \( q = (1,1) \) (see Fig. 9) is formed via the rotation of the part of helix on \( 360^\circ \). As a result, every segment of the helix returns into its initial state. This defect is also characterized by absence of smooth profile with respect to all three components \( r_n, \varphi_n, \) and \( h_n (\omega_0 = 64 \text{ cm}^{-1} > 0) \).

At last, the defect with charge \( q = (-1,1) \) has a smooth profile with respect to all components \( r_n, \varphi_n, \) and \( h_n \) (see Fig. 10). It is formed due to the rotation of the part of the chain on angle \( 2(\pi - \Delta \phi) \) and the shift along the \( z \) axis on \( 2\Delta z \). As a result, the segment with number \( n \) takes the place of the segment \( n + 2 \). The defect with opposite charge \( q = (-1,1) \) also has a smooth profile with respect to all components. For these defects, the first eigenfrequency \( \omega_0 = 0 \), therefore these defects possess solitonlile dynamics, i.e., they can propagate with constant subsonic velocity \( v < v_t \) without change of their profile. In helix elementary cell \( 0 \leq u \leq 1, 0 \leq v \leq 1 \) the topological soliton is realized as a smooth trajectory \( \{(u(n),v(n))\}_{n=-\infty}^{+\infty} \) connecting the ground states \( (1,0) \) and \( (0,1) \). This trajectory corresponds to motion via the bottom of the most deep ravine of a two-dimensional surface of substrate potential \( E = S(0,u,v) \). It is presented in Fig. 5 by a thick line.

The dependence of the energy \( E \), width \( D \), and maximal deformation of the valence bond \( \Delta \rho \), valence \( \Delta \theta \), and torsion \( \Delta \delta \) angles of stationary defect on the value of topological charge \( q = (q_1,q_2) \). The model with torsional potential \( W_1(\delta) \) was accepted.

<table>
<thead>
<tr>
<th>( q )</th>
<th>( E ), kJ/mol</th>
<th>( D )</th>
<th>( \Delta \rho ), Å</th>
<th>( \Delta \theta ), degrees</th>
<th>( \Delta \delta ), degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1, 0)</td>
<td>52.4</td>
<td>24.4</td>
<td>-0.014</td>
<td>-2.77</td>
<td>8.8</td>
</tr>
<tr>
<td>(-1, 0)</td>
<td>129.6</td>
<td>18.1</td>
<td>0.015</td>
<td>3.75</td>
<td>26.5</td>
</tr>
<tr>
<td>(0, 1)</td>
<td>33.6</td>
<td>30.8</td>
<td>0.014</td>
<td>2.66</td>
<td>-10.5</td>
</tr>
<tr>
<td>(0, -1)</td>
<td>70.9</td>
<td>24.3</td>
<td>-0.011</td>
<td>-2.82</td>
<td>13.4</td>
</tr>
<tr>
<td>(1, 1)</td>
<td>28.9</td>
<td>7.6</td>
<td>-0.004</td>
<td>-1.37</td>
<td>8.1</td>
</tr>
<tr>
<td>(-1, -1)</td>
<td>116.4</td>
<td>10.6</td>
<td>0.010</td>
<td>-9.32</td>
<td>90.5</td>
</tr>
<tr>
<td>(-1, 1)</td>
<td>119.4</td>
<td>29.5</td>
<td>0.034</td>
<td>4.96</td>
<td>3.7</td>
</tr>
<tr>
<td>(1, -1)</td>
<td>122.0</td>
<td>30.3</td>
<td>-0.028</td>
<td>-4.94</td>
<td>-4.2</td>
</tr>
</tbody>
</table>

The dependence of eigenfrequencies of stationary defect \( \omega_0, \omega_1 \) (cm\(^{-1}\)) on the value of topological charge \( q = (q_1,q_2) \). The model with torsional potential \( W_1(\delta) \) was accepted.

<table>
<thead>
<tr>
<th>( q )</th>
<th>( \omega_0 )</th>
<th>( \omega_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1, 0)</td>
<td>52</td>
<td>72</td>
</tr>
<tr>
<td>(-1, 0)</td>
<td>67</td>
<td>107</td>
</tr>
<tr>
<td>(0, 1)</td>
<td>50</td>
<td>75</td>
</tr>
<tr>
<td>(0, -1)</td>
<td>46</td>
<td>72</td>
</tr>
<tr>
<td>(1, 1)</td>
<td>64</td>
<td>68</td>
</tr>
<tr>
<td>(-1, -1)</td>
<td>49</td>
<td>68</td>
</tr>
<tr>
<td>(-1, 1)</td>
<td>0</td>
<td>63</td>
</tr>
<tr>
<td>(1, -1)</td>
<td>0</td>
<td>50</td>
</tr>
</tbody>
</table>
V. NUMERICAL MODELING OF THE TOPOLOGICAL SOLITON DYNAMICS

Numerical modeling of the dynamics of topological solitons with the charges \( q = (\pm 1, 1) \), reveals their stability manifested in retaining the velocities and profiles for all rotational potentials \( \varphi_0 = (\pm 9, 10, 11) \).

For definiteness, let us consider the dynamics of topological solitons in the chain with torsional potentials \( \varphi_0 = (\pm 9) \). First consider the interaction of soliton having charge \( q_s = (\pm 1, 1) \) with other stationary topological defects with the charges \( q_d \).

For this we will numerically integrate the system equations of motions

\[
M \ddot{r}_n = M (R_0 + r_n) \varphi_n^2 - \frac{\partial}{\partial r_n} P, \\
M (R_0 + r_n)^2 \varphi_n = -2M (R_0 + r_n) \dot{\varphi}_n \dot{r}_n - \frac{\partial}{\partial \varphi_n} P, \\
M \ddot{h}_n = -\frac{\partial}{\partial h_n} P, \\
\]

\( n = 1, 2, \ldots, N \)

with initial conditions corresponding to a topological soliton [charge \( q_s = (\pm 1, 1) \), velocity \( v = 0.1 v_t \)] and a stationary topological defect with another charge \( q_d \).

If \( q_d = (1, 0) \), the collision of soliton with a defect leads to partial recombination. As a result, the stationary defect with charge \( q = (0, 1) \) appears in the chain. This collision is accompanied by intensive phonon radiation (see Fig. 11). If \( q_d = (-1, 0) \), an elastic reflection of the soliton from a defect occurs. The defect itself remains immobile (see Fig. 12). An elastic reflection is observed also if \( q_d = (0, 1) \), \((-1, -1)\). In all these cases the defect remains immobile. If \( q_d = (0, 1) \), the stationary defect with charge \( q = (-1, 0) \) appears in the chain as a result of partial recombination. The partial recombination occurs also if \( q_d = (1, 1) \). As a result, a stationary defect with a double topological charge \( q = (0, 2) \) arises in the chain. Thus, the stable stationary defects with double topological charges can also exist in the helix chain.

The collision of two topological solitons with similar signs \( q_1 = q_2 \) leads to their elastic reflection. When the signs of solitons are opposite \( (q_1 = -q_2) \) the full recombination occurs.

VI. DYNAMICS OF TOPOLOGICAL DEFECTS IN A THERMALIZED CHAIN

Dynamics of a thermalized chain consisting of \( N \) sites is described by the system of the Langevin equations...
dom forces the relaxation time of the velocity of the molecule. The random force 
\( G \) describing the interaction of the 

\[ \rho \approx n, t \]

where the potential energy of the system 
\( P \), and energy 
\( \varepsilon_n \) in the region of localization of topological defect with charge 
\( q = (1,1) \) for the chain with torsional potential 
\( W_1(\delta) \).

\[
M \ddot{r}_n = M(R_0 + r_n) \ddot{\varphi}_n \frac{\partial}{\partial r_n} P + \xi_n - \Gamma M \dot{r}_n,
\]

\[
M(R_0 + r_n)^2 \dddot{\varphi}_n = -2M(R_0 + r_n) \ddot{\varphi}_n \frac{\partial}{\partial \varphi_n} P + (R_0 + r_n) \eta_n - \Gamma M \dot{r}_n,
\]

\[
M \dddot{h}_n = -\frac{\partial}{\partial h_n} P + \bar{\xi}_n - \Gamma M \dot{h}_n,
\]

where the potential energy of the system 
\( P \) is given by Eq. (20); \( \xi_n \), \( \eta_n \), and \( \bar{\xi}_n \) are random normally distributed forces describing the interaction of the \( n \)th molecule with a thermal bath, and the coefficient of friction is \( \Gamma = 1/\tau_r \) with \( \tau_r \) being the relaxation time of the velocity of the molecule. The random forces \( \xi_n \), \( \eta_n \), and \( \bar{\xi}_n \) have the correlation functions

\[
\langle \xi_n(t_1) \xi_m(t_2) \rangle = \langle \eta_n(t_1) \eta_m(t_2) \rangle = \langle \bar{\xi}_n(t_1) \bar{\xi}_m(t_2) \rangle = 2M\Gamma k_BT \delta_{nm} \delta(t_1 - t_2),
\]

\[
\langle \xi_n(t_1) \eta_m(t_2) \rangle = \langle \xi_n(t_1) \bar{\xi}_m(t_2) \rangle = \langle \eta_n(t_1) \xi_m(t_2) \rangle = \langle \eta_n(t_1) \bar{\xi}_m(t_2) \rangle = 0,
\]

\( n, m = 1, 2, \ldots , N \),

Let us study the soliton dynamics in the chain consisting of 
\( N = 1000 \) segments with the fixed ends. The initial conditions of system (26) correspond to a stationary topological defect.

The numerical integration of the system (26) leads to the conclusion that all topological defects are stable with respect to thermal vibration of the chain if \( T = 100 \) K. Such a stability has a topological nature for the defects with charge 
\( q \not= (1,1) \), because for their breaking, it is necessary to shift half of the chain along the \( z \) axis. The defect with charge 
\( q = (1,1) \), formed via local full rotations of the helix segment, can generally be unstable to thermal vibrations but it has a large enough time of life (\( t > 100 \) ps). The topological soliton [defect with charge 
\( q = \pm (1,1) \)] propagates along the chain as a free Brownian particle. Other topological de-

\[
\begin{array}{cccccc}
\text{q} & E, \text{kJ/mol} & D & \Delta_\rho, \text{Å} & \Delta_\theta, \text{degrees} & \Delta_\delta, \text{degrees} \\
(1, 0) & 43.8 & 26.0 & -0.013 & -2.85 & 20.2 \\
(-1, 0) & 63.3 & 25.1 & 0.016 & 3.78 & 36.2 \\
(0, 1) & 26.9 & 34.0 & 0.013 & 2.50 & -11.3 \\
(-1, 0) & 30.9 & 28.5 & -0.012 & -3.05 & 38.0 \\
(1, 1) & 24.8 & 7.8 & -0.004 & -1.27 & 16.3 \\
(-1, -1) & 50.1 & 10.7 & 0.006 & 2.57 & 49.0 \\
(-1, 1) & 116.7 & 29.6 & 0.035 & 5.12 & 6.0 \\
(1, -1) & 93.0 & 24.7 & -0.021 & -5.84 & 90.7 \\
\end{array}
\]

where \( k_B \) is Boltzmann’s constant and \( T \) is the temperature of a thermal bath.

The system (26) was integrated numerically by the standard fourth-order Runge-Kutta method with a constant step of integration \( \Delta t \). Numerically, the delta function was represented as \( \delta(t)=0 \) for \( |t| > \Delta t/2 \) and \( \delta(t)=1/\Delta t \) for \( |t| < \Delta t/2 \), i.e., the step of numerical integration corresponds to the correlation time of the random force. In order to use the Langevin equation, it is necessary that \( \Delta t = t_r \). Therefore we choose \( \Delta t = 0.002 \) ps and the relaxation time \( t_r = 0.2 \) ps.

Let us study the soliton dynamics in the chain consisting of 
\( N = 1000 \) segments with the fixed ends. The initial conditions of system (26) correspond to a stationary topological defect.

The numerical integration of the system (26) leads to the conclusion that all topological defects are stable with respect to thermal vibration of the chain if \( T = 100 \) K. Such a stability has a topological nature for the defects with charge 
\( q \not= (1,1) \), because for their breaking, it is necessary to shift half of the chain along the \( z \) axis. The defect with charge 
\( q = (1,1) \), formed via local full rotations of the helix segment, can generally be unstable to thermal vibrations but it has a large enough time of life (\( t > 100 \) ps). The topological soliton [defect with charge 
\( q = \pm (1,1) \)] propagates along the chain as a free Brownian particle. Other topological de-

\[
\begin{array}{cccccc}
\text{q} & E, \text{kJ/mol} & D & \Delta_\rho, \text{Å} & \Delta_\theta, \text{degrees} & \Delta_\delta, \text{degrees} \\
(1, 0) & 51.1 & 24.7 & -0.013 & -2.71 & 10.2 \\
(-1, 0) & 91.8 & 21.4 & 0.018 & -7.39 & 55.4 \\
(0, 1) & 32.0 & 31.4 & 0.014 & 2.62 & -10.4 \\
(-1, 0) & 52.8 & 22.0 & -0.012 & 6.34 & 53.5 \\
(1, 1) & 27.6 & 7.4 & -0.004 & 1.39 & 8.9 \\
(-1, -1) & 83.7 & 11.5 & 0.010 & -5.76 & -57.1 \\
(-1, 1) & 118.8 & 29.5 & 0.034 & 4.99 & 4.1 \\
(1, -1) & 121.5 & 30.3 & -0.028 & -4.96 & -4.6 \\
\end{array}
\]
VII. THERMALLY ACTIVATED FORMATION OF TOPOLOGICAL DEFECTS

To model the formation of topological defects in an infinite thermalized chain, the cyclic chain of \( N = 10000 \) segments was considered. The ground state \( r_n = 0, \varphi_n = 0, h_n = 0, \) and \( n = 1,2,\ldots,N \), has been accepted as an initial condition. The system of the equations of motion

\[
\ddot{r}_n + \ddot{\varphi}_n + h_n \frac{\dot{r}_n^2}{r_n^2} + h_n^2 \frac{\dot{\varphi}_n}{\sin \varphi_n} = \frac{1}{3Nk_B T} \sum_{n=1}^{N} M[n^2 + \dot{\varphi}_n^2(R_0 + r_n)^2 + \dot{h}_n^2] / 3Nk_B T,
\]

was integrated numerically during the time \( t = 100 \) ps.

It is convenient to describe the degree of the chain thermalization by the instant dimensionless temperature

\[ c_T(t) = \sum_{n=1}^{N} M[n^2 + \dot{\varphi}_n^2(R_0 + r_n)^2 + \dot{h}_n^2] / 3Nk_B T, \]

the instant dimensionless thermal capacity \( c_E(t) = H(t) / 3Nk_B T \), and their averaged values are

\[ C_T = \lim_{t \to \infty} \int_{0}^{t} c_T(\tau) d\tau, \quad C_E = \lim_{t \to \infty} \int_{0}^{t} c_E(\tau) d\tau. \]

The dependencies \( C_E \) and \( C_T \), on the temperature of a thermal bath for a chain with torsional potentials (9), (10), and (11), are presented in Table VI. The dimensionless temperature of the chain \( C_T \) remains practically always near unity and this confirms the validity of the procedure of thermalization. The dimensionless thermal capacity increases monotonically with the growth of temperature. At small values of temperature, the thermal capacity is close to unity, so that this emphasizes the “harmonicity” of vibrations. With the growth of temperature, the amplitude of vibrations increases and therefore the effect of nonlinearity (“anharmonicity”) of vibrations becomes stronger. The growth of \( C_E \) reflects strengthening of this nonlinear effect in the thermal capacity of the system.

TABLE VI. Dependence of averaged values of the dimensionless temperature \( C_T \) and dimensionless thermal capacity \( C_E \) on the temperature of the thermal bath \( T \) for the chain with torsional potentials \( W_1(\delta), W_2(\delta), \) and \( W_3(\delta) \).

<table>
<thead>
<tr>
<th>( T, \text{K} )</th>
<th>( W_1(\delta) )</th>
<th>( W_2(\delta) )</th>
<th>( W_3(\delta) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.996</td>
<td>1.000</td>
<td>0.997</td>
</tr>
<tr>
<td>100</td>
<td>0.997</td>
<td>1.006</td>
<td>0.998</td>
</tr>
<tr>
<td>150</td>
<td>0.996</td>
<td>1.015</td>
<td>0.996</td>
</tr>
<tr>
<td>200</td>
<td>0.995</td>
<td>1.035</td>
<td>0.997</td>
</tr>
<tr>
<td>250</td>
<td>0.998</td>
<td>1.077</td>
<td>0.998</td>
</tr>
<tr>
<td>300</td>
<td>1.000</td>
<td>1.139</td>
<td>0.998</td>
</tr>
<tr>
<td>350</td>
<td>0.998</td>
<td>1.159</td>
<td>0.998</td>
</tr>
<tr>
<td>400</td>
<td>0.997</td>
<td>1.167</td>
<td>0.998</td>
</tr>
</tbody>
</table>
In the chain with torsional potential (9) at \( T = 250 \text{ K} \), the vibrations of the chain become essentially nonlinear [see Fig. 13(a)]. Topological defects in the chain do not arise. We can see only high-amplitude vibrations of the particles. At \( T = 300 \text{ K} \), the initial state of the chain \( u_0 = 0, v_0 = 0 \) becomes unstable and the states with large energies \( u_0 , v_0 \approx \pm 0.5 \) are stable [see Fig. 13(b)]. When \( T = 350 \text{ K} \), the chain is in the vicinity of these metastable states. The lattice, consisting of the pairs of topological defects with opposite signs \( q = (0, \pm 1) \), is formed [see Fig. 13(c)]. It is seen from Table VI that the most pronounced growth of dimensionless thermal capacity occurs at \( T = 300 \text{ K} \). The saturation of thermal capacity occurs at \( T = 350 \text{ K} \), and a further increase of temperature does not lead to its growth. Therefore, the numerical modeling has shown that accumulation of pointlike topological defects can be considered as one of possible mechanisms of “chain liberation” preceding to phase transition. A satisfactory correspondence of experimental data and numerical estimation with respect to the temperature of structural transformations, confirms to a certain degree our supposition.

As seen from Table VI, an analogous transformation occurs, only a little earlier if using the torsional potential (11) and more earlier in the chain with strongly decreased energetic characteristics of the torsional potential (10). The considered transformation may correspond to the first stage of the phase transition between the II and IV forms of a PTFE crystal, which occur at \( T = 19^\circ\text{C} \). From this viewpoint, the use of the rotation potential (9) is quite justified, because, namely, energetic characteristics are the most important when studying high-amplitude motions and topological structural defects.

Let us note that the phase transition between II and IV forms of a PTFE crystal was also observed in numerical modeling. Despite the fact that we do not take into account a mobility of neighbor chains, our paper leads to the conclusion that the formation and accumulation of pairs of localized pointlike topological defects with opposite signs, may play a noticeable role in the mechanism of the first stage of the phase transition II–IV in crystalline PTFE.

VIII. CONCLUSIONS

The numerical study of topological defects (solitons) in crystalline PTFE has shown that four types of topological solitons can exist in a helix PTFE macromolecule. All these defects are stable with respect to thermal vibrations of the chain. Every defect is characterized by a two-dimensional topological charge. The defect of one type only possesses solitonlike dynamics and can propagate along the chain as a solitary wave. Solitons of this type have a velocity spectrum in subsonic region. Other defects are subjected to pinning and their motion can be presented as thermally activated random jumps. The numerical modeling reveals the existence of a phase transition near \( T = 300 \text{ K} \), which is characterized by fast accumulation of topological defects and increasing thermal capacity of the system.

ACKNOWLEDGMENTS

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