Solitons in crystalline polyethylene: Isolated chains in the transconformation

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This paper is devoted to the investigation of soliton-type excitations in crystalline polyethylene. A numerical solution of the problem of the existence and stability of dynamical solitons in an isolated polyethylene chain has been obtained. In the framework of a realistic model, taking into account deformations of the valence angles and valence bonds, soliton-type excitations describing propagation of the local region of tension along the chain have been found. The existence of the solitons of tension is a direct consequence of a predominance of geometric nonlinearity in a transzigzag chain over a physical one. It is shown that the polyethylene molecule has a comparitively narrow spectrum of soliton velocities in the supersonic region. The modeling performed shows that the solitons of tension are stable over the whole area of their existence. The region of parameters, where interaction between solitons is elastic, has been found. In our numerical analysis we took a refined version of an analytic solution for the limiting case of rigid bonds as the starting point. [S1063-651X(97)03102-4]

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I. INTRODUCTION

Although the problem of linear plane dynamics of the polyethylene molecule was studied by Kirkwood [1] more than half a century ago, its nonlinear generalization has become the subject of theoretical analysis only recently [2]. Such an analysis was stimulated by finding the essential role of localized nonlinear excitations in the process of mechanical degradation of one-dimensional crystals [3,4]. It turned out that a transition from the straight chain to the ''transzigzag'' conformation leads to a qualitative change in the type of soliton solutions: instead of the solitons of compression one can find supersonic solitons of tension as elementary nonlinear excitations [2]. The existence of the solitons of tension is a consequence of geometric nonlinearity of the transzigzag chain which is absent in the case of longitudinal dynamics of a straight chain. This conclusion was, however, obtained in the approximation of infinitely rigid valence bonds; i.e., if only deformations of valence angles are allowed for tension. The problem concerning the influence of inevitable deformations of valence bonds on the dynamics of solitons of this type has remained open.

In this paper the study of solitons of tension in the polyethylene molecule is done in the framework of a more realistic model taking into account deformations of both the valence angles and valence bonds. Previously a refined version of an analytic solution for the limiting case of rigid bonds was obtained. This has been taken as the starting point in the following numerical analysis of the general problem.

II. THE MODEL

In the studies of low-energetic dynamical processes in polyethylene the motion of hydrogen atoms with respect to the main chain is not essential and the approximation of ''united atoms'' can be used [5].

Let us consider a polyethylene molecule $(CH_2)_\infty$ in the transzigzag conformation. In the equilibrium state the backbone of the molecule has a plane zigzag structure which may be characterized by the step $\rho_0 = 1.53$ Å (equilibrium length of the valence bond $H_2C—CH_2$) and by the zigzag angle $\theta_0 = 113°$ (equilibrium valence angle $CH_2—CH_2—CH_2$). A schematic structure of the transzigzag is represented in Fig. 1.

Let the transzigzag be directed along the x axis and be situated in the plane xy. Then the nth unit (CH_2) of the chain has the coordinates

$$x_n^{\circ} = n l_x, \quad y_n^{\circ} = (-1)^n l_y/2,$$

where $l_x = \rho_0 \sin(\theta_0/2)$ and $l_y = \rho_0 \cos(\theta_0/2)$ are longitudinal and transversal steps of the transzigzag chain. It is convenient to introduce the relative coordinates

$$u_n = x_n - x_n^{\circ}, \quad v_n = (-1)^{n+1}(y_n - y_n^{\circ}).$$

Here u_n and v_n determine longitudinal and transversal displacements of the nth united atom from its equilibrium state, respectively, with the positive direction for transversal displacement to the center of the zigzag (Fig. 2). The length of the nth valence bond and the cosine of the nth valence angle are

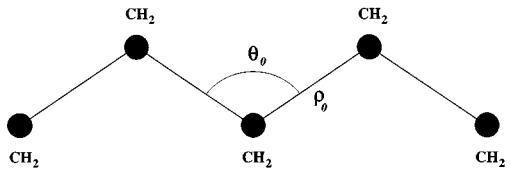

FIG. 1. The structure of polyethylene molecule $(CH_2)_\infty$.

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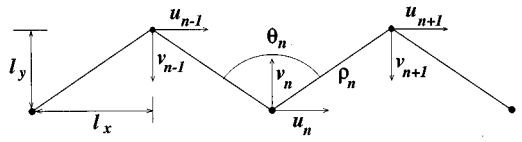

FIG. 2. Reference systems for the displacements of united atoms.

$$\rho_n=\sqrt{(l_x-w_n)^2+(l_y-z_n)^2},$$

$$\cos(\theta_n)=-\frac{a_{n-1}a_n-b_{n-1}b_n}{\rho_{n-1}\rho_n}, \tag{1}$$

where $w_n=u_n-u_{n+1}$ and $z_n=v_n+v_{n+1}$ are longitudinal and transversal deformations of the nth segment of the chain, $a_n=l_x-w_n$, $b_n=l_y-z_n$.

The Hamiltonian of the chain can be written as

$$\mathcal{H}=\sum_n\left[\frac{1}{2}M\dot{u}_n^2+\frac{1}{2}M\dot{v}_n^2+V(\rho_n)+U(\theta_n)\right]. \tag{2}$$

Here the mass of the united atom $M=14m_p$ ($m_p=1.672\,61\times10^{-27}$ kg is the mass of the proton),

$$V(\rho_n)=D_0\{1-\exp[-\alpha(\rho_n-\rho_0)]\}^2 \tag{3}$$

is the potential of the nth valence bond,

$$U(\theta_n)=\tfrac{1}{2}\gamma(\cos\theta_n-\cos\theta_0)^2 \tag{4}$$

is the potential of the nth valence angle. According to Ref. [5], the energy of the valence bond $D_0=334.72$ KJ/mol, the parameters $\alpha=1.91$ Å^{-1}, and $\gamma=130.122$ KJ/mol. The plane mechanical model of the chain is presented in Fig. 3.

If deformations of the bonds and angles are small the parabolic approximation of potentials (3) and (4) can be used

$$V(\rho_n)\approx\tfrac{1}{2}K_1(\rho_n-\rho_0)^2,\quad U(\theta_n)\approx\tfrac{1}{2}K_2(\theta_n-\theta_0)^2, \tag{5}$$

where force constants $K_1=2D_0\alpha^2=405.53$ N/m, $K_2=\gamma\sin^2\theta_0=18.308\times10^{-20}$ J.

Linearization of the equations of motion

$$M\ddot{u}_n=-\frac{\partial H}{\partial u_n},\quad M\ddot{v}_n=-\frac{\partial H}{\partial v_n},\quad n=0,\pm1,\pm2,\ldots, \tag{6}$$

with account of expressions (1) and (5) allows one to obtain the dispersion relation [1]

$$\omega_\pm^2(q)=\omega_0^2(q)\pm\sqrt{\omega_0^4(q)-\omega_1^4(q)}. \tag{7}$$

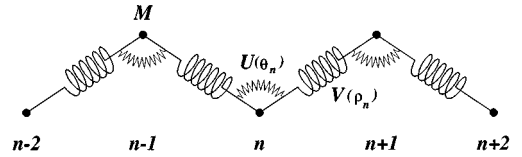

FIG. 3. The plane mechanical model of the polyethylene chain.

Here

$$\omega_0^2(q)=C_1(1+\cos\theta_0\cos2q)+2C_2(1+\cos2q)(1-\cos\theta_0\cos2q),$$

$$\omega_1^4(q)=8C_1C_2(1+\cos2q)\sin^2 2q,$$

and $C_1=K_1/M$, $C_2=K_2/M\rho_0^2$. The upper [$\omega=\omega_+(q)$] and lower [$\omega=\omega_-(q)$] branches correspond to optic and acoustic phonons, respectively.

The velocity of long-length longitudinal phonons (sound velocity)

$$c_0=l_x\lim_{q\to\infty}\frac{\omega_-(q)}{2q}=2\sqrt{K_2/M}\,\tan(\theta_0/2)/\sqrt{1+4\epsilon\,\tan(\theta_0/2)},$$

where the dimensionless parameter

$$\epsilon=C_2/C_1=K_2/K_1\rho_0^2=0.019\,29$$

characterizes the relation of the stiffness of the valence angle to the stiffness of the valence bond. It turns out that the latter far exceeds the former (approximately by two orders). Therefore it seems that one can use the approximation of the infinitely rigid valence bond $\epsilon=0$ ($K_1=\infty$). However, in this approximation the sound velocity

$$\overline{c_0}=2\sqrt{K_2/M}\,\tan^2(\theta_0/2)=8449\ \text{m/s},$$

differs from the exact value $c_0=7790$ m/s$=0.922\,10\overline{c_0}$. Such a shift of the value of the sound velocity, as will be shown further, leads to the necessity of taking into account the finite rigidity of the valence bonds.

III. APPROXIMATION OF INFINITE RIGID VALENCE BONDS

The complexity of the nonlinear system of the equations of motion (6) does not allow an analytical study except when $\varepsilon=0$ (the bonds are infinitely rigid). This limiting case was studied in [2] but there is a need to reconsider in order to account more exactly for the dispersion properties of the model investigated.

It is supposed that geometric nonlinearity is predominant and $U(\theta)=\frac{1}{2}K_2(\theta-\theta_0)^2$. Then the Hamiltonian of the chain has a form

$$\mathcal{H}=\sum_n\left[\frac{1}{2}M\dot{u}_n^2+\frac{1}{2}M\dot{v}_n^2+\frac{1}{2}K_2(\theta_n-\theta_0)^2\right]. \tag{8}$$

Up to the second order the change of the length of the nth valence bond and the nth valence angle are

$$\Delta\rho_n=\rho_n-\rho_0=\mathcal{A}(u_{n+1}-u_n)-\mathcal{C}(v_{n+1}+v_n)+\frac{1}{2\rho_0}[\mathcal{C}(u_{n+1}-u_n)+\mathcal{A}(v_n+v_{n+1})]^2, \tag{9}$$

$$\Delta\theta_n=\theta_n-\theta_0=\frac{c}{\rho_0}(u_{n+1}-u_{n-1})+\frac{s}{\rho_0}(v_{n+1}+2v_n+v_{n-1})$$
$$+\frac{cs}{\rho_0^2}[(v_n+v_{n+1})^2+(v_n+v_{n-1})^2$$
$$-(u_{n+1}-u_n)^2-(u_n-u_{n-1})^2]$$
$$+\frac{c^2-s^2}{\rho_0^2}[(u_n-u_{n-1})(v_n+v_{n-1})$$
$$+(u_{n+1}-u_n)(v_n+v_{n+1})], \quad (10)$$

where $c=\cos(\theta_0/2)$, $s=\sin(\theta_0/2)$.

Supposing that all variables change slowly enough along the chain we can use the continuum approximation: $u_n(t)=u(nl_x,t)$, $v_n(t)=v(nl_x,t)$. Then the equality (9) takes the form

$$\Delta\rho=sl_xu_x-2cv+\frac{1}{2\rho_0}(cl_xu_x+2sv)^2+\cdots .$$

For infinitely rigid bonds $\Delta\rho\equiv 0$, therefore

$$sl_xu_x-2cv+\frac{1}{2\rho_0}(cl_xu_x+2sv)^2+\cdots=0. \quad (11)$$

Equation (11) allows us to decrease a number of variables. Indeed, let us substitute the expressions $v=C_1u_x+C_2u_x^2+\cdots$ into Eq. (11) and equate the coefficients corresponding to different degrees of the variable u_x to zero. Then in the main nonlinear approximation one can obtain the values of C_i $(i=1,2)$: $C_1=s^2\rho_0/2c$, $C_2=\rho_0s^2/4c^3$, i.e.,

$$v=\frac{1}{2}\frac{s^2}{c}\rho_0u_x+\frac{1}{4}\frac{s^2}{c^3}\rho_0u_x^2. \quad (12)$$

Taking into account relation (12), it is easy to transform the discrete equation (10) to the form

$$\Delta\theta=a_1u_x+a_2u_x^2+a_3u_{xxx},$$

where the coefficients $a_1=2s/c$, $a_2=(s/c)^3$, $a_3=s^3(2+s^2)\rho_0/6c$. The third term on the right side of this relation has been neglected in [2]. As we shall see its contribution may be sufficiently perceptible.

Thus, in the case of infinitely rigid bonds, the Lagrange function of the system can be written in the form

$$L=\int\int\left[\frac{1}{2}Mu_t^2+\frac{1}{2}M\left(\frac{1}{2}\frac{s^2}{c}\rho_0u_{xt}+\frac{1}{2}\frac{s^2}{c^3}\rho_0u_xu_{xt}\right)^2\right.$$
$$\left.-\frac{1}{2}K_2(a_1u_x+a_2u_x^2+a_3u_{xxx})^2\right]dxdt. \quad (13)$$

The corresponding equation of motion is

$$\frac{\partial L}{\partial u}-\frac{\partial}{\partial t}\frac{\partial L}{\partial u_t}-\frac{\partial}{\partial x}\frac{\partial L}{\partial u_x}+\frac{\partial}{\partial t\partial x}\frac{\partial L}{\partial u_{xt}}-\frac{\partial^3}{\partial x^3}\frac{\partial L}{\partial u_{xxx}}=0,$$

or

$$-u_{tt}+\overline{c_0^2}u_{xx}+p_1u_xu_{xx}+p_2u_{xxxx}+p_3u_{xxtt}=0, \quad (14)$$

where coefficients

$$p_1=6a_1a_2K_2/M=12s^4K_2/Mc^4,$$
$$p_2=2a_1a_3K_2/M=2s^4(2+s^2)K_2\rho_0^2/6Mc^2,$$
$$p_3=\rho_0^2s^4/4c^2.$$

Let us now use the wave variable $\xi=x-ct$, where c is velocity of the propagation of the stationary wave. Then the equation of motion has the form

$$u_{\xi\xi}(\overline{c_0^2}-c^2)+p_1u_\xi u_{\xi\xi}+(p_2+p_3c^2)u_{\xi\xi\xi\xi}=0. \quad (15)$$

After integration (15) and substituting $w=u_\xi$ one can obtain the equation

$$(\overline{c_0^2}-c^2)w+\tfrac{1}{2}p_1w^2+(p_2+p_3c^2)w_{\xi\xi}=0. \quad (16)$$

In distinction to [2] $p_2\neq 0$, moreover, the ratio $p_2/p_3c^2\sim 0.45$. So, the refinement performed is reasonable.

The multiplication on w_ξ and integration of Eq. (16) leads to the stationary Boussinesq equation

$$(p_2+p_3\overline{c^2})w_\xi^2+\tfrac{1}{3}p_1w^3+(\overline{c_0^2}-c^2)w^2=0. \quad (17)$$

Equation (17) has the soliton solution

$$w(\xi)=A/\cosh^2(\xi/L),$$

where the amplitude $A=3(c^2-\overline{c_0^2})/p_1$, the width $L=2\sqrt{(p_2+p_3c^2)/(c^2-\overline{c_0^2})}$, and the velocity $c>\overline{c_0}$.

Thus in our transzigzag chain with geometric anharmonicity the supersonic solitons of tension

$$u(x,t)=AL\ \tanh\left(\frac{x-ct}{L_1}+x_1\right),$$

exist, where the initial center position is x_1, the soliton velocity $c>\overline{c_0}$. The corresponding transversal displacements $v(x,t)$ can be found from Eq. (12).

The existence of the solitons of tension is a direct consequence of the zigzag structure of the chain. In a straight chain such solitons are impossible. Let us note that in a straight chain a geometric anharmonicity leads to existence of the envelope solitons [7].

IV. NUMERICAL TECHNIQUES FOR REVEALING OF SUPERSONIC SOLITONS

Let us look for a soliton of system (6) in the form of a traveling wave $u_n(t)=u(\xi)$, $v_n(t)=v(\xi)$, where $\xi=nl_x-ct$, c is the wave velocity, the functions u and v are supposed to be smoothly dependent on ξ. Then the Lagrangian corresponding to system (6)

$$\mathcal{L}=\sum_n\left[\frac{1}{2}M\dot{u}_n^2+\frac{1}{2}M\dot{v}_n^2-V(\rho_n)-U(\theta_n)\right]$$

can be written as

$$\overline{\mathcal{L}}=\sum_n \left\{ \frac{c^2M}{24l_x^2}[16w_n^2-(w_n+w_{n+1})^2+16(v_{n+1}-v_n)^2 -(v_{n+2}-v_n)^2]-V(\rho_n)-U(\theta_n)\right\}.$$

A supersonic solitonlike solution always corresponds to the saddle point of the Lagrangian. Consequently, it may be found as a minimum point of the functional

$$\mathcal{F}=\frac{1}{2}\sum_n (\overline{\mathcal{L}_{w_n}^2}+\overline{\mathcal{L}_{v_n}^2}).$$

Thus for the revealing of the solitonlike solution (solitary wave) $\{w_n,v_n\}_{n=1}^N$ the conditional minimum problem

$$\mathcal{F}=\frac{1}{2}\sum_{n=2}^{N-1} (\overline{\mathcal{L}_{w_n}^2}+\overline{\mathcal{L}_{v_n}^2})\rightarrow \min: \quad w_1=w_N=v_1=v_N=0 \tag{18}$$

may be solved numerically.

All solitonic regimes considered are smooth solitary waves with a constant profile. The absence of such solutions for a certain value c means that such a soliton does not exist.

The problem (18) has been solved by the techniques of conjugated gradients [6]. The number of united atoms was supposed to be $N=400$. On the basis of an analytical study in the limiting case $\varepsilon=0$ the initial descent point was taken in the form of two symmetrical bell-like profiles $w(n)$, $v(n)$ with the center at the middle of the chain.

Every soliton solution $\{w_n^0,v_n^0\}_{n=1}^N$ is characterized by the energy

$$E=\sum_{n=2}^{N-1} \left\{ \frac{c^2M}{24l_x^2}[16w_n^2-(w_n+w_{n+1})^2+16(v_{n+1}-v_n)^2 -(v_{n+2}-v_n)^2]+V(\rho_n)+U(\theta_n)\right\},$$

by the overall longitudinal tension of the chain

$$R=\sum_{n=1}^N w_n,$$

which will be named further as a soliton amplitude, by the mean square width measured in the periods of the chain

$$L=2\sqrt{\sum_{n=1}^N (n-m)^2 w_n/R},$$

(the point

$$m=1/2+\sum_{n=1}^N nw_n/R$$

defines the place of the soliton center), by the maximum value of the valence angle $\theta=\max_n(\theta_n)$ and by the maximum length of the valence bond $\overline{\rho}=\max_n(\rho_n)$.

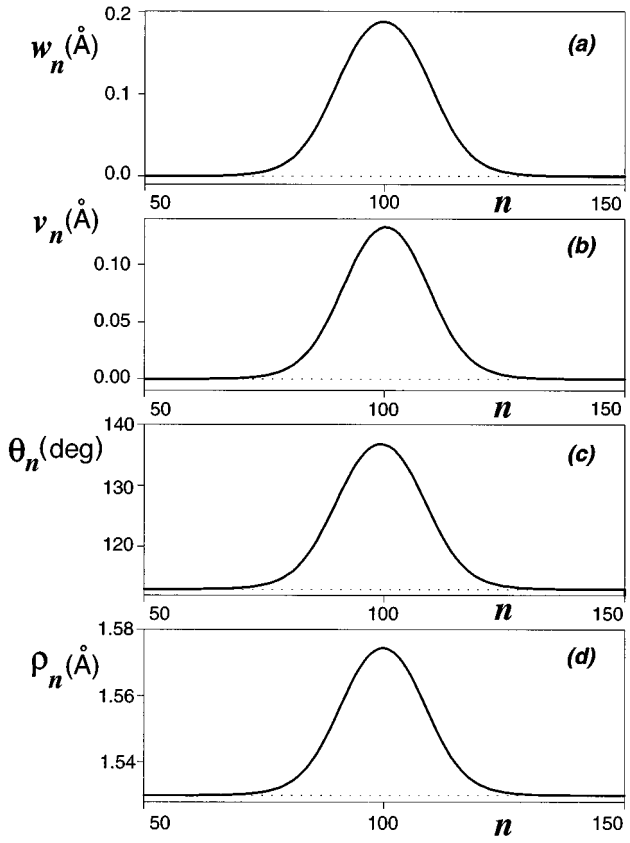

FIG. 4. The profiles of supersonic soliton of tension $w_n=u_{n+1}-u_n$ (a), v_n (b), θ_n (c), ρ_n (d) in the initial ($t=0$) and time $t=160.682$ ps , after soliton approaches 10 000 united atoms. The dimensionless velocity of the soliton $s=0.94$ ($c=7940.21$ m/s).

V. SOLITONS OF TENSION

For real molecular systems the model of infinitely rigid valence bonds turns out to be rough. The soliton form depends essentially on its velocity, but the restriction connected with infinite rigidity of valence bonds leads, as was mentioned above, to a perceptible shift of the sound velocity.

In this section we consider solitons of tension taking into account the finite rigidity of the valence bonds. Let us consider a soliton solution for potentials (3) and (4). Potential (4) is a periodic multiwell barrier potential with minima $\theta=\theta_0$ and $\theta=2\pi-\theta_0$. It reflects correctly the multistability of the transzigzag chain. Indeed, there are energetically equivalent ground states: $x_n^0=nl_x$, $y_n^0=(-1)^n l_y/2$ ($\theta_n\equiv\theta_0$) and $x_n^0=nl_x$, $y_n^0=(-1)^{n+1}l_y/2$ ($\theta_n\equiv 2\pi-\theta_0$). The essential peculiarity of this potential is the existence of inflection point $\theta_1=157.99°$.

Numerical solution of problem (18) has shown that the nonlinear system (6) has solitonic solutions with supersonic velocities. A typical form of the soliton is presented at Fig. 4. The soliton has bell-like profiles for component $w_n=u_{n+1}-u_n$, v_n, θ_n, ρ_n. There is longitudinal tension ($w_n>0$) and transversal compression ($v_n>0$). As this takes place the values of the valence angles increase ($\theta_n>\theta_0$) and valent bonds tense $\rho_n>\rho_0$.

The soliton of tension exists in a narrow supersonic re-

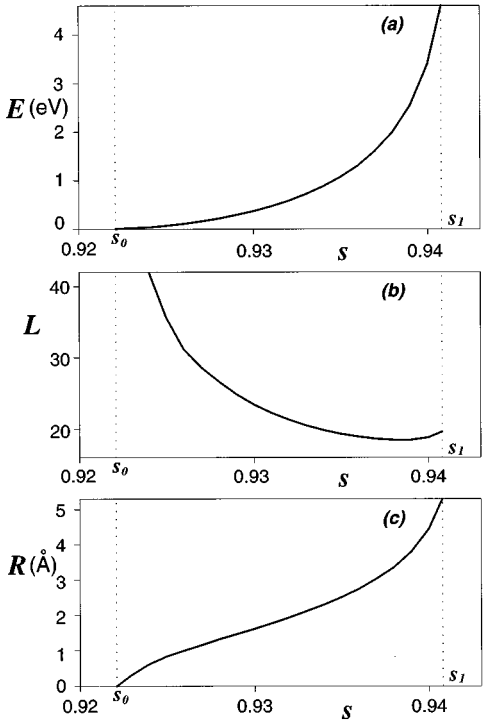

FIG. 5. The dependence of the soliton energy E (a), width L (b), amplitude R (c) on dimensionless velocity s.

gion $s_0<s<s_1$, where dimensionless velocities $s_0=c_0/\overline{c_0}$, $s=c/c_0$, $s_1=0.9408$. The dependence of the energy E, width L and amplitude R of the soliton on dimensionless velocity s are presented in Fig. 5. The finiteness of the velocity spectrum of the soliton is connected with the existence of the inflection point θ_1 for potential (4). With the increasing of the velocity the value of the maximum valence angle $\overline{\theta}=\max\theta_n$ monotonically increases and approaches θ_1 near the right boundary of the spectrum. With the increasing of the velocity the energy and amplitude monotonically grow and approach their maximum values $E_m=4.6$ eV, $R_m=5.3$ Å for $s=s_1$. The width of the soliton decreases, but always exceeds 18 segments of the chain. Therefore, the assumption concerning the smooth dependence of the soliton form on the number of cites is satisfied. Concrete values of the energy E, width L, amplitude R, maximum valence angle $\overline{\theta}=\max\theta_n$ and maximum length of the valence bond $\overline{\rho}=\max\rho_n$ are presented in Table I. As is seen from this table, the tension of the chain occurs mainly due to an increase of the valence angles. The elongation of the valence bonds does not exceed several hundred parts of angstrom, while the valence angles can increase on several decades of degrees.

Numerical solution of the minimum problem (18) has also shown that in the chain with multiwell potential $U_2(\theta)$ the high-amplitude soliton of tension exists with $s=0.990$. The corresponding soliton energy is $E=11.55$ eV. The soliton profile is shown in Fig. 6. In the localization region of the soliton the values of the valence angles exceed 180°, i.e., locally the chain transfers to another ground state. Existence of such a soliton is connected with the multistability of potential. It was shown earlier that in a two-dimensional alpha-

TABLE I. The dependence of soliton energy E, width L, amplitude R, maximum valence angle $\overline{\theta}$, and maximum length of the valence bond $\overline{\rho}$ on dimensionless velocity s.

s	E (eV)	L	R (Å)	$\overline{\theta}$ (deg)	$\overline{\rho}$ (Å)
0.9221	0	∞	0	113.0	1.530
0.924	0.030	41.9	0.63	114.5	1.532
0.926	0.105	31.2	1.00	116.3	1.535
0.928	0.216	26.7	1.32	118.2	1.538
0.930	0.370	23.4	1.62	120.2	1.542
0.932	0.582	21.3	1.94	122.4	1.546
0.934	0.877	19.9	2.30	125.0	1.551
0.936	1.309	18.9	2.74	128.0	1.556
0.938	1.998	18.4	3.36	131.6	1.564
0.940	3.390	18.8	4.44	136.8	1.574
0.9408	4.601	19.6	5.31	139.9	1.581

helix model [8] geometric nonlinearity can also lead to the existence of the soliton of tension with unique velocity.

VI. NUMERICAL SIMULATION OF SOLITON DYNAMICS

For the estimation of the stability of the nonlinear excitations discussed above the modeling of the soliton dynamics in the finite chain consisting of $N_1=400$ sites was per-

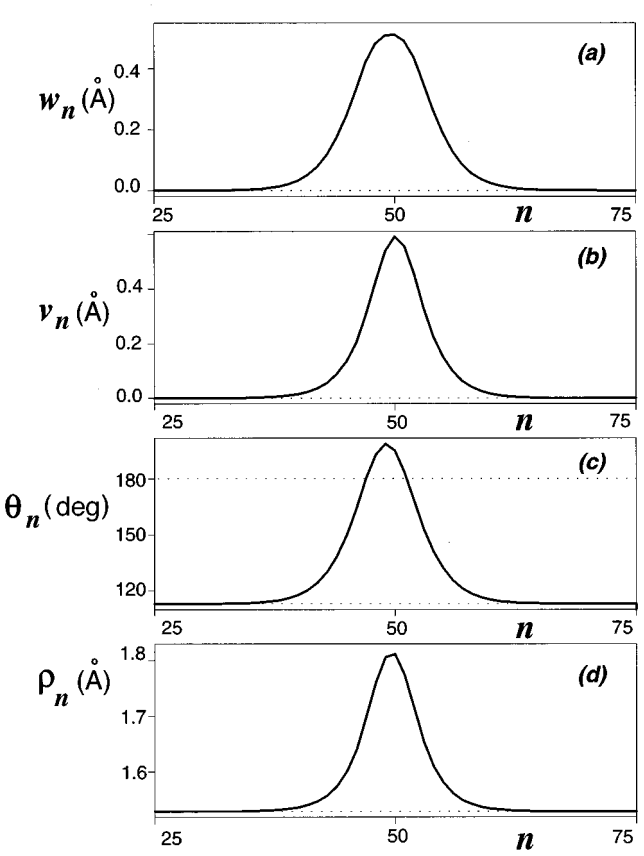

FIG. 6. The profiles of high-amplitude supersonic soliton of tension $w_n=u_{n+1}-u_n$ (a), v_n (b), θ_n (c), ρ_n (d). The soliton velocity $s=0.990$, the energy $E=11.55$ eV.

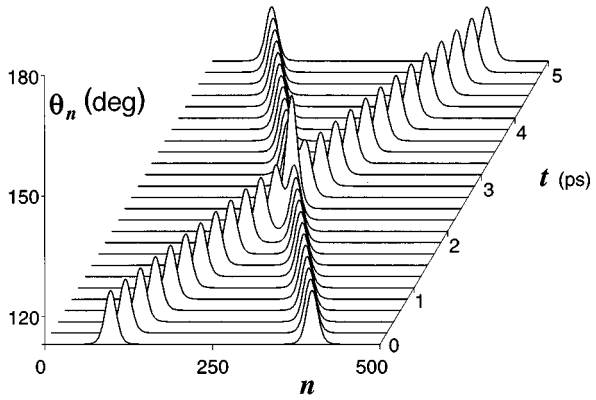

FIG. 7. The elastic collision of two solitons of tension. Dimensionless velocity $s=0.935$.

formed. The system of the equations of motion

$$M\ddot{u}_n=-\frac{\partial H}{\partial u_n},\quad M\ddot{v}_n=-\frac{\partial H}{\partial v_n},\quad n=3,\ldots,N_1-2 \tag{19}$$

was integrated numerically. The end sites of the chain $n=1$, 2, N_1-1, N_1 are supposed to be immobile (the condition of fixed boundary).

The initial conditions for system (19)

$$u_1(0)=R/2,\quad u_{n+1}(0)=u_n(0)-w_n^0,\quad n=2,\ldots,N-1;$$

$$v_n(0)=v_n^0,\quad n=1,\ldots,N;$$

$$\dot{u}_n(0)=s\overline{c_0}[u_{n+1}(0)-u_{n-1}(0)]/2l_x,$$

$$\dot{v}_n(0)=s\overline{c_0}[v_{n+1}(0)-v_{n-1}(0)]/2l_x,$$

$$n=2,\ldots,N-1;\quad u_n(0)=u_N(0),$$

$$v_n(0)=v_N(0),\quad \dot{u}_n(0)=0,\quad \dot{v}_n(0)=0,\quad N<n<N_1$$

correspond to the soliton solution $\{w_n^0,v_n^0\}_{n=1}^N$ of problem (18). As this takes place, the arrangement of the center of the soliton may be defined as the point of intersection of the broken line, which subsequently unites the points $\{(n,u_n)\}_{n=1}^{N_1}$, with the axis n.

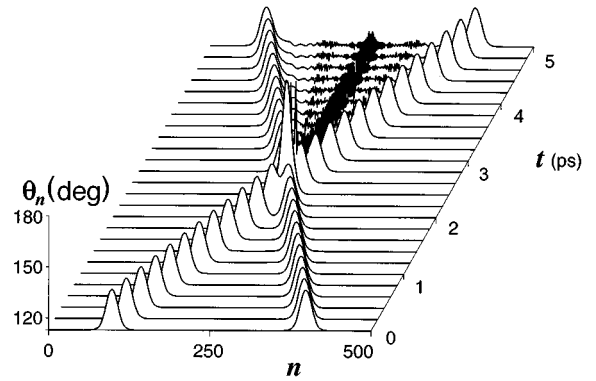

FIG. 8. The unelastic collision of two solitons of tension. Dimensionless velocity $s=0.940$.

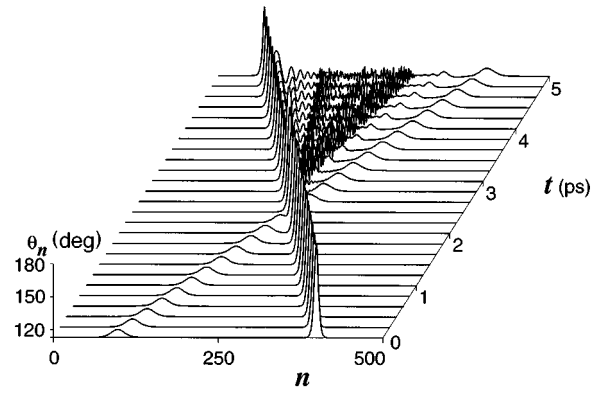

FIG. 9. The collision of the small-amplitude soliton of tension ($s=0.930$) with the high-amplitude soliton ($s=0.990$).

Let us take $N=200$, then the center of the soliton will be initially situated on the 100th particle of the chain. To model the dynamics of the soliton in the infinite chain, every time when it propagates to the right up to the 200th site, the shift of the soliton to the left on these 200 sites is fulfilled

$$u_n(t)=u_{n+200}(t),\quad \dot{u}_n(t)=\dot{u}_{n+200}(t),\quad v_n(t)=v_{n+200}(t),$$

$$\dot{v}_n(t)=v_{n+200}(t),\quad n=1,\ldots,N;$$

$$u_n(t)=u_{N_1}(0),$$

$$\dot{u}_n(t)=0,\quad v_n(t)=v_{N_1}(0),$$

$$\dot{v}_n(t)=0,\quad n=N+1,\ldots,N_1.$$

The system of Eqs. (19) was integrated numerically by the conventional Runge-Kutta method of the fourth order with the constant step of the integration. The accuracy of the numerical integration was controlled by the preservation of the integral of the total energy

$$H=\sum_{n=2}^{N_1-1}\left[\frac{1}{2}M\dot{u}_n^2+\frac{1}{2}M\dot{v}_n^2+V(\rho_n)+U(\theta_n)\right].$$

For example, while the step $\Delta t=10^{-15}$ the full energy was preserved up to seven meaning numbers in the all time of integration.

Numerical simulation of the dynamics has shown that the solitons of tension are dynamically stable at all admissible velocities of the motion. They propagate along the chain with preservation of their form. For example, the soliton of tension with the initial dimensionless velocity $s=0.940$ ($c=7940.21$ m/s) passes 9999.762 sites of the chain during 160.683 ps, i.e., the dimensionless velocity is $\overline{s}=0.939\,756$. The profile of the soliton in finite time coincides fully with the initial one (see Fig. 4).

The collision of two solitons has been numerically simulated also. Let us consider the collision of two solitons which move foward to each other with the same velocity s. The numerical integration of system (19) has shown that the collision occurs elastically only if it does not lead to the increase of the valence angles up to the value which corresponds to the inflection point θ_1 of the potential (4). In the former case the reflection of the solitons occurs without the radiation of the phonons and change of the form of the

solitons—see Fig. 7. Near the right boundary of the velocity spectrum this condition is broken, so that the collision leads to the deformations of the angles exceeding the critical values θ_1 and therefore it occurs unelastically. The reflection of solitons is accompanied by the radiation of the phonons (see Fig. 8).

Let us consider at last the collision of high-amplitude soliton with the low-amplitude solitons of tension. The high-amplitude soliton has only one admissible value of the velocity of propagation $s=0.990$. In the localization region of this soliton the angle deformation exceeds always the value corresponding to the inflection point of the valence angle potential. Therefore the collision of the high-amplitude soliton with the low-amplitude one occurs inelastically with radiation of the phonons (see Fig. 9). Such a collision leads to the breaking of the high-amplitude soliton. Its motion after collision is accompanied by sustained radiation of phonons. The low-amplitude soliton preserves its form and propagates after collision without the radiation of phonons.

VII. CONCLUSION

Nonlinear dynamics of a polyethylene chain is characterized by important peculiarities in comparison with a straight anharmonic atomic chain. First, supersonic solitons of tension (rather than compression) arise due to the predominant role of geometric anharmonicity. Moreover, the spectrum of soliton velocity is restricted if one takes into account the physical anharmonicity. The solitons of tension are stable in the whole region of their existence. The region of velocity where interaction between solitons is elastic is more narrow.

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