Soliton mechanism for propagation of endothermal structural transitions in bistable systems

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A soliton mechanism is proposed, for the first time, for the endothermal structural rearrangement of the asymmetric bistable chain. It is shown that a topological soliton can exist in a two-component asymmetric bistable system, and this soliton can convert the uniform ground state into an intermediate dynamic metastable state which is topologically equivalent to a second, uniform state of the system which is stable (if the disturbance is sufficiently weak). Such a soliton is dynamically stable, and for given parameters of the system it can propagate at only one speed. In the process of propagation, the metastable state relaxes in the region behind the soliton front. As long as the relaxation region is separated from the soliton front by the metastable region, it has virtually no effect on the soliton dynamics. © *1995 American Institute of Physics.*

1. INTRODUCTION

Under certain conditions, structural transitions can occur in condensed systems with two uniform equilibrium states which are separated by an energy barrier. Typical examples are A-B and B-A transitions in DNA molecules,[1–4] structural rearrangement as a result of proton transfer in chains of hydrogen bonds,[5–8] and topochemical reactions in molecular crystals.[9–12] Degenerate bistable systems are especially interesting. In such systems both equilibrium states have the same energy, and this makes possible a soliton mechanism for structural transitions.[13–15] Obviously, the energy degeneracy condition sharply narrows the class of processes studied. Although the existence of topological solitons in nondegenerate systems seems to be impossible at first glance, it has recently been shown[16,17] that, generally speaking, this is not the case. In contrast to the ordinary situation, however, solitons in the degenerate case transfer the system not into a final state, but rather into an intermediate, time-dependent state. There arises the natural question of whether or not the elementary wave mechanism of a structural transition in nondegenerate bistable systems can produce such solitons? The problem is that here the analysis cannot be limited to only the motion of the soliton itself, since a special relaxation process must accomplish the transition of a nondegenerate system from the intermediate into the final state (this stage is absent in degenerate systems).

In Refs. 16 and 17 it is shown that when an exothermal structural transition propagates the velocity of the soliton is supersonic and the relaxation process occurring behind the wave front has virtually no effect on the velocity and shape of the front. This means that the topological soliton adequately describes the intermediate asymptotic process of propagation of an exothermal structural transition. Is this result valid for an endothermal transition? We shall show below that an endothermal topological soliton propagates with a unique subsonic speed, so that a relaxation process propagating with the sound velocity must overtake the soliton. As a result, the soliton will have a finite lifetime, determined by the length of the section where the chain is in the intermediate (metastable) state.

2. TWO-COMPONENT MODEL OF A BISTABLE SYSTEM

We shall study a quasi-one-dimensional molecular system (chain) consisting of bistable monomeric links. The schematic model of such a system is displayed in Fig. 1. Let $R_n(t)$ be the displacement of the nth monomer of the chain and $r_n(t)$ the conformational state of the monomer. Then the Hamiltonian of the system can be represented in the form

$$H=H_1+H_2+H_3, \tag{1}$$

where the energy of the outer sublattice is

$$H_1=\sum_n \left\{\frac{1}{2}M\dot{R}_n^2+\frac{1}{2}K(R_{n+1}-R_n)^2\right\}, \tag{2}$$

the energy of the inner sublattice is

$$H_2=\sum_n \left\{\frac{1}{2}m\dot{r}_n^2+\frac{1}{2}k(r_{n+1}-r_n)^2+\Phi(r_n)\right\}, \tag{3}$$

and the intersublattice interaction energy is

$$H_3=\sum_n (R_{n+1}-R_{n-1})G(r_n). \tag{4}$$

Here M and m are, respectively, the total and reduced mass of a monomer in the chain and K and k are, respectively, the force constants of the outer and inner sublattices.

The asymmetric double-well intramonomer interaction potential which gives rise to the two stable stationary states (conformations) of an isolated monomer is approximated by the function

$$\Phi(r)=\epsilon_0[(r/r_0)^2-1]^2+\epsilon_1 r/r_0+\epsilon_2. \tag{5}$$

The parameter $\epsilon_0>0$ of the potential characterizes the height of the energy barrier separating the two stable conformations of the monomer, and the parameter $0\leqslant\epsilon_1<8\epsilon_0/\sqrt{27}$ characterizes the energy splitting between these conformations.

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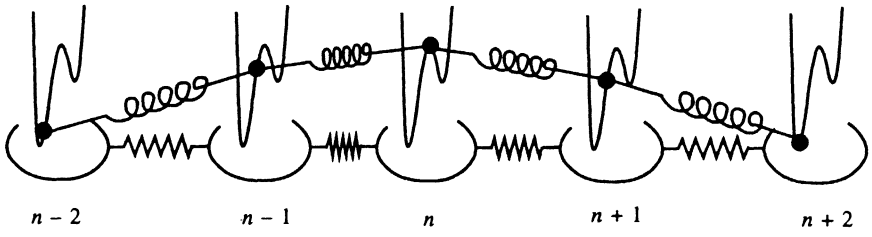

FIG. 1. Schematic representation of a two-component bistable system with inequivalent states.

For $\epsilon_1=0$ the function $\Phi(r)$ describes a symmetric double-well potential with the minima $r=\pm r_0$ and a barrier of height ϵ_0. In the general case the potential $\Phi(r)$ will have two asymmetric minima $r_{\min,1}$ and $r_{\min,2}$, separated by a maximum $r_{\max}$:

$$r_{\min,1}<-r_0<0<r_{\max}<r_{\min,2}<r_0.$$

We choose the reference energy level of the potential ϵ_2 so that in the ground state of the monomer $r=r_{\min,1}$ the energy of the monomer satisfies $\Phi(r_{\min,1})=0$, i.e.,

$$\epsilon_2=-\epsilon_0[(r_{\min,1}/r_0)^2-1]^2-\epsilon_1 r_{\min,1}/r_0.$$

The function

$$G(r)=-X_1(r_{\min,1}-r)/r_0+X_2(r_{\min,1}^2-r^2)/r_0^2 \tag{6}$$

characterizes the interaction of the sublattices. The interaction parameter X_1 describes the effective change introduced in the energy splitting between the two stable conformations of a monomer by a deformation of the outer sublattice, and the parameter X_2 describes the change in the height of the energy barrier separating these conformations. For $\epsilon_1=0$ and $X_1=0$ the Hamiltonian H constructed above is identical to the Hamiltonian proposed in Ref. 15 for describing the soliton dynamics of symmetric two-component bistable systems.

For convenience, we introduce the dimensionless displacements $x_n=r_n/r_0$ and $y_n=R_n/r_0$, the dimensionless time $\tau=t\sqrt{k/m}$, and the dimensionless energy $\mathscr{H}=H/kr_0^2$. Then the Hamiltonian of the system (1) assumes the form

$$\mathscr{H}=\mathscr{H}_1+\mathscr{H}_2+\mathscr{H}_3, \tag{7}$$

where the functions (2), (3), and (4) are defined as follows:

$$\mathscr{H}_1=\sum_n\left\{\frac{1}{2}\mu y_n'^2+\frac{1}{2}\kappa(y_{n+1}-y_n)^2\right\},$$

$$\mathscr{H}_2=\sum_n\left\{\frac{1}{2}x_n'^2+\frac{1}{2}(x_{n+1}-x_n)^2+V(x_n)\right\},$$

$$\mathscr{H}_3=\sum_n(y_{n+1}-y_{n-1})F(x_n).$$

Here a prime denotes differentiation with respect to the dimensionless time τ, $\mu=M/m$, and $\kappa=K/k$.

After substitution of variables, the asymmetric double-well potential (5) becomes

$$V(x)=g_0(x^2-1)^2+g_1x+g_2, \tag{8}$$

where the dimensionless parameters are $g_0=\epsilon_0/kr_0^2$, $g_1=\epsilon_1/kr_0^2$, and $g_2=\epsilon_2/kr_0^2$. For $0\leqslant g_1\leqslant 8g_0/\sqrt{27}$ the potential (8) has two minima ξ_1 and ξ_3 separated by a maximum ξ_2:

$$\xi_1<-1<0<\xi_2<\xi_3<1.$$

Here

$$\xi_1=\frac{2}{\sqrt{3}}\cos((\alpha+2\pi)/3),$$

$$\xi_2=\frac{2}{\sqrt{3}}\cos((\alpha-2\pi)/3),\quad \xi_3=\frac{2}{\sqrt{3}}\cos(\alpha/3),$$

where $\alpha=\arccos(-\sqrt{27}\ g_1/8g_0)$. The parameter $g_2=-g_0(\xi_1^2-1)^2-g_1\xi_1$ is determined from the condition $V(\xi_1)=0$.

After a change of variables the function (6) characterizing the interaction of the sublattices becomes

$$F(x)=-\chi_1(\xi_1-x)+\chi_2(\xi_1^2-x^2),$$

where the parameters characterizing the interaction of the sublattices are $\chi_1=X_1/kr_0$ and $\chi_2=X_2/kr_0$.

We now determine the uniform quasistationary states of the system. Let $x_n\equiv x$, $x_n'\equiv 0$, $y_{n+1}-y_n\equiv\rho$, and $y_n'\equiv s\rho$. The Lagrangian of a system for such a uniform state is proportional to the function

$$f(x,\rho;s)=V(x)+2\rho F(x)+\tfrac{1}{2}(\kappa-\mu s^2)\rho^2,$$

The quasistationary uniform state ($s\neq 0$) corresponds to its minimum.

It is easy to show that for each given value of the velocity $s<s_2$, where $s_2=\sqrt{k/\mu}$ is the dimensionless sound speed in the outer sublattice of the system (the dimensionless sound speed in the inner sublattice $s_1=1$), the function $f(x,\rho;s)$ has two minima only if

$$2\chi_2^2/(\kappa-\mu s^2)g_0<1,\quad 0<(\beta(s)/2)^2-\gamma^2(s)<9\xi_1^2/4, \tag{9}$$

where

$$\beta(s)=3\chi_1\chi_2/g_0\left(1-\frac{2\chi_2^2}{\delta(s)g_0}\right)\delta(s),\quad \delta(s)=\kappa-\mu s^2,$$

$$\gamma(s)=\left[\xi_1^2-1-\frac{\chi_1^2}{g_0\delta(s)}-\frac{1}{4}\left(1-\frac{2\chi_2^2}{g_0\delta(s)}\right)\times\xi_1^2-\frac{1}{2}\frac{\chi_1\chi_2\xi_1}{g_0\delta(s)}\right]\Bigg/\left(1-\frac{2\chi_2^2}{g_0\delta(s)}\right).$$

The first minimum $x=\xi_1$, $\rho=0$ corresponds to the left-hand well of the potential $V(x)$ and the second minimum $x=\eta(s)=-\xi_1/2+\sqrt{(\beta(s)/2)^2-\gamma^2(s)}$, $\rho=\rho_{me}(s)=2F(\eta(s))/\mu(s_2^2-s^2)$ corresponds to the right-hand well of the potential. The stationary uniform state $\{x_n\equiv\xi_1, x_n'\equiv 0, y_{n+1}-y_n\equiv 0, y_n'\equiv 0\}$, which we term the *b* state, corresponds to the first minimum and the uniform metastable (quasistationary) state $\{x_n\equiv\eta(s), x_n'\equiv 0, y_{n+1}-y_n\equiv\rho_{me}(s), y_n'\equiv s\rho_{me}(s)\}$, which we shall term the *me* state, corresponds to the second minimum.

Therefore, the two-component system under consideration has one stationary *b* state and an entire one-parameter class of quasistationary states *me*(s). We shall show below that among all speeds $0\leq s<s_2$ the value

$$s=s_p=s_2\sqrt{1-\frac{2\chi_2^2}{g_0\kappa}-\frac{\chi_1^2}{g_0\kappa(\xi_1^2-1)}},$$

for which the function $f(x,\rho;s)$ has two identical minimal values, is a special value. As $s\to 0$ the quasistationary state *me*(s) changes continuously into the second quasistationary state *me*(0) of the system; in what follows we term this second state the *e* state. As a result, all quasistationary states *me*(s) are topologically equivalent to the *e* state and can transform only into it by relaxation.

Under the condition

$$\frac{2\chi_1^2}{\kappa g_0}+\frac{\chi_1^2}{\kappa g_0(\xi_1^2-1)}<1 \tag{10}$$

the *b* state will be the energy ground state. The uniform stationary states *b* and *e* are always separated from one another by an energy barrier, and for this reason they are topologically inequivalent. We note that in the state *e* the outer sublattice in the system has a relative displacement $\rho_e=\rho_{me}(0)<0$, while for the ground state *b* the relative displacement is $\rho_b=0$.

3. ENDOTHERMAL TOPOLOGICAL SOLITON

The following discrete system of equations of motion corresponds to the dimensionless Hamiltonian (7):

$$x_n''=x_{n+1}-2x_n+x_{n-1}-\frac{dV}{dx}(x_n)-(y_{n+1}-y_{n-1})\frac{dF}{dx}(x_n), \tag{11}$$

$$y_n''=\kappa(y_{n+1}-2y_n+y_{n-1})+F(x_{n+1})-F(x_{n-1}), \tag{12}$$

$n=0,\pm 1,\pm 2,\ldots$.

We assume that a structural excitation encompasses a region which is quite large compared to a step in the chain. Then the continuum approximation $x_n(\tau)\approx x(z,\tau)|_{z=n}$, $y_n(\tau)\approx y(z,\tau)|_{z=n}$ is applicable, and the system of discrete equations (11) and (12) can be replaced by two coupled partial differential equations

$$x_{\tau\tau}=x_{zz}-\frac{dV}{dx}(x)-2y_z\frac{dF}{dx}(x), \tag{13}$$

$$y_{\tau\tau}=s_2^2y_{zz}+\frac{2}{\mu}\frac{d}{dz}F(x), \tag{14}$$

where z is the spatial coordinate, and the subscripts τ and z denote differentiation with respect to the corresponding variable.

The dynamics of structural perturbations of a stationary profile is of great interest from the standpoint of applications. To investigate this class of solutions, we switch to the wave variable $x(z,\tau)=x(\zeta)$, $y(z,\tau)=y(\zeta)$, and $\zeta=z-s\tau$, where s is the propagation speed of the disturbance. Then the system of equations of motion (13) and (14) assumes the form

$$(1-s^2)x_{\zeta\zeta}-\frac{dV}{dx}(x)-2y_\zeta\frac{dF}{dx}(x)=0, \tag{15}$$

$$(s_2^2-s^2)y_{\zeta\zeta}+\frac{2}{\mu}(F(x))_\zeta=0. \tag{16}$$

Integrating Eq. (16), we obtain the relation

$$y_\zeta=\frac{(2/\mu)(F(x)-C_1)}{s^2-s_2^2} \tag{17}$$

where C_1 is a constant of integration. Substituting the expression (17) into Eq. (15), multiplying the latter by x_ζ, and integrating, we arrive at the equation

$$\tfrac{1}{2}(1-s^2)x_\zeta^2-V(x)+\frac{2}{s^2-s_2^2}\left(C_1-\frac{1}{\mu}F(x)\right)F(x)=C_2, \tag{18}$$

where C_2 is an integration constant.

Equation (18) is the law of conservation of energy for a nonlinear oscillator

$$\tfrac{1}{2}x_\zeta^2+Q(x)=0 \tag{19}$$

with the effective potential energy

$$Q(x)=\frac{1}{s^2-1}\left[V(x)+\frac{2}{s_2^2-s^2}\left(C_1F(x)-\frac{1}{\mu}F^2(x)\right)+C_2\right]. \tag{20}$$

For a disturbance which on the right-end of the chain has an asymptotic form corresponding to the state *b* ($x\to\xi_1$, $x_\zeta\to 0$, $y_\zeta\to 0$, and $\zeta\to+\infty$), the integration constants are $C_1=C_2=0$, and the potential (20) has the form

$$Q(x)=a(x-\xi_1)^2[(x+\xi_1)^2+b(x+\xi_1)+c], \tag{21}$$

where the coefficients are defined by the expressions

$$a=\frac{g_0d}{s^2-1},\quad b=\frac{-4\chi_1\chi_2}{g_0\mu(s^2-s_2^2)d},$$

$$c=2\left[\xi_1^2-1+\frac{\chi_1^2}{g_0\mu(s^2-s_2^2)}\right]d^{-1},\quad d=1+\frac{2\chi_2^2}{g_0\mu(s^2-s_2^2)}.$$

Equation (19) admits nontopological soliton solutions, corresponding to a local disturbance of the *b* conformation,[18-20] as well as topological solitons describing an endothermal transition of the chain from the stable state *b* into a quasistationary uniform state *me*(s) which is topologically equivalent to the state *e*. It is significant here that the

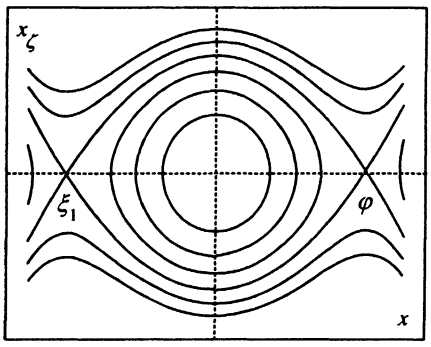

FIG. 2. Phase portrait of the nonlinear oscillator (19) with $s=s_p$ and $a(s_p)<0$.

speed of a topological soliton can have only one value $s=s_p$, for which the potential (21) becomes symmetric:

$$Q(x)=a(s_p)(x-\xi_1)^2(x-\varphi)^2,$$

where $\varphi=\eta(s_p)=-\xi_1-b/2$.

For $a(s_p)<0$ Eq. (19) has a soliton solution with a prescribed behavior at infinity:

$$x(\zeta)=\tfrac{1}{2}(\xi_1+\varphi)+\tfrac{1}{2}(\xi_1-\varphi)\tanh(R\zeta), \tag{22}$$

where $R=(\xi_1-\varphi)\sqrt{-a(s_p)/2}$. The form of the second component of the soliton solution $\rho(\zeta)=dy/d\zeta$ is found from Eq. (17)

$$\rho(\zeta)=2F(x(\zeta))/\mu(s_p^2-s_2^2). \tag{23}$$

In the limit $\zeta\to+\infty$ we have $x(\zeta)\to\xi_1$ and $\rho(\zeta)\to 0$, and in the limit $\zeta\to-\infty$ we have $x(\zeta)\to\varphi$, $\rho(\zeta)\to\rho_{me}=2F(\varphi)/\mu(s_p^2-s_2^2)<0$, i.e., the topological soliton (22), and (23) describes a transition of the chain from the ground state b into the intermediate state $me(s_p)$. The width of the soliton is $L=(\varphi-\xi_1)/x'(0)=2/R$.

The phase portrait of the nonlinear oscillator (19) with $s=s_p$ and $a(s_p)<0$ is displayed in Fig. 2. The saddlepoints correspond to the uniform states b and me, and the separatrices connecting them correspond to a topological soliton.

4. DYNAMICS OF AN ENDOTHERMAL TOPOLOGICAL SOLITON IN AN INFINITE CHAIN

A necessary condition for the existence of a topological soliton in an asymmetric bistable system is $a(s_p)<0$. We note that in a system with the intersublattice interaction parameter $\chi_1=0$ this condition is not satisfied, since in this case $a(s_p)=0$ always holds. For this reason, only nontopological solitons exist in such a system.[18–20] A topological soliton can exist only if $\chi_1\neq 0$.

To simplify the calculations, we consider a two-component system for which the interaction parameter satisfies $\chi_2=0$. Then the conditions for the asymmetric bistability of (9) and (10) reduce for $s=0$ to the single inequality

$$\chi_1<\chi_p=\sqrt{\kappa g_0(\xi_1^2-1)},$$

and the coefficients of the effective potential (21) have the simpler form

TABLE I. η, ρ_e, E_e, ρ_{me}, E_{me}, s_p, and L as functions of the interaction parameter χ_1 of the sublattices.

χ_1	η	$-\rho_e$	$100E_e$	$-\rho_{me}$	$100E_{me}$	s_p	L
0.000	0.930	0.000	0.998	–	–	–	–
0.002	0.932	0.032	0.985	2.500	154.14	0.497	12.3
0.004	0.938	0.064	0.947	1.250	36.95	0.486	12.4
0.006	0.948	0.096	0.883	0.833	15.25	0.469	12.5
0.008	0.961	0.129	0.793	0.625	7.65	0.443	12.7
0.010	0.977	0.163	0.674	0.500	4.14	0.407	12.9
0.012	0.997	0.197	0.527	0.417	2.23	0.358	13.2
0.014	1.018	0.232	0.350	0.357	1.07	0.290	13.5
0.016	1.042	0.269	0.140	0.312	0.33	0.183	13.9
0.017	1.055	0.287	0.023	0.294	0.05	0.074	14.1

$$a=\frac{g_0}{s^2-1},\quad b=0,\quad c=2\left(\xi_1^2-1+\frac{\chi_1^2}{g_0\mu(s^2-s_2^2)}\right).$$

The speed of the topological soliton is

$$s_p=s_2\sqrt{1-\frac{\chi_1^2}{g_0\kappa(\xi_1^2-1)}},$$

and the condition $a(s_p)<0$ of existence of a soliton is equivalent to the inequality

$$\chi_1^2>\kappa g_0(s_2^2-1)(\xi_1^2-1)/s_2^2,$$

which always holds when $s_2<1$. The first and second components of the soliton solution have the form

$$x(\zeta)=\xi_1\tanh(R\zeta),\quad \rho(\zeta)=2\chi_1\xi_1(1-\tanh(R\zeta))/\mu(s_2^2-s_p^2), \tag{24}$$

where $R=2\xi_1\sqrt{g_0/(1-s_p^2)}$.

For definiteness we take $s_2=0.5$, $\mu=1$, $\kappa=0.25$, $g_1=0.01$, and $g_1=0.005$. Then $\xi_1=-1.057454$, $g_2=0.005148$, and $\chi_p=0.017191$. Table I gives the intramonomeric coordinate η, the deformations ρ_e and ρ_{me} of the outer sublattice, the energy levels $E_e=V(\eta)+(1/2)\kappa\rho_e^2+2\chi_1\rho_e(\eta-\xi_1)$ and $E_{me}=V(-\xi_1)+(1/2)\mu(s_2^2+s_p^2)\rho_{me}^2-4\chi_1\rho_{me}\xi_1$ of the states e and me, and the soliton speed s_p and width $L=2/R$ as functions of the parameter χ_1 describing the interactions of the sublattices.

The dynamics of a topological soliton in an infinite chain can be modeled on a finite chain consisting of N links with the left-hand end moving uniformly with speed $s_b=-s_p\rho_{me}$ and a free right-hand end. The corresponding equations of motion are

$$x_1''=x_2-x_1-\frac{dV}{dx}(x_1)-\chi_1(y_2-y_1),\quad y_1=s_b\tau,$$

$$x_n''=x_{n+1}-2x_n+x_{n-1}-\frac{dV}{dx}(x_n)-\chi_1(y_{n+1}-y_{n-1}),$$

$$y_n''=s_2^2(y_{n+1}-2y_n+y_{n-1})+\frac{\chi_1}{\mu}(x_{n+1}-x_{n-1}), \tag{25}$$

$$n=2,3,\ldots,N-1,$$

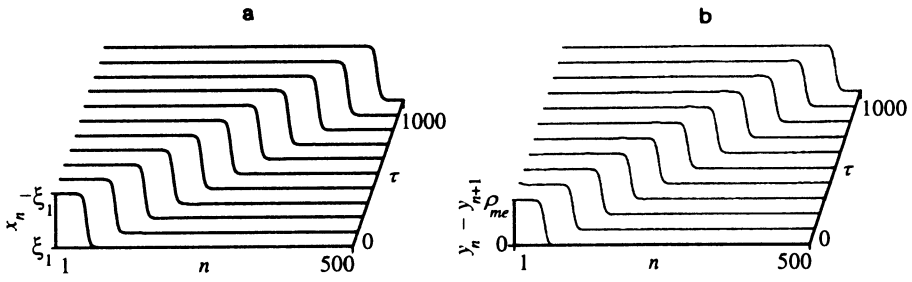

FIG. 3. Dynamics of an endothermal topological soliton in a chain with a uniformly moving left-hand end ($n_0=50$).

$$x_N''=x_{N-1}-x_N-\frac{dV}{dx}(x_N)-\chi_1(y_N-y_{N-1}),$$

$$y_N''=s_2^2(y_{N-1}-y_N)-\frac{\chi_1}{\mu}(x_N+x_{N-1}-2\xi_1),$$

and the initial conditions are

$$\begin{aligned}&x_n(0)=x(n-n_0), \quad n=1,2,\ldots,N,\\ &y_n(0)=y_{n-1}(0)+\rho(n-n_0-1),\\ &x_{n-1}'(0)=-s_p(x_n(0)-x_{n-1}(0)),\\ &y_n'(0)=-s_p\rho(n-n_0),\\ &n=2,3,\ldots,N, \quad x_N'(0)=0,\end{aligned} \tag{26}$$

where $x(\xi)$ and $\rho(\xi)$ are the continuum-approximation soliton solution (24) and n_0 is the initial position of the soliton center.

In summary, the left-hand end of the chain is in an intermediate (metastable) state *me* and the right-hand end is in the ground state *b*. The motion to the right with speed s_p must be accompanied by an increase of the energy of the finite chain ($d\mathcal{H}/d\tau=s_pE_{me}$) as a result of the forced motion of the left-hand end.

We consider now the dynamics of a soliton in a finite chain consisting of $N=500$ links. Let $\chi_1=0.01$. Then the soliton speed is $s_p=0.406699$. Numerical integration of the system of equations of motion (25) showed that a soliton moving with constant speed $s=0.4069$ along the chain and with constant profile (see Fig. 3) is stable. In analyzing the motion of the soliton it is convenient to follow the position of the soliton center, defined as the point $\bar{n}$ on the n-axis where the broken line passing successively through the points $\{n,x_n\}_{n=1}^N$ crosses the n-axis. Table II gives the position of the center $\bar{n}$ of the soliton and the instantaneous speed $\bar{s}$ as a function of the time τ. One can see from this table that the soliton moves virtually uniformly with speed $\bar{s}=0.407\approx s_p$. The small fluctuations of the instantaneous values of $\bar{s}$ are evidently associated with the discreteness of the chain.

TABLE II. Soliton center $\bar{n}$ and instantaneous soliton speed $\bar{s}$ as functions of the time τ.

τ	0	100	200	300	400	500
$\bar{n}$	50.00	90.65	131.38	172.08	212.79	253.50
$\bar{s}$	0.4067	0.4065	0.4072	0.4073	0.4071	0.4071
τ		600	700	800	900	1000
$\bar{n}$		294.21	334.90	375.59	416.28	457.08
$\bar{s}$		0.4071	0.4069	0.4069	0.4069	0.4081

5. DYNAMICS OF AN ENDOTHERMAL TOPOLOGICAL SOLITON IN A FINITE CHAIN

As mentioned above, uniform motion of a topological soliton requires a constant energy input at the left-hand end of the chain. As a result of the motion of the soliton, the entire chain is in a high-energy ($E_{me}\gg E_e$) dynamical intermediate state *me*. The quasistationary state *me* is stable only in an infinite chain, and for this reason in a finite chain a relaxation process that transfers the system from this state into a topologically equivalent stationary state *e* should be observed. A topological soliton will correspond to an intermediate asymptotic process of propagation of a structural transition, if the relaxation process does not influence significantly the dynamics of the soliton.

We now consider the soliton dynamics of a chain with free ends. For this, the second equation in the system (25) must be replaced by the equation

$$y_1''=s_2^2(y_2-y_1)+\frac{\chi_1}{\mu}(x_1+x_2-2\xi_1).$$

After this substitution the system (25) will have as a constant of motion the total energy of the chain

$$\begin{aligned}\mathcal{H}=&\sum_{n=1}^{N}\left\{\frac{1}{2}x_n'^2+\frac{1}{2}\mu y_n'^2+V(x_n)\right\}\\ &+\sum_{n=2}^{N}\chi_1(y_n-y_{n-1})(x_n-\xi_1)\\ &+\sum_{n=1}^{N-1}\left\{\frac{1}{2}(x_{n+1}-x_n)^2+\frac{1}{2}\kappa(y_{n+1}-y_n)^2\right.\\ &\left.+\chi_1(y_{n+1}-y_n)(x_n-\xi_1)\right\}.\end{aligned} \tag{27}$$

We supplement the initial conditions (26) with the conditions $y_1(0)=0$, $y_1'(0)=-s_p\rho(1-n_0)$.

The soliton dynamics of a chain with free ends is displayed in Fig. 4. Initially, at $\tau=0$, the left-hand part of the chain $n<n_0=100$ is in the metastable state *me*. At the same time the soliton begins to move, relaxation of the metastable state starts in the left-hand end: a wave packet moving with

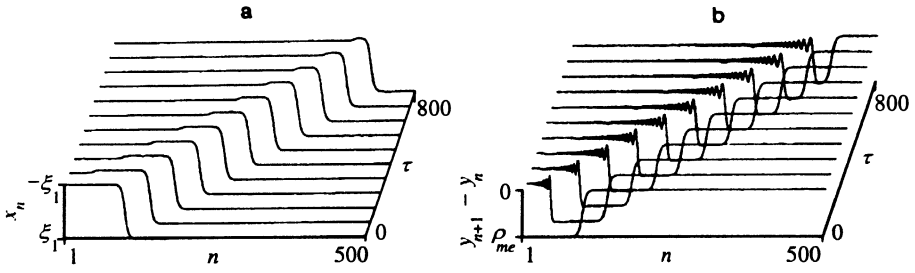

FIG. 4. Dynamics of an endothermal topological soliton in a chain with free ends ($n_0=100$).

the speed of sound $s=s_2$ appears and converts the chain from the state *me* into the state *e*. In the process, a successive stretching of the outer sublattice occurs. Since the soliton speed $s=s_p<s_2$, the relaxation region uniformly overtakes the soliton, shortening the region of the metastable state.

Figure 5 displays the time dependence of the position of the soliton center $\bar{n}$. As long as the relaxation region has not overtaken the front of the soliton disturbance, i.e., $\tau<\tau_0=n_0/(s_2-s_p)$, the soliton moves uniformly with constant speed $s=s_p$, and transforms the chain into the metastable state *me*, which is then transferred in the relaxation region into the state *e* (see Fig. 4). In the process, only a uniform shortening of the section of the chain which is in the state *me* occurs. At $\tau=\tau_0$ the relaxation region overtakes the soliton front, so that the length of the metastable region approaches zero. As a result, the two-component endothermal soliton is destroyed. Therefore, in a chain with free ends an endothermal topological soliton has a finite lifetime τ_0, which is determined by the length of the region of the metastable state. The metastable region is essentially the energy reservoir that is required to maintain the motion of an endothermal soliton.

We now consider in greater detail the dynamics of a soliton in a finite chain whose right-hand end is free. Let $n_0=85$; then $\tau_0=910$. Over this period of time the soliton must reach the 456-th link of the chain. Numerical modeling of the dynamics showed that for $N>452$ the soliton does not reach the right-hand end of the chain. After the soliton stops, an exothermal kink forms, and this kink converts the chain from the state *e* into the ground state *b*. For $N<452$ the soliton reaches the end and is reflected from it, and in the process the soliton is converted into an exothermal kink. (We note that reflection can be avoided if viscous friction, giving rise to absorption of the excess energy of the soliton, is introduced at the right-hand end of the chain. In this case the entire chain would remain in the state *e* after the passage of the soliton.) For $N=452$ the soliton reaches the end but is not reflected from it. As a result, the entire chain is in the second uniform state *e*. Therefore, the soliton energy $E_1=3.6172$ suffices to transform a chain consisting of $N=452$ links from the ground state *b* into the second stable uniform state *e*.

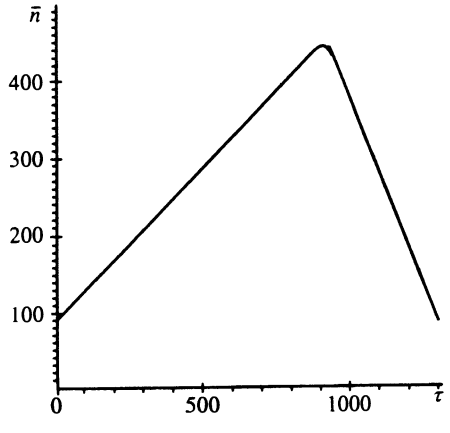

FIG. 5. Center $\bar{n}$ of a soliton moving in a chain with free ends ($N=500$, $n_0=85$) as a function of time τ. The total energy of the chain is $\mathcal{H}=3.6172$.

Our numerical modeling of soliton dynamics shows that for an endothermal transition of a chain consisting of N links from the ground state *b* into the state *e*, it is sufficient to excite an endothermal topological soliton and transform the first $n_0-1=N(1-s_p/s_2)-1$ links into the metastable state *me*. For this, for example, it is sufficient to excite a soliton directly at the left-hand end and then over a time $\tau_1=n_0/s_p$, to uniformly shift the left-hand end of the chain to the right with the speed $s_b=-s_p\rho_e$, i.e., to initiate a sudden early-time intramonomeric conformational transition of the first link of the chain and a prolonged dynamical shock at the left-hand end of the chain. This soliton mechanism of endothermal conformational rearrangement of the chain requires energy input only at the end of the chain.

We now compare the energy of the soliton mechanism of structural rearrangement to that of the nonsoliton mechanism. As was shown above, the rearrangement of a chain consisting of $N=452$ links by the soliton mechanism requires energy $E_1=3.6172$. The nonsoliton mechanism, which in the present case consists of the simultaneous conversion of all monomers of the chain from the state *b* into the state *e*, requires the energy $E_2=NV(\xi_2)=6.989$. Hence one can see that the soliton mechanism is energetically approximately twice as favorable as the nonsoliton mechanism. Moreover, the nonsoliton mechanism requires that energy be supplied to all links of the chain simultaneoulsy, while the soliton mechanism requires only local energy input (for example, at the terminal monomers). This circumstance makes it possible to explain by means of the soliton mechanism some long-range effects in DNA macromolecules.[21-23]

A third scenario of endothermal conformational rearrangement of a chain is also possible. If the right-hand end of the chain is clamped, then motion of the left-hand end can convert the chain into a stressed state. When each monomeric link is compressed by $\rho_0=-g_1/2\chi_1$, the asymmetric

bistable system under study becomes symmetric. It will have two stable uniform states $x_n \equiv \pm 1$ with the same energy. Conformational rearrangement of such a symmetric bistable system can be realized even by the motion of a one-component topological soliton. Conversion of the chain into a stressed state requires energy $E_{\text{stress}} = N(g_2 + g_1\xi_1 + \kappa\rho_0^2/2)$, and the excitation of a stationary soliton requires energy $E_{\text{sol}} = 4\sqrt{2g_0}/3$. Then the conformational rearrangement according to this scenario requires energy $E > E_3 = E_{\text{stress}} + E_{\text{sol}}$. For a chain consisting of $N = 452$ links we have $E_3 = 3.657 > E_1$, i.e., rearrangement of the chain via a transition to a stressed state requires more energy than rearrangement by the soliton mechanism. Moreover, to convert the chain into a stressed state energy must be supplied to all links of the chain.

The system of equations of motion (25) was integrated numerically by the standard fourth-order Runge-Kutta method with a constant integration step. The accuracy of the numerical integration was checked by checking the constancy of the total energy integral (27). For example, with a step $\Delta\tau = 0.1$ energy was conserved to five significant figures.

6. CONCLUSIONS

In the present paper we have given the first proof that a stable topological soliton can exist in a bistable two-component asymmetric system and can convert the system from the uniform ground state *b* into a metastable state *me*. The speed of such a soliton has a unique value equal to $s = s_p < s_2$ and is determined by the parameters of the system. Comparison of the present soliton mechanism of endothermal structural rearrangement with other mechanisms shows that it is energetically favorable. It should also be noted that this mechanism can be initiated by supplying energy locally to the chain.

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