Solitons in nondegenerate bistable systems

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Abstract. Soliton-like elementary excitations in bistable systems with nondegenerate equilibrium positions are considered. Models of specific physical systems, which can be described on the basis of this approach by a single Hamiltonian, are discussed. A detailed analysis of continuum equations of motion demonstrates the existence in such systems both of nontopological solitons participating in energy transfer and of topological solitons responsible for transitions between different equilibrium positions (transfer of a state). The results of a computer simulation are compared with the results of analytic investigations.

1. Introduction

The development of modern nonlinear physics has led to the discovery of new fundamental mechanisms which govern, at the molecular level, many physical processes in crystals and in other ordered molecular systems. The role of non-topological solitons, ensuring the most efficient mechanism of energy transfer in processes such as, for example, heat conduction and fracture of solids [1-3] or propagation of

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signals in biological macromolecules [4], is now fully understood. The passage of such localised excitations does not alter the state of the system, because the topological charge of such excitations is zero. On the other hand, in the case of soliton excitations in those bistable structures where the energy degeneracy of equilibrium states provides favourable conditions for a possible 'transfer of a state' if the interaction between structure elements of the system is sufficiently strong, a topological soliton (kink or antikink) describes a transition from one equilibrium state to another, i.e. it ensures the most efficient (wave) mechanism of this process [4, 5]. This mechanism is encountered, for example, in the motion of domain walls and dislocations [3, 5, 6] and it governs the dynamic nature of structural phase transitions and of plastic flow in crystals. Until recently it has been regarded as self-evident that the existence of topological solitons requires not only more than one equilibrium state, but also energy degeneracy of equilibrium states. This second condition seems quite natural, because otherwise the propagation of a steadystate wave would involve either dissipation or acquisition of energy (depending on the ratio of the energies of the equilibrium states), whereas the investigated dynamic model usually postulates the Hamiltonian structure of the main equations and conservation of the total energy.

In this case the fundamental excitations are topological solitons (kinks) which induce transitions between two equivalent equilibrium states. Such transitions have been considered primarily for one-component models. If the analysis is made of, for example, molecular crystals, the one-component nature of the model implies a weak influence of the intramolecular mobility on structural changes in the system. However, in some cases, particularly in studies of structural transitions in the molecules themselves, this influence becomes of primary importance and it is then essential to allow for the mutual coupling of

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the intramolecular and intermolecular degrees of freedom, i.e. for the multicomponent nature of the molecule. In a degenerate system this coupling does not give rise to any new types of soliton solutions, but it may alter the spectrum of the soliton velocities (a new band may appear in the spectrum [7]).

Naturally, the condition of energy degeneracy greatly reduces the class of processes to be considered. In particular, one should exclude from consideration the structural transitions in nondegenerate systems, the propagation of detonation waves, topochemical reactions in molecular crystals, and conformational changes in polymers and biological macromolecules. However, topological solitons do not exist in one-component nondegenerate systems and nontopological solitons can exist only against the background of a metastable state [8, 9]. On the other hand, studies of the dynamics of nondegenerate bistable quasi-one-dimensional molecular chains within the framework of a two-component model have revealed [10-12] a wider class of nontopological solitons than the onecomponent model [8]. Such solitons describe local perturbations of the stable state of a chain and may exist not only against the background of a metastable state with a higher energy, which is true of the one-component model, but also against the background of the ground state. These solitons have been used to describe B-A conformational transitions in DNA molecules [13-16].

Although at first sight the existence of topological solitons in nondegenerate systems seems to be impossible, recent numerical experiments carried out primarily for the purpose of simulation of propagation of a detonation wave in two-component models of solids (in this case the homogeneous state corresponding to the reaction products can be regarded as displaced to infinity), have revealed a soliton structure of the detonation wavefront and the existence of a preferred velocity of its propagation, in spite of the energy nondegeneracy of the system. In a study of simulation of detonation in a one-dimensional crystal this has been attributed to the occurrence of a specially introduced dissipation [17], but the results reported in Refs [18, 19] apply to structurally more complex, but still Hamiltonian models. An ordered structure of the region near the front is clear evidence of the existence of topological solitons. However, the complexity of such systems prevents precise identification of the elementary process responsible for the 'transfer of a state' in the nondegenerate case. This requires the construction of a simpler model which can be investigated analytically.

Such a model of an infinite one-dimensional molecular crystal, proposed in Ref. [20], has made it possible to reveal explicitly the internal mechanism responsible for the formation of a topological soliton (kink) and for the constancy of the wavefront velocity.

The kink found analytically describes the transition of a system from its initial equilibrium configuration to an intermediate steady (dynamic) state in the region of attraction of the final ground state. The existence of such an intermediate state is a necessary condition for the formation of a topological soliton in a nondegenerate bistable system. The explicitly found solution describes a two-component kink which represents coupled nonlinear waves of intramolecular deformation and displacements of the centres of mass of the molecules. After the passage of such a kink the system undergoes a transition from the

initial configuration to an intermediate steady state in the region of attraction to the final equilibrium state. This intermediate state and, consequently, a topological soliton, exist in a certain range of molecular parameters for a unique value of the wave velocity $V = V_0$. Although this state is of nonequilibrium nature (because the centres of mass of the molecules have nonzero velocities behind the front), in the selected reference frame linked to the travelling wave this state becomes indistinguishable from an equilibrium state with a 'potential' energy equal to the energy of the initial equilibrium state. The formation of a topological soliton becomes possible because of the degeneracy of the potential energy at two stationary points. This means that the class of systems in which the observed soliton 'state transfer' mechanism can take place is much wider than has been assumed hitherto and, consequently, fundamentally new opportunities arise in nonlinear physics of crystal and other ordered systems.

Our aim will be to identify soliton excitations in a wide class of nondegenerate bistable systems, as well as to analyse the conditions for the existence of these excitations and of their stability.

The second section consists of a description of an analytic study of the investigated class of systems in the continuum approximation. It begins with the derivation of the appropriate continuum Hamiltonian and of the equations of motion. The introduction of a kinetic variable resulted in explicit integration of the equations. The conditions of existence of possible soliton excitations are found for bistable nondegenerate systems. The mechanism of selection of a unique wave velocity corresponding to a topological soliton is considered.

The third section gives the results of a numerical investigation of the equations of motion of a discrete model. A study is made of the soliton dynamics under initial conditions which correspond to the exact solutions obtained analytically in the continuum approximation. The nature of propagation of a structural transition is investigated under sufficiently general initial conditions which describe local excitations of the investigated systems. Special attention is given to a comparison of the predicted and observed characteristics of an elementary excitation and to an analysis of the fine structure and stability of the front of a steady-state wave. The role of a topological soliton in the formation of a steady-state wave responsible for a structural transition at the atomic level is studied.

The appendices give several examples from different branches of physics. It is shown that the relevant Hamiltonians are special cases of the general Hamiltonian whose soliton spectrum is considered in Sections 2 and 3.

2. Solitons in molecular systems with nondegenerate bistability

We shall now consider nonlinear lattices in which we can distinguish two interacting degrees of freedom ('external' and 'internal') and find several (at least two) stable equilibrium configurations with unequal energies. The simplest case of such a system is a diatomic lattice with alternating potentials of the interaction between the nearest neighbours, when one of the potentials is of the double-well type and the other nearly harmonic. The natural coordinates are then the mutual displacements of the neighbouring atoms coupled by the double-well potential (internal coordinate) and the mutual displacements of the centres of masses of such atom pairs (external coordinate). A similar lattice, but with a long-range interaction is considered in the Appendix 5.1.

2.1 Generalised model of a bistable system

We shall now consider the class of bistable nondegenerate systems described by the following Hamiltonian:

$$E = \sum_{n} \left[\frac{1}{2} M \dot{R}_{n}^{2} + \frac{1}{2} m \dot{r}_{n}^{2} + \frac{1}{2} K (R_{n+1} - R_{n})^{2} + \frac{1}{2} k (r_{n+1} - r_{n})^{2} + \Phi(r_{n}) + (R_{n+1} - R_{n}) G_{+}(r_{n}) + (R_{n} - R_{n-1}) G_{-}(r_{n}) \right], \qquad (1)$$

which corresponds to the total energy of a two-component system of bistable elements with nonequivalent equilbrium positions, shown schematically in Fig. 1. Here, R_n and r_n are the relative displacements of the links in the external and internal sublattices (external and internal components); M and m are the masses of the links in the sublattices; Kand k are their rigidity constants; $\Phi(r)$ is an asymmetric double-well potential, which can be selected in the form

$$\boldsymbol{\Phi}(r) = \boldsymbol{\varepsilon}_0 \left[1 - (r u_0^{-1})^2 \right]^2 + \boldsymbol{\varepsilon}_1 r u_0^{-1} + \boldsymbol{\varepsilon}_2$$

where the parameters ε_0 and ε_1 represent the barrier height and the difference between the energies of equilibrium states, the parameter ε_2 defines the level from which energies are measured, and u_0 represents the width of the potential barrier. The functions

$$G_{\pm}(r) = X_{1,\pm}(r-u_1)u_0^{-1} + X_{2,\pm}(u_1^2 - r^2)u_0^{-2}$$

represent the interaction between the sublattices. In contrast to the traditionally discussed two-mass lattices (see, for example, Ref. [21]), the parameter k governing the slope

of the optical branch of the dispersion relationship can be both smaller and larger than zero, and the interaction between the sublattices may be asymmetric $(X_{i,+} \neq X_{i,-}, i = 1, 2)$.



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

In the more general case the internal component may be associated with several external components or vice versa. However, the principal characteristics of the dynamic behaviour, which appear because of the interaction between the components, can be revealed even if there are only two components. On the other hand, it is shown in one of the appendices that when the appropriate values of the parameters are selected, the Hamiltonian of Eqn (1) can describe structural transitions and the propagation of chemical reactions in molecular crystals, transport of protons along hydrogen-bonded chains, and the dynamics of local conformational transitions in biological macromolecules of the DNA type.

We shall introduce the following dimensionless variables: the displacements $x_n = r_n/u_0$, $y_n = R_n/u_0$, time $\tau = t\sqrt{|k|/m}$, and energy $H = E/|k|u_0^2$. Then the Hamiltonian (1) becomes

$$H = \sum_{n} \left[\frac{1}{2} \mu y_{n}^{\prime 2} + \frac{1}{2} x_{n}^{\prime 2} + \frac{1}{2} \kappa (y_{n+1} - y_{n})^{2} + \frac{1}{2} \delta (x_{n+1} - x_{n})^{2} + V(x_{n}) + (y_{n+1} - y_{n})F_{+}(x_{n}) + (y_{n} - y_{n-1})F_{-}(x_{n}) \right], (2)$$

where a prime denotes differentiation with respect to the dimensionless time τ , $\mu = M/m$, $\kappa = K/|k|$, and $\delta = +1$ if $\kappa > 0$ and $\delta = -1$ if $\kappa < 0$. A dimensionless asymmetric double-well potential is

$$V(x) = g_0(x^2 - 1)^2 + g_1x + g_2 ,$$

where $g_0 = \varepsilon_0/|k|u_0^2$, $g_1 = \varepsilon_1/|k|u_0^2$, $g_2 = \varepsilon_2/|k|u_0^2$. If $0 \le g_1 < 8g_0/\sqrt{27}$, the potential V(x) has two minima, ξ_1 and ξ_3 , which are separated by a maximum, ξ_2 : $\xi_1 < -1 < 0 < \xi_2 < \xi_3 < 1$, where

$$\begin{split} \xi_1 &= \frac{2}{\sqrt{3}} \cos\left(\frac{\alpha}{3} + \frac{2\pi}{3}\right), \quad \xi_2 &= \frac{2}{\sqrt{3}} \cos\left(\frac{\alpha}{3} - \frac{2\pi}{3}\right) \\ \xi_3 &= \frac{2}{\sqrt{3}} \cos\frac{\alpha}{3} \end{split},$$

and $\alpha = \arccos(-\sqrt{27}g_1/8g_0)$. The parameter g_2 , where $g_2 = -g_0(\xi_0^2 - 1)^2 - g_1\xi_1$, is found from the condition $V(\xi_1) = 0$. The functions $F_{\pm}(x)$ are

$$F_{\pm}(x) = \chi_{1,\pm}(x-\xi_1) + \chi_{2,\pm}(\xi_1^2-x^2) ,$$

where the parameters $\chi_{i,\pm} = X_{i,\pm}/|k|u_0$ (*i* = 1, 2) represent the sublattice interactions.

In the subsequent analysis of the dynamics of the investigated two-component system we need to know its stable homogeneous states. We shall find them on the assumption that $x_n \equiv x$, $x'_n \equiv 0$, $y_{n+1} - y_n \equiv \rho$ and $y'_n \equiv 0$. Then the energy of the system is proportional to the function

$$f(x,\rho) = V(x) + \frac{\kappa}{2}\rho^2 + 2\rho F_s(x) , \qquad (3)$$

where

$$\begin{split} F_s(x) &= \frac{1}{2} \left[F_+(x) + F_-(x) \right] \\ &= \chi_{1,s}(x - \xi_1) + \chi_{2,s}(\xi_1^2 - x^2) \end{split}$$

and

$$\chi_{i,s} = \frac{1}{2} (\chi_{i,+} + \chi_{i,-}), \ i = 1,2$$

Stable homogeneous states of a chain correspond to minima of the function described by Eqn (3) and these are given by the equilibrium equations

$$\frac{\partial f}{\partial x} = \frac{\mathrm{d}V}{\mathrm{d}x} + 2\rho \frac{\mathrm{d}F_s}{\mathrm{d}x} = 0 ,$$

$$\frac{\partial f}{\partial \rho} = \kappa \rho + 2F_s(x) = 0 . \qquad (4)$$

It follows from Eqn (4) that $\rho = -2F_s(x)/\kappa$ and this equality makes it possible to rewrite the function of

Eqn (3) in the form $p(x) = f[x, \rho(x)] = V(x) - 2F_s^2(x)/\kappa$. This function is a fourth-degree polynomial with a double root $x = \xi_1$. We can easily show that a third-degree polynomial p'(x) has not only the simple root $x = \xi_1$, but also two more real roots $\eta_1 = -(\xi_1/2) - \sqrt{D_1}$, $\eta_2 = -(\xi_1/2) + \sqrt{D_1}$, if the discriminant obeys $D_1 = (b_1/2)^2 - c_1 > 0$, where

$$b_{1} = 3\chi_{1,s} \chi_{2,s} \left[\kappa g_{0} \left(1 - \frac{2\chi_{2,s}^{2}}{\kappa g_{0}} \right) \right]^{-1} ,$$

$$c_{1} = \left[\xi_{1,s}^{2} - 1 - \frac{\chi_{1,s}^{2}}{\kappa g_{0}} - \left(1 - \frac{2\chi_{2,s}^{2}}{\kappa g_{0}} \right) \frac{\xi_{1}^{2}}{4} - \frac{1}{2} \frac{\chi_{1,s} \chi_{2,s} \xi_{1}}{\kappa g_{0}} \right] \left(1 - \frac{2\chi_{2,s}^{2}}{\kappa g_{0}} \right)^{-1} .$$

The polynomial p(x) assumes the minimum values at two points ξ_1 and η_2 if the coefficient in front of the term with the highest degree is $1 - (2\chi_{2,s}^2/\kappa g_0) > 0$ and the root is $\eta_1 > \xi_1$.

$$\frac{2\chi_{2,s}^2}{\kappa g_0} < 1, \quad 0 < D_1 < \frac{9}{4}\xi_1^2$$
(5)

the investigated two-component system has two stable homogeneous states: a state **b** lower on the energy scale, $\{x_n \equiv \xi_1, y_{n+1} - y_n \equiv 0\}$, and a higher **e** state $\{x_n \equiv \eta_2, y_{n+1} - y_n \equiv \rho_c\}$, where $\rho_c = -2F_s(\eta_2)/\kappa < 0$. If the asymmetry of the double-well potential $(g_1 = 0 \text{ and} \chi_{1,s} = 0)$ is lifted, both homogeneous states of the chain become equivalent: $x_n \equiv \pm 1, y_{n+1} - y_n \equiv 0$ ($\pm i$ states).

2.2 Equations of motion

The Hamiltonian (2) corresponds to the following discrete system of equations of motion:

$$x_n'' = \delta(x_{n+1} - 2x_n + x_{n-1}) - \frac{\mathrm{d}V}{\mathrm{d}x}(x_n) - (y_{n+1} - y_n) \frac{\mathrm{d}F_+}{\mathrm{d}x}(x_n) - (y_n - y_{n-1}) \frac{\mathrm{d}F_-}{\mathrm{d}x}(x_n) , \quad (6)$$

$$\mu y_n'' = \kappa (y_{n+1} - 2y_n + y_{n-1}) + F_+(x_n) - F_+(x_{n-1}) + F_-(x_{n+1}) - F_-(x_n) , \quad (7) n = 0, \pm 1, \pm 2, \dots .$$

We shall assume that the structural excitation extends over a certain fairly large region (compared with one link of the chain). The continuum approximation $x_n(\tau) = x(z, \tau)|_{z=n}$, $y_n(\tau) = y(z, \tau)|_{z=n}$ can then be applied and the discrete equations of motion [Eqns (6) and (7)] reduce to a system of two coupled partial differential equations:

$$x_{\tau\tau} = \delta x_{zz} - \frac{\mathrm{d}V}{\mathrm{d}x}(x) - 2y_z \frac{\mathrm{d}F_s}{\mathrm{d}x}(x) - y_{zz} \frac{\mathrm{d}F_a}{\mathrm{d}x}(x) , \qquad (8)$$

$$y_{\tau\tau} = s_2^2 y_{zz} + \frac{1}{\mu} \frac{d}{dz} \left[2F_s(x) - \frac{d}{dz} F_a(x) \right] ,$$
 (9)

where z is the spatial coordinate, and the functions in the above equations are

$$F_{a}(x) = \frac{1}{2} \left[F_{+}(x) - F_{-}(x) \right] = \chi_{1,a}(x - \xi_{1}) + \chi_{2,a}(\xi_{1}^{2} - x^{2}) ;$$

 $\chi_{i,a} = (\chi_{i,+} - \chi_{i,-})/2$, i = 1, 2; $s_1 = 1$ and $s_2 = \sqrt{\kappa/\mu}$ are the dimensionless velocities of long-wavelength vibrations in the internal and external sublattices (velocities of

'sound'); the subscripts τ and z indicate differentiation with respect to the indicated variable.

In the approximation of small displacements Eqns (8) and (9) reduce to equations for long-wavelength vibrations of a one-dimensional lattice. The slope of the optical branch of the dispersion curve is then governed by the sign of the parameter δ . If the displacements are not small, then in the system under consideration we can expect nonlinear vibrations and waves. The dynamics of structural excitations with a steady-state profile is of the greatest interest from the point of view of possible applications. We shall study this class of solutions by going over to the wave variables $x(z, \tau) = x(\zeta)$, $y(z, \tau) = y(\zeta)$, $\zeta = z - s\tau$, where s is the velocity of an excitation.

The adoption of the variable ζ transforms the equations of motion (8) and (9) to

$$(\delta - s^2)x_{\zeta\zeta} - \frac{\mathrm{d}V}{\mathrm{d}x}(x) - 2y_{\zeta}\frac{\mathrm{d}F_s}{\mathrm{d}x}(x) - y_{\zeta\zeta}\frac{\mathrm{d}F_a}{\mathrm{d}x}(x) = 0, (10)$$

$$(s_2^2 - s^2)y_{\zeta\zeta} + \frac{1}{\mu} \{2F_s(x) - [F_a(x)]_{\zeta}\}_{\zeta} = 0 \quad . \tag{11}$$

Integration of Eqn (11) gives

$$y_{\zeta} = \left[\left\{ 2F_s(x) - [F_a(x)]_{\zeta} \right\} \mu^{-1} - C_1 \right] (s^2 - s_2^2)^{-1} , \quad (12)$$

where C_1 is the constant of integration the value of which can easily be found from the given asymptotics of the solution at infinity. Substitution of Eqn (12) into Eqn (10), multiplication of the latter by x_{ζ} , and integration gives

$$\frac{1}{2}p(x,s)x_{\zeta}^{2} + q(x,s) = 0 \quad , \tag{13}$$

where

$$p(x,s) = \delta - s^{2} + (\chi_{1,a} - 2x\chi_{2,a})^{2} [\mu(s^{2} - s_{2}^{2})]^{-1} ,$$

$$q(x,s) = -V(x) + 2[C_{1} - F_{s}(x)\mu^{-1}]F_{s}(x)(s^{2} - s_{2}^{2})^{-1} - C_{2} ,$$

and C_2 is the constant of integration.

Eqn (13) represents the law of conservation of energy of a nonlinear oscillator with an effective potential energy Q(x,s) = q(x,s)/p(x,s). An analysis of phase portraits of a nonlinear oscillator of Eqn (13) for different values of the travelling-wave velocity readily identifies possible classes of the wave solutions of Eqns (8) and (9), whereas the solutions themselves can be obtained in quadratures

$$\int_{x(0)}^{x(\zeta)} \frac{\mathrm{d}u}{\sqrt{-2Q(u,s)}} = \pm \zeta \quad . \tag{14}$$

2.3 Soliton excitations of a nondegenerate bistable chain

Among possible solutions of Eqns (10) and (11) we shall seek those dynamic solutions which represent solitary waves with a steady-state profile and an asymptote corresponding to homogeneous states of the system. These solutions are represented by phase paths that are separatrices in the phase space of the nonlinear oscillator of Eqn (13).

We shall first consider the steady-state solution for $\delta = +1$. In this case the asymmetry of the interaction of the sublattices is unimportant. Therefore, we shall limit ourselves just to a discussion of the symmetric interaction when $\chi_{i,+} = \chi_{i,-} = \chi_i$ (i = 1, 2), $F_+(x) \equiv F_-(x) \equiv F_s(x)$, and the function $F_a(x)$ vanishes identically.

2.3.1 Soliton excitations of the b state. We shall now find the solution of the system of equations (10) and (11) with the asymptote

$$x \to \xi_1, \quad x_{\zeta} \to 0, \quad y_{\zeta} \to 0, \quad \zeta \to \pm \infty$$
 (15)

Under these conditions the constants of integration are $C_1 = 0$ and $C_2 = 0$, and the potential Q is described by a fourth-degree polynomial with a double root $x = \xi_1$:

$$Q(x) = a(x - \xi_1)^2 [(x + \xi_1)^2 + b(x + \xi_1) + c_b] , \qquad (16)$$

where

$$a = \frac{g_0}{s^2 - 1} \left[1 + \frac{2\chi_2^2}{g_0\mu(s^2 - s_2^2)} \right] ,$$

$$b = \frac{-4\chi_1\chi_2}{g_0\mu(s^2 - s_2^2)} \left[1 + \frac{2\chi_2^2}{g_0\mu(s^2 - s_2^2)} \right]^{-1} ,$$

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

Thus, Q(x) has not only the double root $x = \xi_1$, but also two more real roots $\varphi_1 = -\xi_1 - (b/2) - \sqrt{D_b}$, $\varphi_2 = -\xi_1 - (b/2) + \sqrt{D_b}$ if $D_b = (b/2)^2 - c_b \ge 0$.

It follows from the explicit expression (16) for the potential Q(x) that the necessary and sufficient conditions for the existence of bounded solutions of Eqn (13) with the asymptote (15) are either the inequalities

$$a < 0, \quad \varphi_1 > \xi_1, \quad D_b > 0 ,$$
 (17)

or the inequalities

$$a > 0, \quad \varphi_1 < \xi_1, \quad D_b > 0$$
 . (18)

If inequalities (17) apply, the differential equation (13) has only one soliton solution $\xi_1 < x_{b_1}(\zeta) \leq \varphi_1$, but if inequalities (18) are obeyed, there are two soliton solutions $\varphi_1 \leq x_{b_2}(\zeta) < \xi_1$ and $\xi_1 < x_{b_3}(\zeta) \leq \varphi_2$ (Fig. 2).

In fact, if inequalities (17) are satisfied, the integral equation (14) becomes



Figure 2. Form of the *b*-soliton solutions $x_{b_1}(\zeta), x_{b_2}(\zeta), x_{b_3}(\zeta)$.

from which we can readily obtain the explicit form of the soliton b_1 :

$$x_{b_1}(\zeta) = \xi_1 + \frac{2(\varphi_1 - \xi_1)(\varphi_2 - \xi_1)}{\varphi_1 + \varphi_2 - 2\xi_1 + (\varphi_2 - \varphi_1)\cosh(R_b\zeta)} , (19)$$

where $R_b = \sqrt{|2a(\varphi_1 - \xi_1)(\varphi_2 - \xi_1)|}$. However, if the inequalities (18)

However, if the inequalities (18) are obeyed, then the integral equation (14) becomes

$$\int_{x(\zeta)}^{x(0)} \frac{\mathrm{d}u}{(u-\xi_1)\sqrt{(u-\varphi_1)(\varphi_2-u)}} = \sqrt{2a} \,\zeta \;\;,$$

where $x(0) = \varphi_1$ applies to the soliton b_2 and $x(0) = \varphi_2$ to the soliton b_3 . Hence, we have the explicit expressions for the solitons b_2 and b_3 :

$$x_{\boldsymbol{b}_{2,3}}(\zeta) = \xi_1 + \frac{2(\varphi_1 - \xi_1)(\varphi_2 - \xi_1)}{\varphi_1 + \varphi_2 - 2\xi_1 \pm (\varphi_2 - \varphi_1)\cosh(R_{\boldsymbol{b}}\zeta)}.$$
(20)

The second component of the solution $\rho_b(\zeta) = dy_b(\zeta)/d\zeta$ can be found from Eqn (12)

$$\rho_{\boldsymbol{b}_k}(\zeta) = \frac{2}{\mu(s^2 - s_2^2)} F[x_{\boldsymbol{b}_k}(\zeta)], \quad k = 1, 2, 3 .$$
⁽²¹⁾

It follows from the explicit form of the **b** solitons of Eqns (19)-(21) that if $\zeta \to \pm \infty$, then $x_b(\zeta) \to \zeta_1$, $\rho_b(\zeta) \to 0$, i.e. the **b** solitons are local perturbations of the **b** state.

The solitons b_1 , b_2 , and b_3 have dome-shaped profiles along the component x and kink-shaped along the component y. The amplitudes of the first and second components are $A_x = x_b(0) - \xi_1$ and $A_y = \rho_b(0)$, and the width is

$$L_{b} = \int_{-\infty}^{+\infty} \left| [x_{b}(\zeta) - \xi_{1}] [x_{b}(0) - \xi_{1}]^{-1} \right| d\zeta ,$$

which is measured in terms of the lattice constants; the energy E is measured from the energy level of the **b** state.

The spectrum of the velocities of the soliton b_1 is governed by inequalities (17) and that of the solitons b_2 and b_3 is determined by inequalities (18). The condition $D_b > 0$ is equivalent to the inequality $s_{p_1} < s < s_2$, where

$$s_{p_1} = s_2 \sqrt{1 - \frac{2\chi_2^2}{g_0\kappa} - \frac{\chi_1^2}{g_0\kappa(\xi_1^2 - 1)}}$$

It should be noted that on the basis of inequalities (5), we have $0 < s_{p_1} < s_2$.

The inequality a < 0 determines the range of the velocities $0 \le s < \min(1, s_{p_2})$, $\max(1, s_{p_2}) < s < s_2$ if $s_2 > 1$, but $0 \le s < s_{p_2}$, $s_2 < s < 1$, if $s_2 < 1$. Here,

$$s_{p_2} = s_2 \sqrt{1 - 2\chi_2^2 (g_0 \kappa)^{-1}} \ge s_{p_1}$$
.

The condition $\varphi_1 > \xi_1$ determines the range of values $0 \le s < \min(1, s_{p_3})$, and $\max(1, s_{p_3}) < s < s_2$, where

$$s_{p_3} = s_2 \sqrt{1 - (\chi_1 - 2\chi_2\xi_1)^2 [g_0\kappa(3\xi_1^2 - 1)]^{-1}} \ge s_{p_1}$$
.

Consequently, the soliton \boldsymbol{b}_1 generally has a two-band velocity spectrum:

$$s_{p_1} < s < \min(1, s_{p_2}, s_{p_3}), \quad \max(1, s_{p_2}, s_{p_3}) < s < s_2$$
. (22)

If $s_2 > 1$, the velocity spectrum is of the two-band type only if $s_{p_1} < 1$, s_{p_2} , $s_{p_3} > s_{p_1}$, and $s_{p_2} < s_2$. If $s_2 < 1$, the soliton \boldsymbol{b}_1 can only have a one-band spectrum.

The inequality a > 0 governs the range of velocities $\min(1, s_{p_2}) < s < \max(1, s_{p_2})$, and the condition $\varphi_1 < \xi_1$ governs the range $0 \le s < \min(1, s_{p_3})$, and $\max(1, s_{p_3}) < s < s_2$. Hence, the solitons b_2 and b_3 have a one-band velocity spectrum with $\min(1, s_{p_2}) < s < \min(1, s_{p_3})$ if $s_{p_2} < s_{p_3}$ and a one-band spectrum with $\max(1, s_{p_3}) < s < (1, s_{p_3}) < s < (1, s_{p_3})$ if $s_{p_2} > s_{p_3}$.

In addition to the **b**-soliton solutions found here and representing local perturbations of the **b** state, the system of equations (10) and (11) has a solution which describes a transition from the state **b** to a metastable state **me**, which is topologically close to the state **e**.

In fact, if $s = s_{p_1}$ and a < 0, the potential of Eqn (25) has two double roots $x = \xi_1$ and $x = \varphi^0 = -\xi_1 - (b/2)$. The integral equation (14) becomes

$$\int_{(\xi_1+\varphi^0)/2}^{x(\zeta)} \frac{\mathrm{d}u}{(u-\xi_1)(\varphi^0-u)} = \pm \sqrt{-2a}\,\zeta \ .$$

Hence, we obtain the explicit form of the topological soliton tb_{\pm}

$$x_{tb_{\pm}}(\zeta) = \frac{1}{2}(\zeta_1 + \varphi^0) \pm \frac{1}{2}(\varphi^0 - \zeta_1) \tanh(R_{tb}\zeta) , \qquad (23)$$

where $R_{tb} = (\xi_1 - \varphi^0) \sqrt{-a/2}$ (Fig. 3). The second component of the solution $\rho_{tb_{\pm}}(\zeta) = dy_{tb_{\pm}}(\zeta)/d\zeta$ is found from the equation

$$\rho_{tb_{\pm}}(\zeta) = 2F[x_{tb_{\pm}}(\zeta)][\mu(s_{p_1}^2 - s_2^2)]^{-1} .$$
⁽²⁴⁾

If $\zeta \to \pm \infty$, $x_{ib_{\pm}}(\zeta) \to \xi_1$, $x_{ib_{\mp}}(\zeta) \to \varphi^0$, $\rho_{ib_{\pm}}(\zeta) \to 0$, $\rho_{ib_{\mp}}(\zeta) \to \rho_{me} = 2F(\varphi^0)/\mu(s_{\rho_1}^2 - s_2^2)$, the topological soliton tb_{\pm} describes the transition of a chain from the state **b** to the metastable state $me \{x_n \equiv \varphi^0, y_{n+1} - y_n \equiv \rho_{me}, y'_n \equiv s_b\}$, $s_b = -s_{\rho_1}\rho_{me}$. The energy of the metastable state me is higher than the energy of the state **b**, so that — depending on the direction — the motion of the soliton tb is accompanied either by the evolution or absorption of energy. The soliton width is $L_{tb} = (\varphi^0 - \xi_1)/x'_{tb}(0) = 2/R_{tb}$.

The necessary condition for the existence of the soliton tb_{\pm} is the inequality $a(s_{p_1}) < 0$. It should be noted that if $\chi_1 = 0$, then $s_{p_1} = s_{p_2}$ and $a(s_{p_1}) = 0$, so that the soliton tb_{\pm} can exist only if $\chi_1 \neq 0$.



Figure 3. Topological soliton $x_{tb}(\zeta)$.

2.3.2 Soliton excitations of the e state. We shall find the solution of the system of equations (10) and (11) with the asymptote

$$x \to \eta_2, \quad x_{\zeta} \to 0, \quad y_{\zeta} \to \rho_e, \quad \zeta \to \pm \infty$$
 (25)

Under these conditions the constants of integration are $C_1 = 2F(n_2)s^2\kappa^{-1}$

$$C_2 = -V(\eta_2) + 2F^2(\eta_2)(2s^2 - s_2^2)[\kappa(s^2 - s_2^2)]^{-1} .$$

Then the potential Q is of the form

$$Q(x) = a(x - \eta_2)^2 [(x + \eta_2)^2 + b(x + \eta_2) + c_e] , \qquad (26)$$

where

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

$$d = \eta_2^2 - 1 + \frac{2\chi_2 F(\eta_2)}{\kappa g_0} < 0 .$$

The fourth-degree polynomial Q(x) not only has the double root $x = \eta_2$, but two more real roots

$$\theta_1 = -\eta_2 - \frac{1}{2}b - \sqrt{D_e}, \ \theta_2 = -\eta_2 - \frac{1}{2}b + \sqrt{D_e},$$

if $D_e = (b/2)^2 - c_e \ge 0$. It follows from the form of Eqn (26) describing the potential Q that the necessary and sufficient condition for the existence of bounded solutions of Eqn (13) with the asymptote (25) is either the satisfaction of the inequalities

$$a < 0, \quad \theta_2 < \eta_2, \quad D_e > 0 ,$$
 (27)

or of the inequalities

$$a > 0, \quad \theta_2 > \eta_2, \quad D_e > 0$$
 . (28)

When conditions (27) are satisfied, the differential equation (13) has one soliton solution $\theta_2 < x_{e_1}(\zeta) \leq \eta_2$, but in the case of inequalities (28) there are two soliton solutions $\theta_1 \leq x_{e_2}(\zeta) < \eta_2$ and $\eta_2 < x_{e_3}(\zeta) \leq \theta_2$. The explicit form of the solitons e_1, e_2, e_3 can be found in the same way as the explicit form of the solitons b_1, b_2, b_3 . The solution e_1 is

$$x_{e_1}(\zeta) = \eta_2 + \frac{2(\theta_1 - \eta_2)(\theta_2 - \eta_2)}{\theta_1 + \theta_2 - 2\eta_2 - (\theta_2 - \theta_1)\cosh(R_e\zeta)} , \quad (29)$$

and the solutions e_2 and e_3 are

$$x_{e_{2,3}}(\zeta) = \eta_2 + \frac{2(\theta_1 - \eta_2)(\theta_2 - \eta_2)}{\theta_1 + \theta_2 - 2\eta_2 \pm (\theta_2 - \theta_1)\cosh(R_e\zeta)} , \quad (30)$$

where $R_e = \sqrt{|2a(\theta_1 - \eta_2)(\theta_2 - \eta_2)|}$. The second component of the solution $\rho_e(\zeta) = dy_e(\zeta)/d\zeta$ follows from Eqn (12)

$$\rho_{e_k}(\zeta) = 2\{s_2^2 F[x_{e_k}(\zeta)] - s^2 F(\eta_2)\} [\kappa(s^2 - s_2^2)]^{-1} ,$$

$$k = 1, 2, 3 .$$
(31)

It follows from the explicit form of the *e* solitons described by Eqns (29), (30), and (31) that if $\zeta \to \pm \infty$, then $x_e(\zeta) \to \eta$, $\rho_e(\zeta) \to \rho_e$, i.e. the *e* solitons are local perturbations of the *e* state.

The solitons e_1, e_2 , and e_3 have dome-shaped profiles along the component x and are kink-shaped along y. They have the following amplitudes along the first and second components, $A_x = \eta_2 - x_e(0)$ and $A_y = \rho_e(0) - \rho_e$, and their width is

$$L_{e} = \int_{-\infty}^{+\infty} \left| [x_{e}(\zeta) - \eta_{2}] [x_{e}(0) - \eta_{2}]^{-1} \right| d\zeta ,$$

which is measured in terms of the lattice constants, and the energy is E, measured from the energy level of the e state. The velocity spectrum of the soliton e_1 is determined by inequalities (27), and that of the solitons e_2 and e_3 is governed by inequalities (28).

In addition to these e-soliton solutions, the system of equations (10), (11) has a solution which describes a transition from the state e to the metastable state mb, topologically close to the state b.

In fact, if the velocity is $s = s_{p_4}$, described by

$$s_{p_4} = s_2 \sqrt{1 - \frac{2\chi_2^2}{g_0 \kappa} - \frac{\chi_1^2}{g_0 \kappa d}},$$

the discriminant is $D_e = 0$, so that the potential (26) is a fourth-degree polynomial with two double roots $x = \eta_2$, $x = \theta^0 = -\eta_2 - (b/2)$. The soliton solution te_{\pm} exists only if $a(s_{p_4})$ and has the form

$$x_{te_{\pm}}(\zeta) = \frac{1}{2}(\eta_2 + \theta^0) \pm \frac{1}{2}(\eta_2 - \theta^0) \tanh(R_{te}\zeta) , \qquad (32)$$

where $R_{te} = (\eta_2 - \theta^0) \sqrt{-a/2}$. The second component of the solution $\rho_{te_{\pm}}(\zeta) = dy_{te_{\pm}}(\zeta)/d\zeta$ is found from Eqn (12):

$$\rho_{te_{\pm}}(\zeta) = 2\{s_2^2 F[x_{te_{\pm}}(\zeta)] - s_{p_4}^2 F(\eta_2)\}[\kappa(s_{p_4}^2 - s_2^2)]^{-1} \quad . \tag{33}$$

If $\zeta \to \pm \infty$, then $x_{te_{\pm}}(\zeta) \to \eta_2$, $x_{te_{\mp}}(\zeta) \to \theta^0$, $\rho_{te_{\pm}}(\zeta) \to \rho_e$, $\rho_{te_{\mp}}(\zeta) \to \rho_{mb} = 2[s_2^2 F(\theta^0) - s_{\rho_4}^2 F(\eta_2)]/\kappa(s_{\rho_4}^2 - s_2^2)$, i.e. the topological soliton te_{\pm} describes a transition of a chain from the state e to the metastable state $mb \ \{x_n \equiv \theta^0, y_{n+1} - y_n \equiv \rho_{mb}, y'_n \equiv s_e\}$, $s_e = -s_{\rho_4}(\rho_{me} - \rho_e)$.

The energy of the metastable state mb is higher than the energy of the state e, so that the motion of the soliton te is accompanied by the evolution or absorption of energy, depending on the direction of its motion. The soliton width is $L_{te} = (\eta_a - \theta^0)/x'_{te}(0) = 2/R_{te}$.

The necessary condition for the existence of the topological soliton te_{\pm} is the inequality $a(s_{p_4}) < 0$. It should be noted that if $\chi_1 = 0$, then $s_{p_4} = s_{p_2}$, $a(s_{p_4}) = 0$, so that the soliton te_{\pm} , like the soliton tb_{\pm} , can only exist if $\chi_1 \neq 0$.

We shall consider the steady-state solutions corresponding to $\delta = -1$. For simplicity, we shall confine ourselves to the case when $\chi_{2,+} = \chi_{2,-} = 0$.

As in the case when $\delta = +1$, we shall first consider the soliton excitation of the **b** state, i.e. we shall find the solutions of the system of equations (10) and (11) with the asymptote (15). The effective potential Q of the nonlinear oscillator (13) is then a fourth-degree polynomial given by Eqn (16) and the coefficients in this polynomial are

$$a = g_0 \left[1 + s^2 + \frac{\chi_{1,a}^2}{\mu(s^2 - s_2^2)} \right]^{-1}, \quad b = 0 ,$$

$$c_b = 2 \left[\xi_1^2 - 1 - \frac{\chi_{1,s}^2}{g_0 \mu(s^2 - s_2^2)} \right] .$$

In this case the condition a < 0 is incompatible with the condition $c_b \leq 0$, so that the solitons b_1 and tb_{\pm} cannot exist. For example, only the nontopological solitons b_2 and b_3 can exist against the background of the *b* state.

We shall next consider the soliton excitations of the estate. We shall find the solutions of the system (10), (11) with the asymptote (25). In this case the effective potential Q is a fourth-degree polynomial of Eqn (26) with the coefficient $c_e = 2\{\eta_2^2 - 1 + [\chi_{1,s}^2/g_0\mu(s^2 - s_2^2)]\}$. Here, the conditions a < 0 and $c_e \leq 0$ are compatible and they determine the velocity spectrum of the soliton e_1 : $s_{p_5} < s < s_{p_6}$, where the velocity of the topological soliton s_{p_5} is found from the condition $c_e(s) = 0$ and the velocity s_{p_5} is deduced from the condition a(s) = 0. In the former case the velocity is $s_{p_5} = s_2 [1 + \chi_{1,s}^2/g_0 \kappa (1 - \eta_2^2)]^{1/2} > s_2$, and in the latter case it is $s_{p_6} = [\{s_2^2 - 1 + [(s_2^2 + 1)^2 + 4\chi_{1,a}^2]^{1/2}\}/2]^{1/2}$. We note that when the interaction between the sublattices is symmetric ($\chi_{1,a} = 0$), the solitons e_1 and te_{\pm} cannot exist, because in this case we have $s_{p_{\epsilon}} = s_2 < s_{p_5}$. Therefore, if $\delta = -1$, the asymmetry of the lattice interaction $(\chi_{1,a} > \chi_p)$, where χ_p is found from the condition $s_{p_6} = s_{p_5}$) is the necessary condition for the existence of the solitons e_1 and te_{\pm} .

The soliton te_{\pm} exists only for one velocity $s = s_{p_5}$ and it has the form $x_{te_{\pm}}(\zeta) = \pm \eta_2 \tanh(R_{te}\zeta)$, where $R_{te} = \eta_2 \sqrt{-2a(s_{p_5})}$. The second component of the solution is found from Eqn (12).

An analysis carried out in this section shows that in a bistable chain with *nondegenerate* ground states we can expect the existence, not only of nontopological solitons, but also (at fixed values of the velocity) of the topological solitons tb_{\pm} and te_{\pm} , which induce a transition of a chain from its initial equilibrium state to an intermediate steady state in the region of attraction to another equilibrium state. These solitons exist because of the sublattice interaction that results in a dynamic degeneracy of the effective potential of a phase transition at a specific value of the velocity.

3. Computer simulation of soliton dynamics in a bistable chain

Our analytic investigation of soliton motion is based on the long-wavelength approximation. The question therefore arises of the influence of the discrete nature of the lattice. Moreover, it is necessary to study the stability of the soliton solutions.

We shall consider the dynamics of solitons for two limiting types of sublattice interaction: $\chi_{2,\pm} = 0$ and $\chi_{1,\pm} = 0$. In the former case the main effect of a reduction by ρ in the step (period) of the external sublattice is a reduction of the difference between the energy levels of the ground states of the effective double-well potential $V(x) + 2\chi_{1,s}\rho(x-\xi_1)$. This sublattice interaction has been used before [20, 22, 23] in simulation of the propagation of exothermal reactions in quasi-one-dimensional molecular crystals. In the case of the latter type of sublattice interaction a reduction by ρ in the step (period) of the external sublattice is related to a change in the height of the barrier between the two ground states of the effective double-well potential $V(x) + 2\chi_{2,s}\rho(\xi_1^2 - x^2)$. This type of the sublattice interaction has been used [7, 24, 25] in simulation of the transport of protons in quasi-one-dimensional chains of hydrogen bonds and later [10-12, 26] in simulation of the dynamics of local conformational transitions in DNA molecules.

$$\chi_1 < \chi_{p_1} = \sqrt{\kappa g_0(\xi_1^2 - 1)}$$
 (34)

When this inequality is satisfied the two-component system under discussion has two stable states: the state b more favourable from the energy point of view, and the state e, which is less favourable from this point of view.

The spectrum of the permissible velocities of the solitons b_1, b_2 , and b_3 is derived in the preceding section. In the sublattice interaction case considered here, we have

$$s_{p_1} = s_2 \sqrt{1 - \chi_1^2 [g_0 \kappa (\xi_1^2 - 1)]^{-1}}, \quad s_{p_2} = s_2$$
$$s_{p_3} = s_2 \sqrt{1 - \chi_1^2 [g_0 \kappa (3\xi_1^2 - 1)]^{-1}}.$$

When the bistability condition (34) is obeyed, it is found that $0 < s_{p_1} < s_{p_3} < s_2$. Therefore, the soliton \boldsymbol{b}_1 has a two-band velocity spectrum (22):

$$s_{p_1} < s < \min(1, s_{p_3}), \quad \max(1, s_{p_3}) < s < s_2$$

if $s_2 > 1$, and the one-band spectrum $s_{p_1} < s < s_{p_3}$, if $s_2 < 1$. The solitons b_2 and b_3 have a one-band velocity spectrum $\max(1, s_{p_3}) < s < \max(1, s_2)$, i.e. they exist only if $s_2 > 1$.

The topological soliton *tb* has only one permissible velocity $s = s_{p_1}$ and it exists for values of χ_1 such that $s_{p_1} < 1$.

The velocity spectrum of the soliton e_1 is found from the inequalities (27). The inequality a < 0 defines the range s < 1, and the condition $D_e > 0$ defines the range $0 \le s < s_2$, $s_{p_4} < s < \infty$ if $\chi_1 < \chi_{p_2}$ and the range $s_{p_4} < s < s_2$ if $\chi_{p_2} < \chi_1 < \chi_{p_1}$, where $s_{p_4} = s_2(1-R)^{1/2}$ for $R = \chi_1^2/g_0\kappa(\eta_2^2 - 1) < 1$ and $s_{p_4} = 0$ for $R \ge 1$, but $\chi_{p_2} = [\kappa g_0(\xi_1^2 + \xi_1)]^{1/2} < \chi_{p_1}$. If $\chi < \chi_{p_2}$, then $\eta_2 < 1$, $s_{p_4} > s_2$, but if $\chi_{p_2} < \chi_1 < \chi_{p_1}$, then $1 < \eta_2 < \xi_1$, $s_{p_4} < s_2$. The condition $\theta_2 < \eta_2$ defines the range $0 \le s < s_{p_7}$, $s_2 < s < \infty$, where

$$s_{p_7} = s_2 \sqrt{1 - \chi_1^2 [g_0 \kappa (3\eta_2^2 - 1)]^{-1}} > s_{p_1}$$
.

Hence, subject to the condition $\chi_1 < \chi_{p_2}$, the soliton e_1 has a two-band velocity spectrum

$$0 \leq s < \min(1, s_{p_7}), \quad s_{p_4} < s < 1$$
,

and for $\chi_{p_2} < \chi_1 < \chi_{p_1}$ it has a one-band spectrum $s_{p_4} < s < \min(1, s_{p_7})$.

The velocity spectrum of the solitons e_2 and e_3 is found subject to the inequalities (28). The inequality a > 0 defines the range of values s > 1 and the condition $\theta_2 < \eta_2$ corresponds to the range $s_{p_7} < s < s_2$. Therefore, these solitons have a one-band velocity spectrum $\max(1, s_{p_7}) < s < s_2$, i.e. they exist only if $s_2 > 1$.

The topological soliton *te* has only one permissible value of the velocity $s = s_{p_4}$ and exists for $\chi_1 < \chi_{p_3}$, where the threshold value $\chi_{p_3} < \chi_{p_2}$ is found from the condition $s_{p_4}(\chi_{p_3}) = 1$.

In molecular chains the displacements along the component x are intramolecular and they deform relatively rigid valence bonds, whereas the displacements along the external component y represent displacements of the molecules relative to one another, leading solely to deformations of the soft nonvalence bonds. Therefore, the rigidity of the internal sublattice is as a rule higher than that of the external sublattice: $s_1 = 1 > s_2$. We shall now consider the soliton dynamics in that typical case when the solitons b_1 , tb, e_1 , and te can exist.

We shall now consider the specific case when $s_2 = 0.5$, $\mu = 1$, $\kappa = 0.25$, $g_0 = 0.01$, $g_1 = 0.005$. We then have $\xi_1 = -1.057454$, $g_2 = 0.005148$, $\chi_{p_1} = 0.017191$, $\chi_{p_2} = 0.012324$. The dependences of the intramolecular coordinate η_2 , of the compression of the external sublattice ρ_e , of the energy level E_e of the *e* state, and of the boundary values of velocities $s_{p_1}, s_{p_3}, s_{p_4}, s_{p_7}$ on the sublattice interaction parameter χ_1 are listed in Table 1. It is clear from this table that the soliton *te* exists only for $\chi_1 \leq 0.011$, when its velocity is $s_{p_4} > s_2$.

The soliton b_1 has a one-band velocity spectrum (s_{p_1}, s_{p_3}) . If $\chi_1 = 0.01$, then $s_{p_1} = 0.406699$, $s_{p_3} = 0.495735$. The dependences of the amplitudes A_x and A_y of the width L_b , and of the energy E of the soliton b_1 on the velocity s are shown in Fig. 4. Only the amplitude A_x depends monotonically on s. If $s \to s_{p_3}$, then $A_x \to 0$, $A_y \to 0$, $L_b \to \infty$, $E \to 0$. The profiles of the soliton b_1 are shown in Fig. 5 for different velocities. The width and the energy of the soliton increase monotonically on approach to $s \to s_{p_1}$. In this limit, one soliton b_1 splits into two topological solitons tb_+ and tb_- . The increase in the width of the soliton b_1 is due to the movement apart of the centres of the topological solitons. The rise of its energy is a consequence of the higher energy, compared with the

Table 1. Dependences of the parameters η_2 , ρ_e , and E_e of the *e* state and of the limiting values in the velocity spectra s_{p_1} , s_{p_3} , s_{p_4} , and s_{p_7} on the sublattice interaction parameter χ_1 .

χ1	η_2	$ ho_{ m e}$	$E_{\mathbf{e}}$	s_{p_1}	<i>s</i> _{<i>p</i>₃}	<i>S</i> _{<i>P</i>7}	s_{p_4}
0.000	0.930403	0.000000	0.009980	0.500000	0.500000	0.500000	0.500000
0.002	0.932390	-0.031884	0.009853	0.496605	0.499830	0.499751	0.503052
0.004	0.938292	-0.063864	0.009472	0.486276	0.499320	0.499024	0.513203
0.006	0.947945	-0.096259	0.008832	0.468557	0.498469	0.497873	0.534325
0.008	0.961097	-0.129187	0.007925	0.442559	0.497275	0.496373	0.577830
0.010	0.977440	-0.162792	0.006742	0.406699	0.495735	0.494612	0.688594
0.011	0.986705	-0.179886	0.006043	0.384238	0.494834	0.493660	0.841482
0.012	0.996641	-0.197193	0.005271	0.358024	0.493847	0.492673	1.548257
0.013	1.007207	-0.214725	0.004423	0.327159	0.492770	0.491660	0.000000
0.014	1.018363	-0.232491	0.003497	0.290157	0.491605	0.490628	0.000000
0.016	1.042287	-0.268767	0.001404	0.182848	0.489007	0.488537	0.000000
0.017	1.054981	-0.287291	0.000233	0.074274	0.487572	0.484870	0.000000



Figure 4. Dependences of the amplitudes A_x and A_y , of the width L_b (in chain periods), and energy *E* (measured from the energy level of the *b* conformation) of the *b*₁ soliton on the velocity *s*, calculated for $g_0 = 0.01$, $g_1 = 0.005$, $\mu = 1$, $\kappa = 0.25$ ($s_2 = 0.5$), $\chi_1 = 0.01$, $\chi_2 = 0$.



Figure 5. Transformation of the soliton b_1 into a pair of topological solitons tb_+ and tb_- in the limits $s \to s_{p_1}$ for a chain with $g_0 = 0.01$, $g_1 = 0.005$, $\mu = 1$, $\kappa = 0.25$, $\chi_1 = 0.01$, and $\chi_2 = 0$. The soliton b_1 is shown for s = 0.49, 0.46, 0.42, 0.407 and 0.4067 (curves 1-5).

state b of the ends of the chain, of the metastable conformation me in the part of the chain between the centres of the topological solitons.

The dynamics of the nontopological solitons b and e can be investigated conveniently subject to periodic boundary

conditions. This can be done by replacing Eqns (6) and (7) with the system

$$x_n'' = x_{n+1} - 2x_n + x_{n-1} - \frac{dV}{dx}(x_n) - (\rho_n + \rho_{n-1})\frac{dF_s}{dx}(x_n) ,$$
(35)
$$\mu \rho_n'' = \kappa(\rho_{n+1} - 2\rho_n + \rho_{n-1}) + F_s(x_{n+2}) - F_s(x_{n+1}) - F_s(x_n) + F_s(x_{n-1}) ,$$
(36)

where $\rho_n = y_{n+1} - y_n$ are the relative displacements of the *n*th site in the external sublattice, and n = 1, ..., N, where *N* is the number of links in the chain (n + 1 = 1, n + 2 = 2) if n = N, but n + 2 = 1 for n = N - 1, and n - 1 = N for n = 1). The initial conditions are selected to correspond to the exact soliton solutions of Eqns (19), (20), (21), and (29), (30), (31).

Computer simulation of the dynamics of the soliton b_1 reveals that it is stable only at velocities *s* close to s_{p_1} . For example, for a cyclic chain with N = 200 molecules and the initial velocity s = 0.40699 or s = 0.41, this soliton travels at a constant velocity conserving its profile; in the time $\tau = 1200$ it crosses 489 'cells' or links of the chain when the initial velocity is s = 0.40699 and 492 such links if s = 0.41. The energy of this soliton decreases monotonically on increase in the velocity in the range s < 0.42, but for s > 0.42 the energy rises monotonically (Fig. 4). The energy minimum corresponds to s = 0.42. If $s \ge 0.42$ the soliton is unstable. The soliton motion results in its deceleration to a velocity close to s_{p_1} and then the soliton moves at a constant velocity.

The soliton e_1 has a two-band velocity spectrum $0 \le s < s_{p_7}$, $s_{p_4} < s < 1$ ($s_{p_7} = 0.494612$, $s_{p_4} = 0.688594$) if $\chi_1 = 0.01$. In the first band of the velocity spectrum in the localisation region the external sublattice becomes elongated and in the case of the second band this sublattice is



Figure 6. Profiles of the soliton e_1 in a chain with $g_0 = 0.01$, $g_1 = 0.005$, $\mu = 1$, $\kappa = 0.25$, $\chi_1 = 0.01$, and $\chi_2 = 0$ for *s* from the second band in the velocity spectrum: s = 0.6886, 0.7, 0.8, 0.9, and 0.99 (curves 1-5).

compressed. The profile of the soliton travelling at the velocity s from the second subband is shown in Fig. 6.

Near the limit $s \rightarrow s_{p_4}$ the soliton width and its energy increase monotonically. In this limit, one soliton e_1 splits into two topological solitons te_- and te_+ . The increase in the soliton width e_1 is explained by spreading apart of the centres of the topological solitons and the rise of the energy is due to the fact that the metastable state mb of the part of the chain between the centres of the topological solitons, has a higher energy than the state e of the ends of the chain. As the velocity approaches the right-hand edge of the second band of the velocity spectrum the soliton amplitude decreases monotonically, its width approaches zero, and the energy approaches infinity.

Computer simulation of the dynamics of the soliton e_1 has revealed its instability in both intervals of the velocity spectrum. During its motion the soliton either splits into two kinks, which take the chain from the state e to the conformation b, which is more favourable from the energy point of view, or the soliton is transformed in a twocomponent breather and this process is accompanied by the emission of low-amplitude phonons.

The dynamics of the topological solitons *tb* and *te* was simulated for a finite system of N = 400 molecules with a free right-hand end and a clamped left-hand end, the latter moving uniformly at a velocity s_k , where $s_k = s_b = -s_{p_1}\rho_{mb}$ for the soliton *tb* and $s_k = s_e = -s_{p_4}(\rho_{me} - \rho_e)$ for the soliton *te*.

The dynamics of a chain is described by the system of equations

$$x_{1}'' = x_{2} - x_{1} - \frac{dV}{dx}(x_{1}) - (y_{2} - y_{1})\frac{dF_{s}}{dx},$$

$$y_{1} = s_{k}\tau,$$

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

$$\mu y_{n}'' = \kappa(y_{n+1} - 2y_{n} + y_{n-1}) + F_{s}(x_{n+1}) - F_{s}(x_{n-1}), \quad (37)$$

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

$$y_{n}'' = x_{n} - \frac{dV}{dx}(x_{n}) - (y_{n} - y_{n-1})\frac{dF_{s}}{dx}(x_{n}),$$

$$x_N'' = x_{N-1} - x_N - \frac{y_N}{dx}(x_N) - (y_N - y_{N-1}) \frac{y_N}{dx}(x_N)$$
$$\mu y_N'' = \kappa (y_{N-1} - y_N) - F_s(x_N) - F_s(x_{N-1})$$

subject to the initial conditions

$$\begin{aligned} x_n(0) &= x(n), \quad n = 1, 2, \dots, N, \quad y_n(0) &= y_{n-1}(0) + \rho_{n-1}(n) , \\ x'_{n-1}(0) &= -s[x_n(0) - x_{n-1}(0)], \quad y'_n(0) &= -s[\rho(n) - \rho^0] , \\ n &= 2, 3, \dots, N, \quad x'_N(0) &= 0 , \end{aligned}$$

where $x(\zeta)$, $\rho(\zeta)$ are the soliton solutions of Eqns (23), (24), (32), and (33) obtained in the continuum approximation, $\rho^0 = \rho_b = 0$ applies to the soliton tb_+ , and $\rho^0 = \rho_e$ applies to the soliton te_{\pm} . If $\chi_1 = 0.01$, the soliton tb has the width L = 12.92 and its velocity is $s = s_{p_1} = 0.406699$; in the case of the soliton te, we have L = 10.26 and $s = s_{p_4} = 0.688594$, which confirms the validity of the continuum approximation used to find the soliton profile in Section 2.

It therefore follows that in simulation of the dynamics of the soliton tb_+ (and te_+) the left-hand end of the chain is in the metastable state me (mb), and the chain at the righthand end is in the state b (e). The soliton motion to the right at the velocity $s = s_{p_1}$ ($s = s_{p_4}$) is accompanied by an increase in the energy of the finite chain because of the



Figure 7. Decay of the topological te_+ soliton with $s = s_{p_4}$ in a chain with $g_0 = 0.01, g_1 = 0.005, \mu = 1, \kappa = 0.25, \chi_1 = 0.01$, and $\chi_2 = 0$.

induced leftward motion of the left-hand end $s_k = s_b$ $(s_k = s_e)$ and the motion to the left at the velocity $s = -s_{p_1}$ $(s = -s_{p_4})$ is accompanied by a reduction in the energy because of the induced rightward motion of the lefthand end $s_k = -s_b$ $(s_k = -s_e)$.

Computer simulation of the dynamics of the soliton tb_+ demonstrates its stability. For example, if $s = s_{p_1}$ then in the time $\tau = 800$ it crosses, at a constant velocity and retaining its profile, 326 links of the chain, but for $s = -s_{p_1}$ it crosses 325 such links. Simulation of the dynamics of the te_+ soliton reveals its instability, manifested by the loss of matching of the sublattice motion. If $s = s_{p_4}$, a onecomponent kink is formed from the soliton and after formation this kink begins to move opposite to the initial direction (Fig. 7), but for $s = -s_{p_4}$ a one-component kink is formed and it becomes detached from the soliton component moving in the direction of the initial motion (Fig. 8).

We shall now consider the transition from the metastable state e to the state b which is more favourable from the energy point of view, and we shall do this for the case of a chain of N = 400 links with free ends. Let the first 15 links be in the state b, and the other links in e. Then the chain dynamics is described by the following system of equations



Figure 8. Decay of the topological te_{-} soliton with $s = -s_{p_4}$ in a chain with $g_0 = 0.001$, $g_1 = 0.005$, $\mu = 1$, $\kappa = 0.25$, $\chi_1 = 0.01$, and $\chi_2 = 0$. The soliton profile is given at the initial moment $\tau = 0$ (curves *l* and *2*), at $\tau = 200$ (curves *3* and *4*), and at $\tau = 400$ (curves *5* and *6*).

$$\begin{aligned} x_1'' &= x_2 - x_1 - \frac{dV}{dx}(x_1) - (y_2 - y_1)\frac{dF_s}{dx}(x_1) ,\\ \mu y_1'' &= \kappa(y_2 - y_1) + F_s(x_1) + F_s(x_2) ,\\ x_n'' &= x_{n+1} - 2x_n + x_{n-1} - \frac{dV}{dx}(x_n) - (y_{n+1} - y_{n-1})\frac{dF_s}{dx}(x_n) ,\\ \mu y_n'' &= \kappa(y_{n+1} - 2y_n + y_{n-1}) + F_s(x_{n+1}) - F_s(x_{n-1}) , \quad (38)\\ n &= 2, 3, \dots, N-1 ,\\ x_N'' &= x_{N-1} - x_N - \frac{dV}{dx}(x_N) - (y_N - y_{N-1})\frac{dF_s}{dx}(x_N) ,\\ \mu y_N'' &= \kappa(y_{N-1} - y_N) - F_s(x_N) - F_s(x_{N-1}) \end{aligned}$$

subject to the initial conditions

$$x_{1}(0) = \dots = x_{14}(0) = \eta_{2}, \quad x_{15}(0) = 0,$$

$$x_{16}(0) = \dots = x_{N}(0) = \xi_{1},$$

$$y_{1}(0) = \dots = y_{15}(0) = 0, \quad y_{n+1}(0) = y_{n}(0) + \rho_{e},$$

$$n = 15, 16, \dots, N - 1,$$

$$x'_{1}(0) = \dots = x'_{N}(0) = 0, \quad y'_{1}(0) = \dots = y'_{N}(0) = 0.$$

The total energy of the system

$$H = \sum_{n=1}^{N} \left(\frac{1}{2} x'_{n}^{2} + \frac{\mu}{2} y'_{n}^{2} + V(x_{n}) \right) + \sum_{n=1}^{N-1} \left[\frac{1}{2} (x_{n+1} - x_{n})^{2} + \frac{\kappa}{2} (y_{n+1} - y_{n})^{2} + (y_{n+1} - y_{n}) F_{s}(x_{n}) + (y_{n+1} - y_{n}) F_{s}(x_{n+1}) \right]$$
(39)

is an integral of motion, which can be used conveniently to check the precision of numerical integration.

Numerical integration of the system of equations (38) shows that the conformational transition can occur in accordance with two scenarios.

If the sublattice interaction is weak (i.e. when $\chi_1 < \chi_{p_3}$) the transition splits into two stages: first a one-component kink forms in the chain and moves at supersonic velocity $s > s_2$ without dilation of the external sublattice and then a wave of dilation of this sublattice travels at the velocity of sound s_2 (Fig. 9). Depending on the sublattice interactionparameter χ_1 , the dissipation of energy may occur mainly during the first or second stage of this exothermal process. The first stage corresponds to the motion of a supersonic reaction wave and is not accompanied by an increase in the linear dimensions of the molecular system. The topological soliton *te* then approximates the profile of the front of a supersonic wave. The second stage is accompanied by dilation and active thermalisation of the external sublattice quite far behind the front.

If the sublattice interaction is strong (i.e. if $\chi_1 > \chi_{p_3}$), when there is no topological soliton *te*, the conformational transition does not split into two stages. A subsonic two-component soliton ($s < s_2$) forms in the chain and immediately transforms the chain from the state *e* to *b* (Fig. 10). Energy is then released in the soliton localisation region.

This transition mechanism corresponds to dynamic propagation of an exothermal reaction [27]. The first scenario with a nonthermalised supersonic detonation wave may be attributed to an explosive reaction in which the energy is released behind the reaction front. The second scenario represents smooth combustion when the energy is released in the region of the reaction front.



Figure 9. Conformational $e \rightarrow b$ transition in a chain with $g_0 = 0.01$, $g_1 = 0.005$, $\mu = 1$, $\kappa = 0.25$, $\chi_1 = 0.01$, and $\chi_2 = 0$. The displacements x_n and ρ_n are given at the initial moment $\tau = 0$ (curves 1 and 2), at $\tau = 180$ (curves 3 and 4), and $\tau = 360$ (curves 5 and 6). The velocity of the conformational transition front is s = 0.92.



Figure 10. Conformational $e \rightarrow b$ transition in a chain with $g_0 = 0.01$, $g_1 = 0.005$, $\mu = 1$, $\kappa = 0.25$, $\chi_1 = 0.012$ and $\chi_2 = 0$. The displacements x_n and ρ_n are given at the initial moment $\tau = 0$ (curves *I* and *2*), at $\tau = 180$ (curves *3* and *4*), and $\tau = 360$ (curves *5* and *6*). The velocity of the conformational transition front is s = 0.38.



Figure 11. Evolution of a topological soliton in a diatomic chain with free ends ($g_0 = 0.014$, $g_1 = 0.011$, $\mu = 5$, $\chi_{1,s} = 0.026$, $\chi_{1,a} = 0.634$, $s_2 = 0.155$). The initial soliton velocity is s = 0.246 (1 is the internal coordinate x_n , and 2 is the external coordinate ρ_n).

We shall now consider the dynamics of the topological solitons for such parameters of a chain when $\chi_{1,a} \neq 0$. In this case we can expect the existence of the topological te solitons both for $\delta = +1$ and $\delta = -1$. These solitons travel at a supersonic velocity $s_{te} = s_{p_5} > s_2$. Computer simulation of the *te*-soliton dynamics has revealed a number of features that distinguish such dynamics from the cases discussed earlier. The te soliton is also unstable, but its decay occurs in accordance with a different scenario. Supersonic te solitons have a finite lifetime, which depends on the lattice parameters. Simulation of the dynamics of the te soliton in a chain with free ends shows clearly that there are several stages of its evolution (Fig. 11). The first stage is characterised by the absence of deceleration and the front velocity is practically identical with the calculated value. A postfrontal region is established in this stage. In this region an intermediate dynamic state, corresponding to the metastable conformation mb, relaxes to the final state with oscillations near the equilibrium configuration of the products (b state). The subsequent soliton evolution is associated with the emission of radiation, which transfers the energy of the frontal region itself to a region occupied by molecules in the intermediate state. During this stage the soliton is decelerated slightly and its profile is distorted in the region of the intermediate state which follows directly behind the front. The final stage begins with a strong deceleration of the front and is completed by its total stoppage and formation of a clear boundary which



Figure 12. Dependence of the range of the soliton *te* on the width of its profile.

separates the reagents from the reaction products. The process of formation of this boundary begins with the formation of an extended transition region, which then breaks up. The total range of the *te* soliton is 20-100 unit cells, depending on the lattice parameters. This scenario of the stoppage of the reaction front is similar to the deceleration and stoppage of spinodal decomposition in mixtures of polymers observed over quite different spatial and temporal scales [28].

Another unexpected feature of the case under discussion is an unusual dependence of the lifetime (range) of the te soliton on its width (or, which is equivalent, on its velocity). Traditionally it is assumed that an increase in the width of a topological soliton reduces the influence of the discrete structure of the lattice and, consequently, increases the lifetime. However, in the system under discussion the dependence of the lifetime on the width is opposite (Fig. 12). Very wide solitons, with the velocity close to that of sound s_2 , decay practically immediately, so that it is not possible to determine their range. An increase in the velocity of a kink (and a reduction of its width) increases its range, which reaches the maximum value $N_t = 65$ of unit cells when the velocity is $S_{te} \approx 1.8s_2$. To the right of the maximum value the soliton range falls slightly. This behaviour of the lifetime of a topological soliton can be explained by a competition between two mechanisms. The decay of wide ('slow') solitons is related to a longwavelength instability, whereas in the case of narrow ('fast') solitons the discrete nature of the lattice is the decisive effect.

Numerical investigation of the soliton dynamics in a chain with $\chi_{1,\pm} = 0$, $\chi_{2,\pm} = \chi_2$, $\delta = +1$ is reported in Ref. [12]. For this type of the sublattice interaction only nontopological solitons can exist in a bistable nondegenerate chain and only topological solitons ti_{\pm} , describing the

transition of a chain from one equivalent state to another, can appear in a degenerate chain $(g_1 = 0)$.

If the bistability condition $\chi_2 < \sqrt{\kappa g_0/2}$ is satisfied, a degenerate chain $(g_1 = 0)$ has two equivalent stable homogeneous states $x_n = \pm 1, y_{n+1} - y_n = 0$ } ($\pm i$ states). In the limit $g_1 \rightarrow 0$ the state **b** goes over to a state -i and the state **e** to +i. The soliton solution of the system of equations (10) and (11) should have the asymptote

$$x \to \pm 1(\mp 1), \quad y_{\zeta} \to 0, \quad \zeta \to \pm \infty$$

when the effective potential of the nonlinear oscillator of Eqn (13) has the form $Q(x) = a(1 - x^2)^2$. Therefore, only if $a = g_0\{1 + [2\chi_2/g\mu(s^2 - s_2^2)]\}$ $(s^2 - 1)^{-1} < 0$ can the system of equations (10) and (11) have the solutions

$$x_{ii_{\pm}}(\zeta) = \pm \tanh(\sqrt{-2a\zeta}) ,$$

$$\rho_{ii_{\pm}}(\zeta) = 2\chi_{2}[\mu(s^{2} - s_{2}^{2})\cosh^{2}(\sqrt{-2a}\zeta)]^{-1} ,$$
(40)

which correspond to the topological solitons ti_{\pm} describing a localised transition from one steady state $(\mp i)$ to another $(\pm i)$.

The existence of the topological solitons ti_{\pm} requires that the inequality a < 0 should be satisfied, which determines the spectrum of the permissible velocities: $0 \le s < s_{p_2}$, $s_2 < s < 1$ if $s_2 < 1$ and $0 \le s < \min(1, s_{p_2})$, $\max(1, s_{p_2}) < s < s_2$ if $s_2 > 1$. Because of the bistability condition we have $s_{p_2} > 0$, so that the ti_{\pm} solitons always have a spectrum of velocities consisting of two bands separated by a gap of width $s_2 - s_{p_2}$ if $s_2 < 1$ and of width $|s_{p_2} - 1|$ if $s_2 > 1$. For $s_2 > 1$ the external sublattice is compressed in the soliton localisation region, but if $s_2 < 1$, the compression occurs in the lower velocity band and dilation in the upper band.

The width of the topological soliton is

$$L_{ti} = 2[x_{\zeta}(0)]^{-1} = \sqrt{2(1-s^2)(s^2-s_2^2)[g_0(s^2-s_{p_2}^2)]^{-1}}$$

and its energy is

$$E_{ti} = \int_{-\infty}^{+\infty} \left\{ \frac{2}{1-s^2} V[x_{\pm i}(\zeta)] - \frac{4(s^4 - 2s^2 + s_2^2)F_s^2[x_{\pm i}(\zeta)]}{\mu(s^2 - s_2^2)^2(1-s^2)} \right\} d\zeta$$
$$= \frac{4}{3} \sqrt{\frac{2g_0(1-s^2)}{(s^2 - s_{p_2}^2)(s^2 - s_2^2)^3}} \times \frac{(s^2 - s_2^2)^2 - (s_2^2 - s_{p_2}^2)(s^4 - 2s^2 + s_2^2)}{1-s^2} .$$

The dependences of E_{ti} and L_{ti} on s when $s_2 > 1$ are plotted in Fig. 13, whereas those for $s_2 < 1$ are given in Fig. 14. It should be noted that if $s \to \max(1, s_{p_2})$ when $s_2 > 1$ and if $s \to s_{p_2}$ when $s_2 < 1$, the soliton width goes to the limit $L_{ti} \to \infty$, so that for these values of the velocities the discrete system of equations (6) and (7) always has smooth soliton solutions. The soliton energy increases monotonically in the first band of the velocity spectrum and inside the second band the energy has a minimum at the velocity s = s'.

The stability of the topological solitons ti_{\pm} at velocities corresponding to the lower band of the spectrum has been demonstrated analytically [7, 25]. A numerical investigation of the stability has shown [7] that solitons are stable in the upper band of the spectrum if s > s' and unstable if s < s'. This allows us to conclude that the topological solitons ti_{\pm} are stable only at velocity values such that $dE_{ti}/ds > 0$.

If $g_1 > 0$ the bistability condition of Eqn (5) becomes

$$\chi_2 < \chi_{p_3} = \sqrt{\frac{1}{2}\kappa g_0} \left[1 - \frac{4(\xi_1^2 - 1)}{\xi_1} \right] ,$$

and the limiting values of the velocities are

$$s_{p_1} = s_{p_2} = s_2 \sqrt{1 - \frac{2\chi_2^2}{g_0 \kappa}} < s_{p_3} = s_2 \sqrt{1 - \frac{4\chi_2^2 \xi_1^2}{g_0 \kappa (3\xi_1^2 - 1)}} .$$

The soliton b_1 has a one-band velocity spectrum $\max(1, s_{p_3}) < s < s_2$ and the solitons b_2 and b_3 have a one-band spectrum $\min(1, s_{p_2}) < s < \min(1, s_{p_3})$. Therefore, the necessary condition for the existence of the soliton b_1 is the inequality $s_2 > 1$ and the necessary condition for the existence of the solitons b_2 and b_3 is the inequality $s_{p_2} < 1$.



Figure 13. Dependences of the energy E_{ti} and width L_{ti} (expressed in terms of the chain periods) of the topological soliton ti on the velocity s, calculated f or $g_0 = 0.1$, $g_1 = 0$, $\mu = 1$, $\kappa = 4$, $s_2 = 2$, $\chi_1 = 0$, and $\chi_2 = 0.33$ ($s_{p_2} = 1.34981$).



Figure 14. Dependences of the energy E_{ti} and width L_{ti} (in chain periods) of the topological siliton ti on the velocity s, calculated for $g_0 = 0.02$, $g_1 = 0$, $\mu = 1$, $\kappa = 0.25$, $s_2 = 0.5$, $\chi_1 = 0$, and $\chi_2 = 0.04$ ($s_{p_2} = 0.3$).

The dependences of the amplitudes A_x and A_y , of the width L_b , and the energy E_b , measured from the energy level of the **b** state, of the soliton b_1 on its velocity *s* are plotted in Fig. 15. The energy of the soliton b_1 is a monotonic function of *s* only for fairly high values of the asymmetry parameter g_1 . At low values of g_1 the function $E_b(s)$ has a local minimum. Near the limit $g_1 \rightarrow 0$ the width of the soliton b_1 increases monotonically and in the limit it decays into two topological solitons ti_{\pm} and ti_{-} (Fig. 16). The interval of the velocities of the soliton b_1 then goes over to the upper band of the velocity spectrum of the topological soliton. A numerical investigation of the dynamics of the soliton b_1 shows that it is stable only for such velocities *s* that $dE_b/ds > 0$.

The velocity spectrum of the soliton e_1 is found from the system of inequalities (27). For a chain with $d = \eta_2^2 - 1 + [2\chi_2F_s(\eta_2)/\kappa g_0] < 0$ the spectrum consists of two bands $0 \le s < \min(1, s_{p_8})$, $s_2 < s < 1$, if $s_2 < 1$ and of one band $0 \le s < \min(1, s_{p_8})$ if $s_2 > 1$, where

$$s_{p_8} = s_2 \sqrt{1 - \frac{2\chi_2^2}{\kappa g_0 [1 + (d/2\eta_2^2)]}}$$
.

A soliton can exist in a chain with d > 0 only if $s_2 > 1$, when the soliton has a one-band velocity spectrum $\max(1, s_{p_8}) < s < s_2$. The velocity spectrum of the solitons e_2 and e_3 is found from the system of inequalities (28). For d < 0 it consists of the interval $\max(1, s_{p_8}) \leq s < s_{p_2}$, whereas for d > 0 the interval is $s_{p_2} < s < \min(1, s_{p_8})$.



Figure 15. Dependences of the amplitudes A_x and A_y , width L_b (in chain periods), and energy *E* (measured from the conformational energy level **b**) of the soliton **b**₁ on the velocity *s*, calculated for $g_0 = 0.1$,

 $\mu = 1$, $\kappa = 4$, $\chi_1 = 0$, $\chi_2 = 0.33$, $g_1 = 0.05$ ($s_{p_3} = 1.389727$, curve 1), $g_1 = 0.005$ ($s_{p_3} = 1.354726$, curve 2), and $g_1 = 0.005$ ($s_{p_3} = 1.350318$, curve 3).



Figure 16. Transformation of the soliton b_1 into a pair of topological solitons i_+ and i_- , calculated for $g_1 \rightarrow 0$, $g_0 = 0.1$, $\mu = 1$, $\kappa = 4$, $\chi_1 = 0$, $\chi_2 = 0.33$, s = 1.6. The profile of the soliton b_1 is given for $g_1 = 0.05$, 0.005, 0.0005, 0.00005, and 0.0000005 (curves 1-5).

Numerical simulation of the dynamics of the e solitons has demonstrated their instability at all velocities.

4. Conclusions

A full classification is given above of localised nonlinear excitations that exist in a wide class of bistable energetically nondegenerate systems. One of the conclusions that follows from the analysis of the results obtained is the existence of a cooperative fundamental mechanism of structural transitions and of chemical reactions in bistable systems which are nondegenerate from the energy point of view. This mechanism is realised by topological solitons of a new type, which (in contrast to the conventional topological solitons) have a unique velocity of motion, convert a region behind a wavefront into an intermediate dynamic state; this is followed by relaxation to the final state quite far behind the front and in practice without any influence on the front dynamics. It is shown that such very (physically) different processes as structural transitions and chemical reactions in molecular crystals, transport of protons in hydrogenbonded lattices, and conformational transitions in DNA can all be described by various specific realisations of the general Hamiltonian of Eqn (1). Therefore, the conclusions drawn apply equally well to a wide class of bistable systems and make it possible to explain a number of 'anomalies' revealed by real experiments and computer simulations [27].

The above analysis of the models, based on linearisation of the equation associated with one of the components of the system (according to the current terminology this is called the 'external sublattice' deformation), is an important stage in the development of realistic models of the dynamics of complex molecular systems. At this stage it is possible to investigate analytically the soliton solutions of the equations of motion so as to identify the nature of elementary excitations in complex systems which are energy-nondegenerate. Therefore, a basis can then be provided as a starting point of a more detailed investigation of nonlinear dynamics, thermodynamics, and kinetics of specific systems.

One of the potential directions of further research is the construction of models of solid-phase reactions of the dissociative type (similar to the dissociation of solid explosives), which requires allowance for the anharmonicity of the intermolecular interactions and an analysis of the behaviour of soliton-like solutions when the energy minimum corresponding to the final stage is shifted to infinity.

The question of initiation of soliton excitations in real systems is particularly important. Local initiation of solitons seems to be the most likely process. However, preliminary investigations have shown that formation of a kink-antikink pair by thermal fluctuations is also possible. It follows from our results that in the case of exothermal reactions or structural transitions the relevant soliton solution is unstable and has a finite lifetime. This makes the problem of the influence of the anharmonicity of the intermolecular interaction on the dynamics of solitons particularly important.

We shall conclude by noting that soliton-type excitations, similar to those discussed in the present paper, may exist in many other physical systems.

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Appendices

A.1 Exothermal reactions in a diatomic molecular crystal. Detonation of solid explosives

For a long time the propagation of shock waves in chemically active media has been the subject of close attention both of physicists and of chemists working in various specialised fields. On the one hand, analytic and experimental methods based on the macroscopic approach to the propagation of a detonation wave are being developed extensively [17-20] and, on the other, the subject of molecular structure and of possible paths of the reactions of explosives [21-24] are being investigated actively. However, there still remain many unsolved problems. There have been several recent investigations which in truth can be regarded as the 'missing link' between the macroscopic approach to the phenomenon of propagation of high-temperature processes in a condensed medium, on the one hand, and molecular methods for active media, on the other. The methods of molecular-dynamic simula-



Figure 17. Qualitative representation of the intramolecular potential U(r) in the case of a structural transition (a) and dissociation of the chain molecules (b).

tion have been applied to the propagation of shock and detonation waves in gaseous and condensed media [13-15, 25-29]. In fact, the processes of physicochemical transformations, which occur in the region of the shock wavefront, require a time comparable with the intermolecular vibration time ($\leq 10^{-12}$ s) and are localised in ordered regions extending over just a few interatomic states ($\leq 10^{-9}$ m). Therefore, these processes represent an ideal object for the investigation by the molecular-dynamic method, both from the point of view of the temporal and spatial resolution. However, as pointed out in the Introduction, an analytically soluble model is essential to provide an unambiguous interpretation of numerical experiments.

We shall consider the quasi-one-dimensional model of a diatomic crystal proposed in Ref. [20]. We shall assume that a one-dimensional chain consists of alternating particles of two types: A and B. To be specific, we shall assume that $m_{\rm A} \leq m_{\rm B}$, where $m_{\rm A}$ and $m_{\rm B}$ are the masses of the molecules A and B. A molecular chain is formed as a result of consecutive attachment of diatomic AB molecules because of the intermolecular interactions. The qualitative form of the intramolecular potential U is shown in Fig. 17. The intermolecular interactions of atoms can be described by harmonic potentials, which is justified by the fact that in the shock wavefront the chain is compressed and the molecules interact only by repulsion. Compression makes the harmonic potential physically equivalent to that encountered in reality and characterised by a positive curvature in this range of values

Let us assume that the link in the initial state of a chain is l and that the equilibrium length of intramolecular bonds is r_0 . The Hamiltonian of the chain is

$$E = \sum_{n} \left[\frac{1}{2} m_{\rm A} \dot{z}_{\rm A_n}^2 + \frac{1}{2} m_{\rm B} \dot{z}_{\rm B_n}^2 + U(z_{\rm B_n} - z_{\rm A_n}) + \frac{1}{2} K_1 (z_{\rm A_n} - z_{\rm B_{n-1}} - l + r_0)^2 + \frac{1}{2} K_2 (z_{\rm B_{n+1}} - z_{\rm A_n} - l - r_0)^2 + \frac{1}{2} K_3 (z_{\rm B_{n+1}} - z_{\rm B_n} - l)^2 + \frac{1}{2} K_4 (z_{\rm A_{n+1}} - z_{\rm A_n} - l)^2 \right], \quad (41)$$

where z_{A_n} and z_{B_n} are the coordinates of the *n*th chain particles A_n and B_n ; U(z) is the potential of the intramolecular interaction, which has a minimum at $z = r_0$; K_1, K_2, K_3, K_4 are the rigidities of the intermolecular interactions; the dot implies differentiation with respect to the dimensionless time *t*. A schematic model of the lattice is shown in Fig. 18.



Figure 18. Schematic model of a diatomic molecular chain.

We shall now go over from absolute coordinates to relative displacements $u_{A_n} = z_{A_n} - nl + r_0 - u_1$, $u_{B_n} = z_{B_n} - nl$. Then Hamiltonian (41) becomes[†]

$$E = \sum_{n} \left[\frac{1}{2} m_{\rm A} \dot{u}_{\rm A_{n}}^{2} + \frac{1}{2} m_{\rm B} \dot{u}_{\rm B_{n}}^{2} + \varPhi(u_{\rm B_{n}} - u_{\rm A_{n}}) \right. \\ \left. + \frac{1}{2} K_{1} (u_{\rm A_{n}} - u_{\rm B_{n-1}} + u_{1})^{2} + \frac{1}{2} K_{2} (u_{\rm B_{n+1}} - u_{\rm A_{n}} - u_{1})^{2} \right. \\ \left. + \frac{1}{2} K_{3} (u_{\rm B_{n+1}} - u_{\rm B_{n}})^{2} + \frac{1}{2} K_{4} (u_{\rm A_{n+1}} - u_{\rm A_{n}})^{2} \right] , \qquad (42)$$

where the intramolecular potential is $\Phi(r) = U(r + r_0 - u_1)$.

In simulation of the structural modification of the chain it is convenient to use the potential $\varphi - 4$ (a quartic double-well potential) with a linear asymmetry

$$\Phi(u) = \varepsilon_0 [(uu_0^{-1})^2 - 1]^2 + \varepsilon_1 u u_0^{-1} + \varepsilon_2 , \qquad (43)$$

where the parameter $\varepsilon_0 > 0$ represents the height and $u_0 > 0$ the width of the energy barrier between two stable states of a molecule. The parameter $\varepsilon_1 > 0$ represents the difference between the energies of the ground states. If $\varepsilon_1 = 0$, then Eqn (43) is a double-well symmetric potential with minima $\pm u_0$ and a barrier ε_0 , whereas for $0 < \varepsilon_1 < 8\varepsilon_0/\sqrt{27}$ it is an asymmetric double-well potential with a minimum u_1 corresponding to the initial state of the chain. The parameter ε_2 (from which energies are measured) is selected on the basis of the condition $\boldsymbol{\Phi}(\boldsymbol{u}_1)=0,$ i.e. it assumed that is $\varepsilon_{2} = -\varepsilon_{0}[1 - (u_{1}u_{0}^{-1})^{2}]^{2} - \varepsilon_{1}u_{1}u_{0}^{-1}.$

Let us also introduce variables representing the motion of a molecule as a whole: a displacement of the centre of mass $R_n = (m_A u_{A_n} + m_B u_{B_n})/M$, where the total mass of the molecule is $M = m_A + m_B$ and the intramolecular displacement (reaction coordinate) is $r_n = u_{B_n} - u_{A_n}$. We then have

$$u_{A_n} = R_n - m_B r_n M^{-1}$$
, $u_{B_n} = R_n - m_A r_n M^{-1}$.

Using these expressions, we can transform Hamiltonian (42) with the aid of elementary procedures into

$$E = \sum_{n} \left\{ \frac{1}{2} M \dot{R}_{n}^{2} + \frac{1}{2} m \dot{r}_{n}^{2} + \Phi_{1}(r_{n}) + \frac{1}{2} k (r_{n+1} - r_{n})^{2} + \frac{1}{2} K (R_{n+1} - R_{n})^{2} + (r_{n} - u_{1}) \times [X_{+} (R_{n+1} - R_{n}) + X_{-} (R_{n} - R_{n-1})] \right\}, \quad (44)$$

[†]A different form of Hamiltonian (41) is used in Ref. [20] and the asymmetry of the potential $\Phi(u)$ is ensured by a term proportional to u^3 . However, we can easily show that these two formulations are equivalent. where $m = m_{\rm A}m_{\rm B}/M$ is the reduced mass of a molecule in a chain, $\Phi_1(r) = \Phi(r) + [(K_1 + K_2)(r - u_1)^2/2]$ is the reduced intramolecular potential, and $k = [K_3m_{\rm A}^2 + K_4m_{\rm B}^2 - m_{\rm A}m_{\rm B}(K_1 + K_2)]/M^2$, $K = K_1 + K_2 + K_3 + K_4$, $X_+ = [m_{\rm B}(K_2 + K_4) - m_{\rm A}(K_1 + K_3)]/M$, $X_- = [m_{\rm A}(K_2 + K_3) - m_{\rm B}(K_1 + K_4)]/M$.

Hamiltonian (44), which is a special case of the generalised Hamiltonian of Eqn (1), allows us to consider a diatomic chain as a system of two interacting sublattices: the intramolecular (internal) sublattice with relative displacements of the sites r_n , with the site mass m, and with the rigidity k, as well as the external sublattice, which describes the motion of molecules with the relative displacements of the sites R_n , with the site mass $M \ge m$, and the rigidity K. The parameters X_+ and X_- represent the sublattice interaction. In contrast to the traditionally investigated twomass lattices (see, for example, Ref. [21]), the parameter k governing the slope of the optical branch of the dispersion equation can be both less or more than zero.

In our model the topological *te* soliton corresponds to the motion of the reaction front, whereas the nontopological e solitons may form a front with a complex structure when the detonation is initiated by impact. Since the velocities of the nontopological solitons are higher than the velocity of the topological soliton, it is the former that form the visible edge of the front of a detonation wave. This mechanism can account for the results of computer experiments [17-19] and in particular we can see why steady-state motion of the front of a detonation wave appears only on introduction of a dissipative term in the equation of motion [17]. It can be shown that in the model of a solid explosive considered in Ref. [17] the longwavelength Hamiltonian does not contain the term $\rho_z F(x)$, which governs the existence of the topological solitons similar to the te solitons and responsible for the soliton mechanism of the propagation of a detonation front. On the other hand, the model of an elementary cell, which admits the existence of both *te* and *e* solitons, has been used [18, 19] and this leads to the existence of a steady-state front of a detonation wave. It follows from the results of computer simulations of the stability of the *te* solitons that even a weak nonlinearity of the potential increases considerably the lifetime of a reaction kink. The last comment should be made about the profile of the intramolecular potential. The propagation of a detonation wave has been simulated with the aid of a potential of the dissociative type (Fig. 17), for which a minimum corresponding to the reaction products is shifted to infinity. We have used a double-well potential in which the equilibrium states, corresponding to the reagents and reaction products, are separated by a finite distance. However, the effective potentials Q in Eqn (13) are qualitatively equivalent for these two cases, i.e. they have two minima separated by a finite distance [20]. It therefore follows that a change of the potential from the double-well to the dissipative form does not fundamentally alter the reaction propagation mechanism. An important feature of the investigated models is relaxation of the intermediate state to the final state of the products. Such a process cannot be described within the framework of the adopted analytic model, but it appears clearly in the computer simulation results. It follows that an analytic solution corresponds to the intermediate asymptote of the process and describes only the region of the front.

Biological macromolecules exhibit a strong polymorphism of their secondary structures. Relatively small barriers, which separate stable states, and the small differences between the free energy of possible structural forms means that the relative positions of the structure elements (conformation) of the cells macromolecules can vary within wide limits, which both ensures reliable storage of genetic information and easy transfer of this information. These polymorphic properties are manifested most strikingly by the DNA macromolecule [29]. Under physiological conditions DNA molecules are in the B conformation of a double helix, but in local regions they may go over to the A, C, D, Z, and other conformations [30]. It is assumed that it is the transitions to the metastable states that are responsible for the high reactivity of biological macromolecules [31, 32]. Studies of the dynamics of localised excitations (conformational solitons) should make it possible to interpret the experimental data on the longrange effects in biological systems and to gain a better understanding of the mechanisms of regulation of the biological activity of the cells. Some progress in this direction has been made in studies of the B-A transitions in DNA macromolecules [13-16].

In general, the model of a DNA-type macromolecule is a double chain of bistable components, which corresponds to the presence of two of the lowest-energy forms of the sugar ring of a nucleoside [16, 33]. The mobility of a monomer link in a chain can be described simply by considering a unit cell with four components, two of which correspond to nucleosides, whereas the other two correspond to the phosphate groups of the 'backbone' [16]. The positions of these components of the double helix of DNA determine the parameters of the model, which are calculated from the known x-ray structure data. The masses of the backbone units (m_0) are constant along the whole macromolecular chain, but the masses of the nucleosides (m_i) are different, because they include the masses of the nucleic bases. Here the index i = 1, 2 labels the macromolecular chains. The energy of a macromolecule, considered in the four-component approximation, is

$$E = \frac{1}{2} \sum_{n,i} \left\{ m_0 \dot{\mathbf{R}}_i^2(n) + m_i \dot{\mathbf{r}}_i^2(n) + U[\mathbf{r}_i(n), \mathbf{R}_i(n)] \right\} , \quad (45)$$

where the summation over *n* includes all the monomers in the chain; the position vectors \mathbf{R}_i and \mathbf{r}_i describe the displacements of the centres of mass of the backbone and nucleosides, respectively; *U* is the potential energy which depends on the coordinates of the conformational displacements. In the linear approximation the model of Eqn (45) makes it possible to describe qualitatively and quantitatively the vibrations of the structure elements of DNA and to interpret the lf (low frequency) Raman scattering spectra [34].

This model of the conformational mobility of DNA is fairly complex, but in studies of the dynamics of specific conformational transitions, such as $B \rightarrow A$, it can be reduced to the two-component form [16]. Allowance is then made for the fact that the conformational transition occurs simultaneously in both strands of the double chain of the macromolecule. The nuclear acid bases move simultaneously in coupled pairs without a significant change in the lengths of the hydrogen bonds. In the course of the $B \rightarrow A$ transition the shape of the sugar ring and of the nucleoside as a whole changes. The changes in the geometry of a monomeric link are accompanied by simultaneous twisting (torsion) and bending of the backbone of the macromolecule. Bearing these points in mind, we can now use the four-component model to describe simultaneous motion of the structure elements in the double-chain links. It is shown in Ref. [16] that the dynamics of a conformational transition can be described in terms of displacements of the centres of mass of monomeric links $[\mathbf{R} = (m_p \mathbf{r}_p + 2m_0 \mathbf{r}_q)/M]$ and of displacements of the pairs of nucleosides relative to the core $(\mathbf{r} = \mathbf{r}_p - \mathbf{r}_q)$. Such a description is possible because of neglect of the relative displacements of nucleosides in pairs, which is typical of the $A \rightarrow B$ transitions. It is important to stress that the difference between the masses of the nucleic acid bases has no influence on the macromolecular dynamics.

In the derivation of an explicit Hamiltonian it is convenient to adopt variables which describe torsion of a monomeric link (φ) and a shift of a pair of bases along the dyad axis (r) (Fig. 19). As is known [29, 30], these components are mutually linked and are used traditionally in calculations of the energy of the double helix. Flexural deformation of a chain varies symbatically with the torsional deformation and allowance for it does not give qualitatively new results [35]. The Hamiltonian can therefore be retained in the form

 $E = E_1 + E_2 + E_3$,

where the torsional energy of the chain is

$$E_1 = \sum_{n} \frac{1}{2} I \dot{\varphi}_n^2 + \frac{1}{2} K (\varphi_{n+1} - \varphi_n)^2 ,$$

the energy of the intramonomer conformational modification is

$$E_2 = \sum_n \frac{1}{2}m\dot{r_n}^2 + \frac{1}{2}k(r_{n+1} - r_n)^2 + \Phi(r_n) ,$$



Figure 19. Two-component model of the conformational mobility of the double-helix DNA molecule.

and the energy of the interaction of the torsional deformation and of the intramonomer conformational coordinate is

$$E_3 = \sum_n G(r_n)(\varphi_{n+1} - \varphi_{n-1})$$
.

Here, *I* and *m* are, respectively, the moment of inertia and the reduced mass of monomeric link of the chain; *K* and *k* are the force constants of the interaction between neighbouring monomers; $\Phi(r)$ is a double-well potential function of a structural transition between stable states of a monomer. In view of the energy inequivalence of stable states of the system, the function $\Phi(r)$ may be asymmetric. It can be described conveniently by means of Eqn (43) and the function *G* representing the sublattice interaction can be taken as $G(r) = X(u_1^2 - r^2)/u_0^2$. The parameter *X* is responsible for the change in the height of the effective barrier of the intramonomer potential in the course of twisting of the DNA macromolecule.

An analysis of this model demonstrates that a chain has two stable homogeneous states: the ground state $\{r_n = u_1 < 0, \rho_n = 0\}_{n=-\infty}^{+\infty}$, which corresponds to the B state of the DNA molecule, and a state higher on the energy scale $\{r_n = u_2 > 0, \rho_n = \rho(u_2) < 0\}_{n=-\infty}^{+\infty}$, corresponding to the metastable A conformation, where $\rho_n = \varphi_{n+1} - \varphi_n$ is the relative displacement of the *n*th monomer of the chain. The inequivalence of these states corresponds to the inequivalence of the B and A conformations under physiological conditions.

Such quantitative estimates show that there may be an effective long-range mechanism mediated by the motion of the nontopological b_1 solitons [13–15]. The proposed soliton mechanism should make it possible to provide a self-consistent interpretation of the experimental results [36–38].

A.3 Topochemical polymerisation of diacetylenes

The solid-phase polymerisation of diacetylene is a true topochemical reaction, which occurs in an undeformed crystal in the absence of lattice defects. It begins at the points distributed at random throughout the volume of a crystal and occurs homogeneously inside a monomer crystal [39-42]. Growing polymer macromolecules form a solid solution of these molecules in a monomer crystal. This preserves the continuity of the original crystal. It follows that the solid-phase polymerisation of diacetylene represents effectively a special phase transition between a solid monomer and a solid polymer, as a result of which a perfect monomer single crystal is transformed into a perfect polymer single crystal without participation of a liquid-like intermediate state in this transition.

A monomeric link of diacetylene and the configuration of the resultant polymer molecule are shown in Fig. 20, where the symbols R and R' denote radicals that are side substituents. The polymerisation reaction represents the 1,4-trans-addition process, which occurs because of specific rotations of the monomer molecules relative to their centres of masses, accompanied by the approach of these macromolecules by 0.04-0.1 of the lattice constant of the monomer crystal. The result of this stereospecific polymerisation is a stereoregular polymer with a small number of defects. In some cases the length of the chain formed in this way is comparable with the size of a single crystal.



Figure 20. Topochemical polymerisation of diacetylene. The initial monomer (a) and final polymer (b) crystals are shown.

The schematic diagram in Fig. 20 makes it possible to understand readily the processes that occur in topochemical polymerisation of diacetylene. The molecules in a monomer crystal are distributed in piles around one of the crystallographic directions in such a way that the last carbon atom of one of the molecules approaches to a distance $r \sim 4$ Å the first carbon atom of the adjacent molecule. Polymerisation involves successive rotation of each molecule, which alters the angle of slope of the monomer units toward the pile axis. In ideal cases such a change in the angle of slope occurs even without displacement of the centres of mass of the individual molecules. If this condition is satisfied or nearly satisfied, we have the 'principle of small displacements' in topochemical reactions, which has been formulated earlier [43]. Moreover, the type of the spatial packing of the side substituents R, as well as the specific volume and the space symmetry of the crystal lattice do not change in the course of polymerisation. The majority of polydiacetylenes have approximately the same lengths of the repeated macromolecular link (~ 4.91 Å) and also of the same lengths and angles of the bonds between the carbon atoms, which form the backbone of the chain [44].

The results of experimental investigations support qualitatively the geometric model shown in Fig. 20. In some cases the same diacetylene monomer can be obtained in different crystalline modifications, which are very different in respect of their reactivity. Consequently, in the solid phase the reactivity of diacetylenes is controlled by the geometric packing of the monomer and not by the chemical nature of the side substituents R and R' [39]. On the other hand, knowledge of just these packing parameters is sometimes insufficient to judge reliably the reactivity of one particular diacetylene. It is known that there are several monomers of this compound and they have practically identical crystallographic packings, but they differ very greatly in respect of their reactivities.

In the approximation of a quasi-one-dimensional isolated chain the process of solid-phase topochemical polymerisation of diacetylene can be described by the 'molecular mechanical' model. In this model the monomer molecules are replaced by absolutely rigid 'dumbbells' each of mass M and with a moment of inertia I. The exothermal potential $U(\varphi)$ determines the dependence of the energy of a monomer link on the angle of its tilt relative to the crystallographic axis. This angle plays the role of the reaction coordinate. Displacements of the centres of masses of monomer links and the geometric deformation of the unit cell are controlled by harmonic bonds of rigidities K_1, K_2, K_3 , and K_4 : bonds with the rigidities K_3 and K_4 should connect identical ends of the dumbbells (in the case of different side substituents, R and R' and the

rigidities are different); the bonds with rigidities K_1 and K_2 connect the opposite ends, i.e. they are diagonal. The potential $U(\varphi)$ for $-\pi \leq \varphi \leq \pi$ has only one minimum at the point $0 < \varphi_m < \psi_0$, where $\psi_0 < \pi$ is the equilibrium value of the angle of tilt of the monomer relative to the crystallographic axis of a monomer crystal.

The deformation energy of the model lattice is

$$E_d = \sum_n \left[\frac{1}{2} K_1 (L_n - L_0)^2 + \frac{1}{2} K_2 (S_n - S_0)^2 + \frac{1}{2} K_3 (l_n^u - l_0)^2 + \frac{1}{2} K_4 (l_n^d - l_0)^2 + U(\varphi_n) \right] ,$$

where L_n, S_n, l_n^u, l_n^d are the actual lengths of the bonds; L_0, S_0 , and l_0 are their equilibrium lengths in a monomer crystal. The length l_0 is the lattice constant of a monomer crystal, and $L_0 = (l_0^2 + a^2 + 2al_0 \cos \psi_0)^{1/2}$ and $S_0 = (l_0^2 + a^2 - 2al_0 \cos \psi_0)^{1/2}$ are the lengths of the diagonal bonds (*a* is the length of the monomer molecule).

If we bear in mind the deformation of the intermonomer links during polarisation of diacetylene, we can write the Hamiltonian of the system in terms of variables representing the displacements of the centres of mass of a monomer unit R and of the slope angles φ :

$$\begin{split} E &= \sum_{n} \left(\frac{1}{2} M \dot{R}_{n}^{2} + \frac{1}{2} I \dot{\varphi}_{n}^{2} \right) + E_{d} \\ &= \sum_{n} \left\{ \frac{1}{2} M \dot{R}_{n}^{2} + \frac{1}{2} I \dot{\varphi}_{n}^{2} + \frac{1}{2} K (R_{n+1} - R_{n})^{2} \right. \\ &+ \frac{1}{2} k (\varphi_{n+1} - \varphi_{n})^{2} + (\varphi_{n} - \psi_{0}) [X_{+} (R_{n+1} - R_{n}) \\ &+ X_{-} (R_{n} - R_{n-1})] + U_{1} (\varphi_{n}) \right\} , \end{split}$$

where

$$\begin{split} &K = (l_0 + a\cos\psi_0)^2 (K_1L_0^{-2} + K_2S_0^{-2}) + K_3 + K_4 , \\ &k = \frac{a}{4}(K_3 + K_4) - al_0\sin\psi_0 (K_1L_0^{-2} + K_2S_0^{-2}) , \\ &\lambda = 2al_0\sin\psi_0 (K_1L_0^{-2} + K_2S_0^{-2}) , \\ &\lambda_+ = \frac{a}{2}(K_3 - K_4) - al_0\sin\psi_0 (K_1L_0^{-2} + K_2S_0^{-2}) , \\ &X_- = \frac{a}{2}(K_4 - K_3) - al_0\sin\psi_0 (K_1L_0^{-2} + K_2S_0^{-2}) . \end{split}$$

The effective potential $U_1(\varphi) = U(\varphi) + \lambda(\varphi - \psi_0)^2$ can in general now have two minima: one at $\psi_1 \approx \varphi_m$, and the other at $\psi_2 \approx \psi_0$. The absolute minimum ψ_1 corresponds to

the polymer state of the chain and the higher value of ψ_2 corresponds to its monomer state.

In this model the motion of the topological te soliton corresponds to an elementary event in the growth of a polymer chain and the finite range of a soliton may reduce considerably the observed activation energy. The deceleration of solitons and the formation of a monomer – polymer interface corresponds to chain breaking and formation of a defect in a single crystal. On the other hand, the influence of external stresses and of the process of relaxation of a crystal from the monomer phase to the polymer can influence significantly the lifetime of the te soliton, which alters the molecular-mass distribution as the degree of conversion to the polymer increases.

A.4 Model of the proton mobility in a strongly polarised chain of hydrogen bonds

Proton transport in molecular systems with hydrogenbonded chains is one of the important topics in biophysics. For example, transmembrane proton transport is an intermediate mechanism in energy conversion in biosystems [45]. According to the well-known hypothesis of Mitchell, the intermediate stage in realisation of the energy from the oxidation of food products in mitochondria is the energisation of their coupled membranes, which is achieved by increasing the proton concentration on the outer surfaces by proton 'pumps'.

The molecular mechanism of transmembrane proton transport was first discussed by Onsager [46, 47] who postulated that proton channels are formed from continuous chains of polar groups of amino acid residues of transmembrane protein molecules. This hypothesis has been developed further [48–50] and confirmed by studies of the structure of the proton channels in the bacteriorhodopsin molecule, which is a light-controlled proton pump. For example, according to Ovchinnikov et al. [51], the proton path in the bacteriorhodopsin molecule passes along amino acid residues containing a hydroxyl group.

It is currently assumed that the transport of protons across a membrane via protein proton channels occurs along hydrogen-bond chains $O-H\cdots O-H\cdots O H\cdots O-H\cdots$, which are formed by amino acid residues containing O-H groups (serine, threonine, tyrosine). Tyrosine residues, which occur in seven transmembrane alphahelical segments of the molecule, for a chain of hydrogen bonds in the bacteriorhodopsin molecule [52– 53] (Fig. 21).

A chain of hydrogen bonds may also be in a different state: $H - O \cdots H - O \cdots H - O \cdots H - O \cdots$. In the absence of an external field the two states of the chain are equivalent. A high proton gradient at the 'energy membrane' of a cell gives rise to a transmembrane electric field of intensity $\mathcal{E} \sim 10^7 \, \mathrm{V \, m^{-1}}$, which polarises the hydrogen-bond chain forming a proton channel. The two ground states of the chains are then no longer energy-equivalent. Therefore, the transmembrane chains of hydrogen bonds in biosystems are bistable and have energy-nondegenerate ground states.

In the absence of an external electric field directed along a chain, a proton (H) in each $O-H\cdots O$ hydrogen bond has two energy-equivalent stable equilibrium positions, separated by a barrier of a symmetric-well potential. This potential can be derived as a sum of two single-well oxygen-proton potentials.



Figure 21. Structure of the proton-conducting path of the molecule of bacteriorhodopsin [53].

The interaction of a proton with an atom of oxygen can be described conveniently by the Morse potential

$$U(r) = D_0 \{ \exp[-b(r - r_0)] - 1 \}^2 ,$$

where D_0 and r_0 are the energy and length of the O-H valence bond in an isolated hydroxyl group; b is the phenomenological parameter of the potential, which can be determined from the frequency of the longitudinal vibration of the valence bond; r is the actual length of the valence bond. It is assumed that the proton is always located on the hydrogen-bond line. Then its double-well symmetric potential can be defined as the sum of two Morse potentials [54-56]

$$V(u,\rho) = U\left(\frac{l+\rho}{2}+u\right) + U\left(\frac{l+\rho}{2}-u\right)$$
$$-U\left(\frac{l}{2}+u_0\right) - U\left(\frac{l}{2}-u_0\right)$$
$$= \varepsilon_0(\alpha-1)^{-2}\left\{\left[\alpha-\cosh(bu)\exp\left(-\frac{1}{2}b\rho\right)\right]^2$$
$$+\frac{1}{2}[1-\exp(-b\rho)]\right\}, \qquad (46)$$

where l is the lattice period (step), ρ is the relative elongation of the hydrogen bond, and u is the coordinate of the proton measured from the midpoint of the line joining the neighbouring oxygen atoms. At an equilibrium position of the chain the potential of Eqn (46) has two minima $u = \pm u_0$, where u_0 is found from $\alpha = \cosh(bu_0) = \frac{1}{2}\exp\{b[(l/2) - r_0]\}$, separated by a barrier of height $\varepsilon_0 = D_0(1 - \alpha^{-1})^2$. If $\rho \neq 0$, the minima of the potential $\pm u(\rho)$ are found from the equation $\cosh(bu) = \alpha \exp(b\rho/2)$, and the barrier height is $\varepsilon(\rho) = D_0[1 - \alpha^{-1}\exp(-b\rho/2)]^2$. The potential (46) is of the double-well type only if $\rho > \rho_0 = -2b^{-1}\ln \alpha$. If the bond is strongly compressed, so that $\rho \leq \rho_0$, it becomes a symmetric single-well potential.

The energy of a hydrogen bond in which the proton is in one of its two ground states can be described by the harmonic potential $V_{OO}(\rho) = \frac{1}{2}K\rho^2$, where K is the rigidity constant of the hydrogen bond. In this case the last term of the potential described by Eqn (46) should be replaced with the potential $V_{OO}(\rho)$ in such a way that the total energy of the O-H...O bond is $W(u, \rho) = V_{OH}(u, \rho) + V_{OO}(\rho)$, where

$$V_{\rm OH}(u,\rho) = D_0 \left[1 - \alpha^{-1} \cosh(bu) \exp\left(-\frac{1}{2}b\rho\right) \right]^2 . \quad (47)$$

Let us now assume that the chain is in an external static electric field of intensity \mathcal{E} . Then the total energy of the chain can be represented by the expression

$$E = \sum_{n} \frac{1}{2} m \dot{r}_{n}^{2} + \frac{1}{2} M \dot{R}_{n}^{2} + \frac{1}{2} k (r_{n+1} - r_{n})^{2} + \frac{1}{2} K (R_{n+1} - R_{n})^{2} + V_{\text{OH}} (u_{n}, \rho_{n}) + e \mathcal{E} u_{n} , \qquad (48)$$

where R_n is the displacement of the *n*th oxygen atom of mass M from its equilibrium position and r_n is the displacement of the *n*th proton of mass m, measured from the midpoint of the *n*th step in the chain which is in an equilibrium position, k is the strength of the proton – proton interaction, e is the proton charge, and the variables are

$$u_n = r_n - \frac{1}{2}(R_n + R_{n+1}), \quad \rho_n = R_{n+1} - R_n.$$

In an analytic investigation it is desirable to replace the double-well potential of Eqn (47) in the Hamiltonian (48) by a simpler expression

$$\Phi(r_n) + [G_1(r_n) + G_2(r_n)](R_{n+1} - R_n) ,$$

which differs little from Eqn (48) if ρ_n is small and where the potential $\Phi(r)$ is given by Eqn (43) and the functions $G_i(r_n)$ are defined as follows:

$$G_1(r) = X_1(r-u_1)u_0^{-1}, \quad G_2(r) = X_2(u_1^2 - r^2)u_0^{-2}$$

Here, one parameter is $\varepsilon_1 = e\mathcal{E}u_0 > 0$, $X_1 = e\mathcal{E} du(\rho) d\rho|_{\rho=0}$ represents the change in the asymmetry of the potential when the bond is deformed, and $X_2 = d\varepsilon(\rho)/d\rho|_{\rho=0}$ is the change in the barrier height. We shall select the reference point ε_2 for the proton energy in such a way that in the ground state $r = u_1 < 0$ the energy is $\Phi(u_1) = 0$. Then the Hamiltonian of the system can be represented by the sum $E = E_1 + E_2 + E_3$, where

$$E_{1} = \sum_{n} \left[\frac{1}{2} M \dot{R}_{n}^{2} + \frac{1}{2} K (R_{n+1} - R_{n})^{2} \right]$$

is the energy of the oxygen sublattice,

$$E_{2} = \sum_{n} \left[\frac{1}{2} m \dot{r}_{n}^{2} + \frac{1}{2} k (r_{n+1} - r_{n})^{2} + \boldsymbol{\Phi}(r_{n}) \right]$$

is the energy of the proton sublattice, and

$$E_3 = \sum_{n} [G_1(r_n) + G_2(r_n)](R_{n+1} - R_n)$$

is the energy of the interaction of the oxygen and proton sublattices. The Hamiltonian E represents a natural generalisation of the two-component function first used to describe proton transport in a chain of hydrogen bonds [7, 24, 57].

In the proton transport model the motion of the *te* soliton corresponds to an elementary event as a result of which all the protons are transferred, in some part of the chain, from the 'left' oxygen atom to its 'right' neighbour. The resultant proton current represents a series of consecutive runs of topological solitons.

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