New elementary mechanism of structural transition in bistable non-degenerate systems

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Abstract. A topological soliton of a new type which may exist in bistable energetically non-degenerate systems (BENDSs) is revealed. Such a soliton realizes the transition from the initial equilibrium state to the intermediate dynamic state, the latter relaxing to the final equilibrium state in the post-frontal region. Results of computer simulations lead to the conclusion that all the characteristics of the process just beyond the front are well described by the analytical solution for an infinite lattice. On the basis of analytical and numerical studies the cooperative mechanism of structural transitions in BENDSs is proposed.

1. Introduction

The ordered systems (molecular and polymer crystals, and macromolecules), which have at least two stable equilibrium states with different energies (absolutely stable and metastable states) can exhibit under certain conditions structural transitions or chemical reactions. Such objects will be referred to below as bistable energetically non-degenerate systems (BENDSs). The conventional approach to the description of the dynamic mechanism of structural transitions and chemical reactions in BENDSs deals with local elementary events, each consisting in overcoming an energy barrier. However, there are experimental and computer simulation data which point to abnormal (from the common viewpoint) behaviour of a number of BENDSs [1].

The main goal of this article is to show that the structural transitions in BENDSs may be realized at an atomic level not only by localized processes but also in a cooperative *manner through the motion of localized non-linear excitations. It is necessary to note* that this alternative mechanism of molecular mobility in BENDSs cannot be considered in terms of the usual topological solitons. The reason is that the latter correspond to the transition between two equilibrium states of the same energy and therefore they may appear in a particular class of bistable energetically degenerate systems (BEDSs) only [2, 3]. Our approach to structural transitions in BENDSs is based on revealing topological solitons of a new type, which realize at an atomic level a transition from the initial equilibrium state to an intermediate dynamic state. This relaxes then to the final state, but the front propagation is described adequately by the soliton motion. In contrast with topological solitons in BEDSs with a continual velocity spectrum, topological solitons in BENDSs have the only possible value of velocity.

Despite the fact that the existence of the usual topological solitons in BENDSs is forbidden, nevertheless the computer simulation data relating to the particular cases of detonation in models of crystalline explosives [4–6] and of proton transfer in complex

lattices in the presence of an external field [7] indicate the propagation of a stationary wave with a soliton-like structure of the front region†.

Explanations of such an unexpected behaviour proposed to date imply the presence of dissipative effects [4] or (in the Hamiltonian case, when dissipation is absent) of energy outflow from leading degrees of freedom through a radiation mechanism [5, 6]. In both cases, however, we do not deal with elementary solitonic excitations. Existing numerical data do not allow one to make unambiguous conclusions about the nature of solitonic excitations in BENDSs. Therefore, there is a need in the analytical treatment of the problem with the help of simplified models, for further computer simulation on the basis of both simple and complicated models as well as experimental study. In this connection the following fundamental questions arise.

(i) Does an elementary excitation exist whose motion corresponds to reaction propagation in Hamiltonian BENDSs at the atomic level?

(ii) What are the conditions of its existence, stability and initiation?

(iii) What is the relationship between the microscopic and macroscopic levels in the different processes where such excitations are manifested?

A basis for answering these questions was given in our previous article [8] where the simplest model of an infinite diatomic molecular crystal with two equilibrium states, whose energies are different, has been constructed. The main result of [8] is analytical, revealing in Hamiltonian BENDSs a topological soliton of a new type which realizes at the atomic level a transition from an initial metastable state to a certain intermediate dynamic state.

2. The analytically solved model

Let us consider the model of a diatomic molecular crystal suggested in [8] (figure 1). Such a model, as mentioned above, may be an adequate approximation for the problems of structural (in particular conformational) transitions or topochemical reactions in solids. The Hamiltonian function of this system may be written in the form

$$H = \sum_j \left(\frac{M}{2} \dot{u}_j^2 + \frac{m}{2} \dot{w}_j^2 + U(w_j - u_j) + \frac{a}{2}(u_{j+1} - w_j)^2 \right.$$
$$\left. + \frac{K}{2}(u_{j+1} - u_j)^2 + \frac{k}{2}(w_{j+1} - w_j)^2 \right) \tag{1}$$

where M and m are the masses of 'large' and 'small' particles, u_j and w_j are their displacements from the equilibrium position in crystal lattice, and a, K and k are the rigidities of intermolecular bonds. The intramolecular potential has two energetically unequal minima (figure 2). Intermolecular interactions are harmonic. The points over the symbols denote the time derivatives. One possible realization of the intramolecular potential U which is convenient to describe the structural transition is represented in appendix 1.

It is more convenient to write the corresponding equations of motion in terms of intramolecular coordinates $\varphi_j = w_j - u_j$ and displacements $\chi_j = (Mu_j + mw_j)/(M + m)$ of the centre of molecular masses:

$$\ddot{\chi}_j - V_0^2(\chi_{j+1} - 2\chi_j + \chi_{j-1}) + \alpha(\varphi_{j+1} - \varphi_{j-1})/2M_t - \beta(\varphi_{j+1} - 2\varphi_j + \varphi_{j-1})/M_t = 0$$

$$\ddot{\varphi}_j + \omega^2\varphi_j + \nu V_1^2(\varphi_{j+1} - 2\varphi_j + \varphi_{j-1}) + U'(\varphi_j)/\mu - \alpha(\chi_{j+1} - \chi_{j-1})/2\mu \tag{2}$$

$$- \beta(\chi_{j+1} - 2\chi_j + \chi_{j-1})/\mu = 0$$

† In the case of detonation the absolutely stable energy minimum may be considered as shifted to infinity.
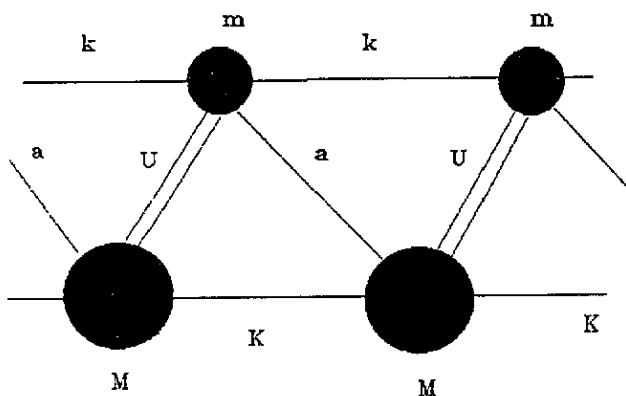
Figure 1. Simple quasi-one-dimensional model for a diatomic molecular crystal. The large atoms (of mass M) and small atoms (m) atoms are coupled by both intermolecular bonds (single lines) with rigidities a, K and k and intramolecular bands (double lines) described by a non-linear potential U such as in figure 2.
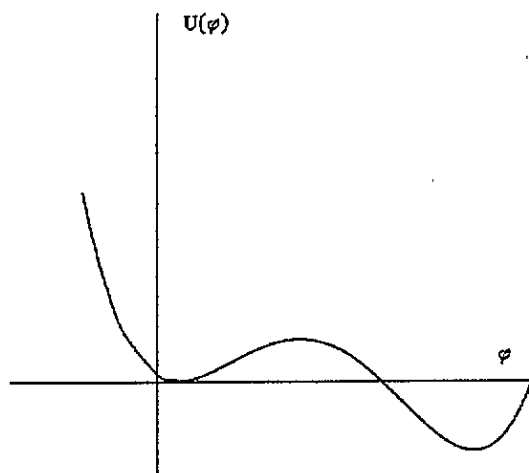

Figure 2. Double-well intramolecular potential U; the higher sate at $\varphi = 0$ corresponds to the reagents and the lower state to the products of reaction.

where the constants V_0, V_1, α, β and ω are defined by the intermolecular rigidities a, K and k (see appendix 1), $U'(\varphi) = dU/d\varphi$, $M_t = M + m$, $\mu = Mm/m_t$ and $\nu = \pm 1$.

In the continual approximation, which is justified if the front width is at least several lattice constants, the dynamics of molecular crystals is described by a coupled system of two partial equations:

$$\chi_{\tau\tau} - V_0^2 \chi_{xx} - h\chi_{xxxx} + \frac{\alpha}{M_t}\varphi_x - \frac{\beta}{M_t}\varphi_{xx} + \frac{\gamma}{M_t}\varphi_{xxx} = 0$$

$$\varphi_{\tau\tau} + \nu V_1^2 \varphi_{xx} + \omega^2\varphi + \frac{U'(\varphi)}{\mu} - \frac{\alpha}{\mu}\chi_x - \frac{\beta}{\mu}\chi_{xx} - \frac{\gamma}{\mu}\chi_{xxx} = 0.$$

(3)

Here the subscripts denote the partial derivatives with respect to the time (τ) or space (x) coordinates†.

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† It is easy to show that equations (3) written in such a form corresponds to the first terms of respective Hamiltonian decomposition of the general diatomic system with arbitrary interatomic interactions.

Introduction of the kinematic variable $\zeta = x - V\tau$ (V is the velocity of the travelling wave) allows us to solve asymptotically the first of equations (3) with respect to a 'lattice deformation' χ_ζ:

$$\chi_\zeta = -\frac{1}{M_t(V^2 - V_0^2)}\left[\alpha\varphi - \beta\varphi_\zeta + \left(\gamma + \frac{\alpha h}{V^2 - V_0^2}\right)\varphi_{\zeta\zeta}\right]. \tag{4}$$

Excluding the lattice deformation χ_ζ from the second of equations (3), one may reduce the system (3) to the equation of the 'non-linear oscillator':

$$p(V)\varphi_{\zeta\zeta} + \Phi'(\varphi; V) = 0 \tag{5}$$

where the effective potential $\Phi(\varphi; V)$ includes the wave velocity V as a parameter:

$$\Phi(\varphi; V) = \left[\omega^2 + \frac{\alpha^2}{\mu M_t(V^2 - V_0^2)}\right]\frac{\varphi^2}{2} + \frac{U(\varphi)}{\mu}. \tag{6}$$

The factor $p(V)$ is given by

$$p(V) = V^2 + \nu V_1^2 - \frac{\beta^2 - \alpha[\gamma + h/(V^2 - V_0^2)]}{M_t\mu(V^2 - V_0^2)}. \tag{7}$$

This equation is valid when looking for a stationary elementary excitation which propagates with velocity V in the infinite lattice. A specific form of solution is defined both by the profile of the potential function Φ and by the sign of the factor $p(V)$. This statement becomes evident on looking at the phase portrait in equation (5), most specific cases of which are shown in figure 3 for different wave velocities V, while the relative depth of potential wells is changed with the sign of $p(V)$. If the latter is positive, we have only periodic solutions, located near the bottom of the right- or left-hand well (figure 3(a)). On the other hand, if the condition $p(V) < 0$ holds, the solution describing the transition from one well to the vicinity of the other is possible, as shown in figures 3(b) and 3(c). Figure 3(c) partly relates to the stationary wave describing a transition from one to other stationary point, which corresponds to initial ($\varphi = 0$) and certain asymptotic ($\varphi = \varphi_k$) states.

Let us analyse the conditions when such a solution is possible. The presence of a velocity-dependent term in the effective potential Φ means that the relative depths of the left- and right-hand wells are changed with variation in V. Most specific profiles of potential function are shown in figure 4. It is fundamental that a certain velocity V_k exists such that the potential minima have equal values (figure 4(c)). If φ_k denotes the reactional coordinate at $\zeta \to -\infty$, one can write the following equation:

$$\Phi(0; V_k) = \Phi(\varphi_k; V_k). \tag{8}$$

It is necessary to note that the coordinate φ_k is not equal to the coordinate of the absolute minimum potential energy of the original system, despite the fact that the relative distance may be small (appendix 2).

The second equation defining the condition of localized solution existence follows from the requirement of stationarity of the asymptotic state†:

$$(d/d\varphi)\Phi(\varphi_k; V_k) = 0. \tag{9}$$

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† For a potential function of the general type, equation (8) may be added to the equation defining the stationarity of the initial point too:

$$(d/d\varphi)\Phi(\varphi_{in}; V_k) = 0.$$

However, this requirement is trivial for the potential U represented in figure 2.
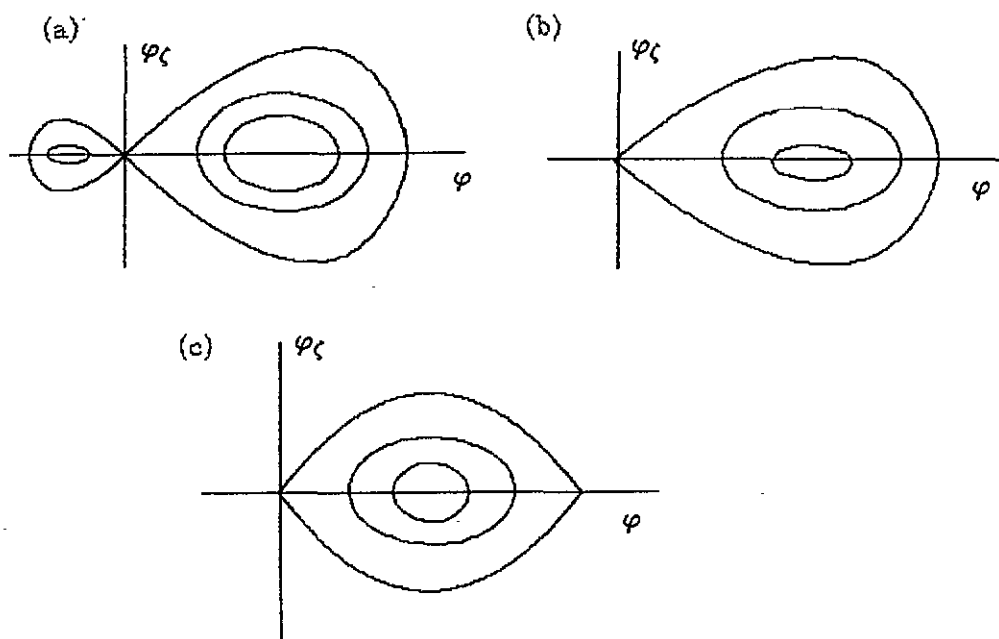
Figure 3. The phase portrait of an effective non-linear oscillator: (a) if the velocity of the travelling wave is not in the region where $p(V)$ is negative, then the solution of equation (5) is a periodic function; (b) if the supersonic velocity of the wave is not equal to the velocity of the topological soliton, the closed separatrix is associated with a non-topological soliton with homogeneous boundary conditions; (c) at the velocity of the travelling wave which is equal to the velocity of the topological soliton, the separatrix corresponds to the topological soliton solution, which describes the conversion of reagents to intermediate products of reaction.
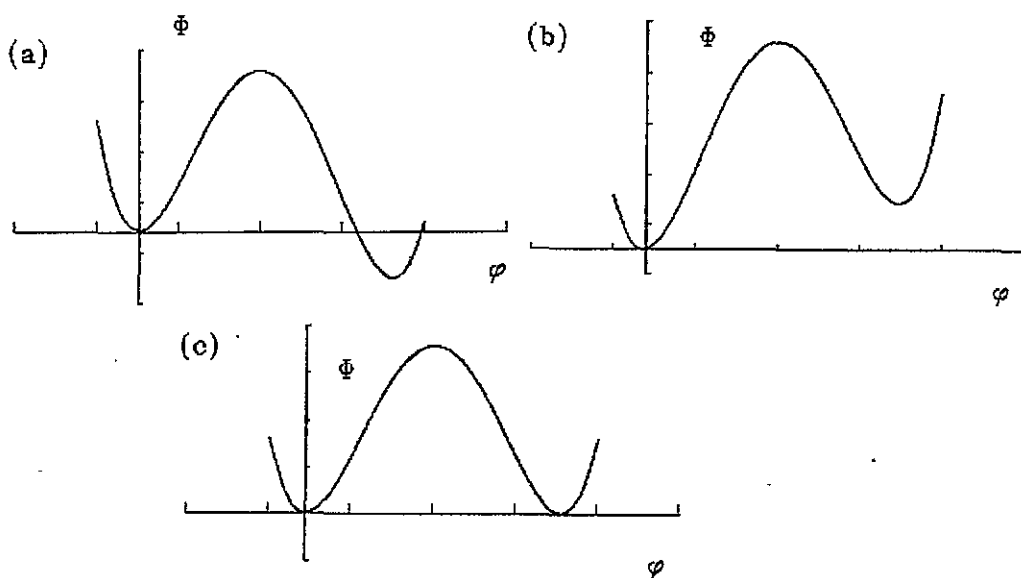

Figure 4. The effective potential $\Phi(\varphi; V)$ for different velocities of the travelling wave.
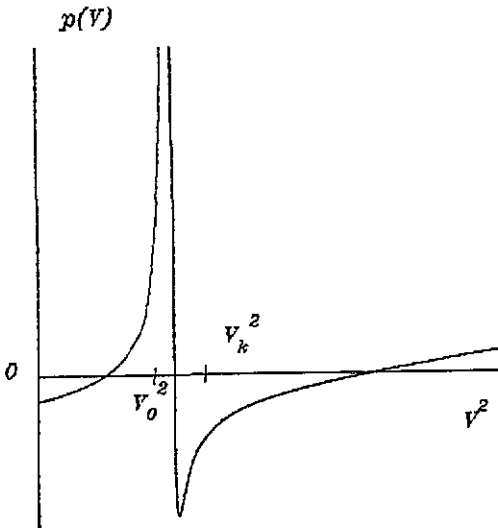
Figure 5. The factor p versus the wave velocity V.

The solutions of equations (8) and (9) allow us to define the topological kink velocity V_k and the reaction coordinate φ_k in the intermediate state. The corresponding lattice deformation χ_ζ is defined by equation (4).

By analysing the factor p in equation (7) we can see that it may have a positive or negative dependence on the wave velocity V. One of the specific dependences of p on V is represented in figure 5. In this case, p is negative both in the subsonic and in the supersonic region. If V_k is the solution of equations (8) and (9) and $p(V_k)$ is negative, the solutions of equation (5) are defined by the trajectories shown in figure 3(c). The solution which satisfies the homogeneous boundary conditions at $\zeta \to +\infty$ (i.e. $\varphi = 0$, $\chi_\zeta = 0$) is partly represented by the separatrix travelling through points $\varphi = 0$, $\varphi_\zeta = 0$ and $\varphi = \varphi_k$, $\varphi_\zeta = 0$. When this is the case, the non-linear localized wave, namely the topological soliton, will be the solution of equation (3):

$$\varphi = \varphi_k[1 - \tanh(\zeta/\delta)]/2$$

$$\chi_\zeta = -\frac{\varphi_k}{2M_t(V^2 - V_0^2)} \left\{ \alpha\left[1 - \tanh\left(\frac{\zeta}{\delta}\right)\right] - \frac{\beta}{\delta}\mathrm{sech}^2\left(\frac{\zeta}{\delta}\right) \right. \tag{10}$$

$$\left. - \left(\gamma + \frac{\alpha h}{M_t(V^2 - V_0^2)}\right)\frac{\mathrm{sech}^2(\zeta/\delta)\tanh(\zeta/\delta)}{2\delta^2} \right\}$$

where δ is the half-width of the frontal region.

What are the main peculiarities of the solution obtained, which causes it to differ from the topological soliton in a BEDS?

The principal difference is that the soliton solution (10) describes the transition from an initial state to a certain intermediate state which does not correspond to any equilibrium state of the system studied. Really, the asymptotic values of the reaction coordinate φ and lattice deformation χ_ζ at $\zeta \to -\infty$ (it relates to the region well behind the front of the chemical reaction (CR) or the structural transition (ST)) are

$$\varphi = \varphi_k$$

$$\chi_\zeta^{(k)} = -\frac{\alpha\varphi_k}{M_t(V_k^2 - V_0^2)} \qquad \zeta \to -\infty. \tag{11}$$

These values are not the same as the values defined by equilibrium equations of the homogeneous state (see appendix 1). Moreover this intermediate state is not static because the constant velocities of molecules well behind the front are not zero:

$$\chi_\tau^{(k)} = V_k \frac{\alpha \varphi_k}{M_t(V_k^2 - V_0^2)} \neq 0. \tag{12}$$

Therefore the displacement χ on the left-hand edge of the lattice increases while the reaction front moves to the right-hand edge. It is a natural consequence of the change in the lattice constant.

So the asymptotics (11) of a topological soliton in a BENDS differs qualitatively from the analogous soliton in a BEDS, where it corresponds to the equilibrium point of the system. However, as shown in appendix 2, the intermediate state (11) is localized in the vicinity of the global minimum potential energy of the system under consideration (final state). Therefore, in a real system (such as a crystal with free edges), one can expect some relaxation process which transfers the lattice from the intermediate state to the final state. This is the second peculiarity of a topological soliton in a BENDS. (It is necessary to note that such a relaxation cannot be described in term of a stationary wave, and the solution of this problem exceeds the limits of the analytical model.)

The last peculiarity of the topological soliton in a BENDS is that its velocity is unique and is defined by equation (8) and (9), while the topological soliton in a BEDS has a wide spectrum of velocities from $V = 0$ up to the speed of sound.

It is useful to note that solution (10) possesses translational invariance in the case of an infinite lattice. It corresponds to unactivated motion of the interface between the lattice in different states (in other words, the reaction front) from the physical point of view.

In the next section we shall consider the results of numerical simulations of the topological soliton motion in a simple model of a molecular crystal.

3. Numerical study

Numerical investigations of the system under consideration have been made for one-dimensional lattices with various parameters of interatomic interactions (a, K, k, M, m and U as denoted in figure 1). First it is necessary to note that such lattices can exhibit a strong different dynamical behaviour depending on the parameters mentioned above. A full study will be published in the near future [9] and here we discuss the computer simulation results which are interesting from a chemical reaction and/or a structural transition viewpoint.

To answer the questions relating to the existence and stability of a topological soliton the initial profile and velocity of the topological soliton have been chosen in accordance with the analytical solution for an infinite continuum model (figure 6). The first test was made for kink propagation in an 'infinite crystal', i.e. in a lattice with boundary conditions which are in accordance with the analytical solution (10) during the full time of the numerical experiment. The most characteristic case of soliton propagation modelling is shown in figure 6, where one can see both the reaction coordinate (figure 6(a)) and the lattice deformation (figure 6(b)) profiles. We observed that the soliton had a finite lifetime under these conditions. The specific path of the soliton is changed from a few lattice constants to a few tens of lattice constants depending on the parameters of the interatomic interactions. It is very interesting that narrower solitons have a larger lifetime. One can see that the profile of the soliton
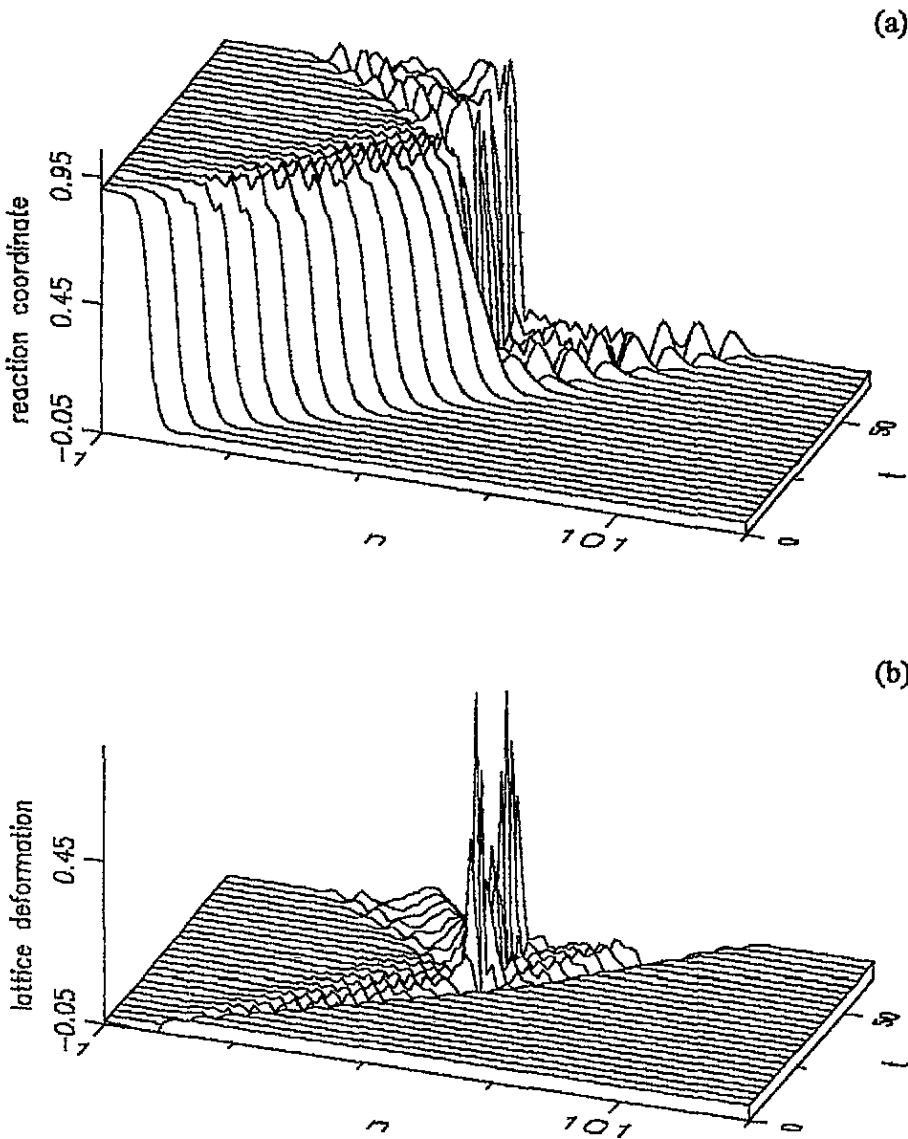
Figure 6. The evolution of coupled topological solitons in the 'infinite' chain: (a) reaction coordinate φ_n; (b) lattice deformation $\chi_{n+1} - \chi_n$, n is the number of molecules and τ is the time in relative units. For example, the system parameters in this simulation are (see appendix 1) $a = 1.510$, $K = 0.150$, $k = 17.000$, $m = 1.00$, $M = 2.60$, $U_0 = 2.933$, $\lambda = -5.100$ and $\kappa = 3.750$; the initial kink velocity is equal to $V_k = 1.589 V_0$ for these chain parameters.

and its velocity are not distinguished noticeably from the analytical solution (10) during its lifetime excluding a short time before the soliton stops.

To study the effect of boundary conditions (and the size of the system) on the soliton propagation a lattice with the same parameters and free edges has been used (figure 7). The initial conditions were the same as in the 'infinite' lattice, i.e. they were in accordance with the analytical solution (10) at time $t = 0$. As the process progresses further, one can observe that a complex structure of the post-frontal region is formed (figures 7 and 8). Propagation
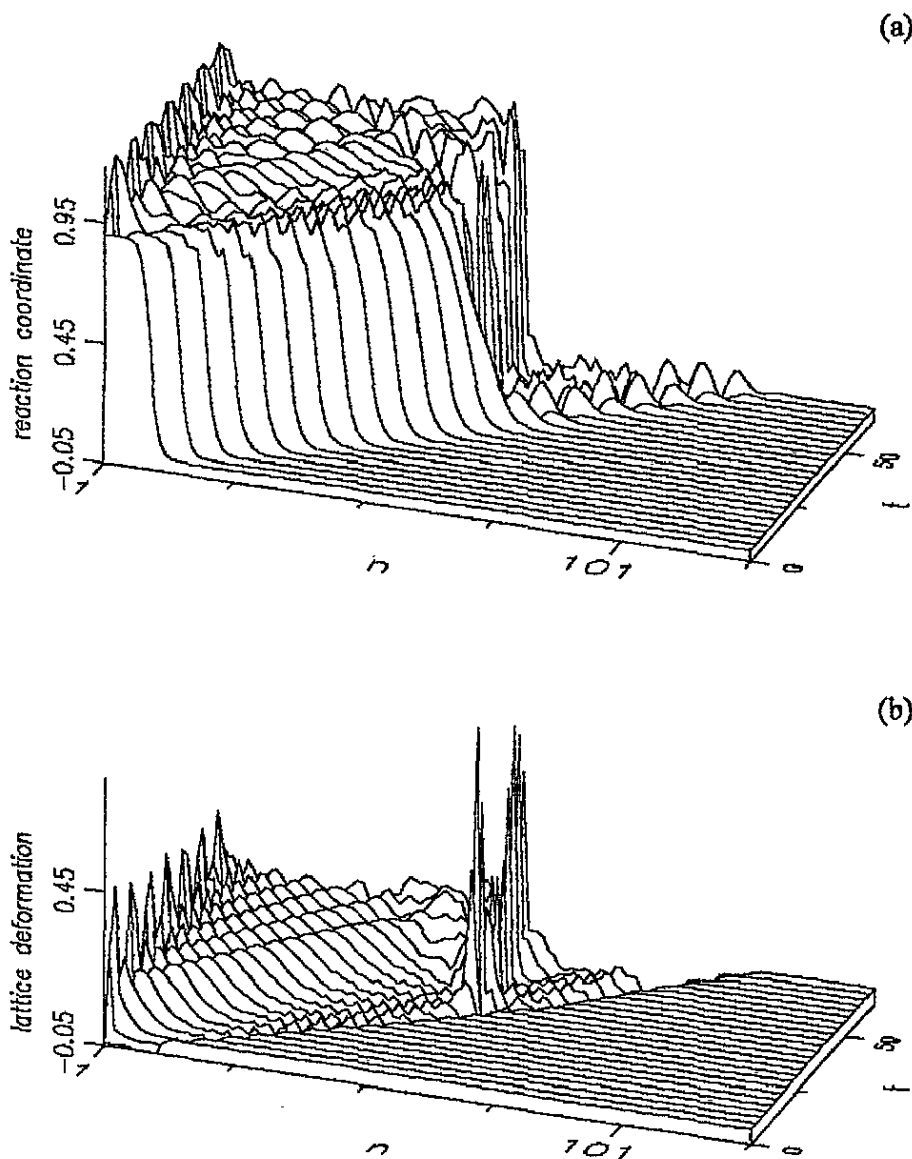
(a)

(b)

Figure 7. The same as figure 6 but for a chain with free edges.

of the front corresponds reasonably well to the analytical predictions for an infinite lattice. A small radiation just beyond the front may be related to the effect of discreteness. On the other hand, as expected the relaxation to the final state (with additional vibrations) occurs in the region well beyond the wave front. Let us emphasize that such a relaxation process does not affect noticeably the main characteristics of the frontal region.

So by observing the fine structure of the reaction kink during its progress one can distinguish three very different regions (figure 8). The first is the region of sharp transformation from the initial to intermediate state. Its length is equal to several lattice constants. The profiles of the reaction coordinate and accompanying lattice deformation inside this region differ weakly from the analytical solution (10) excluding the last period
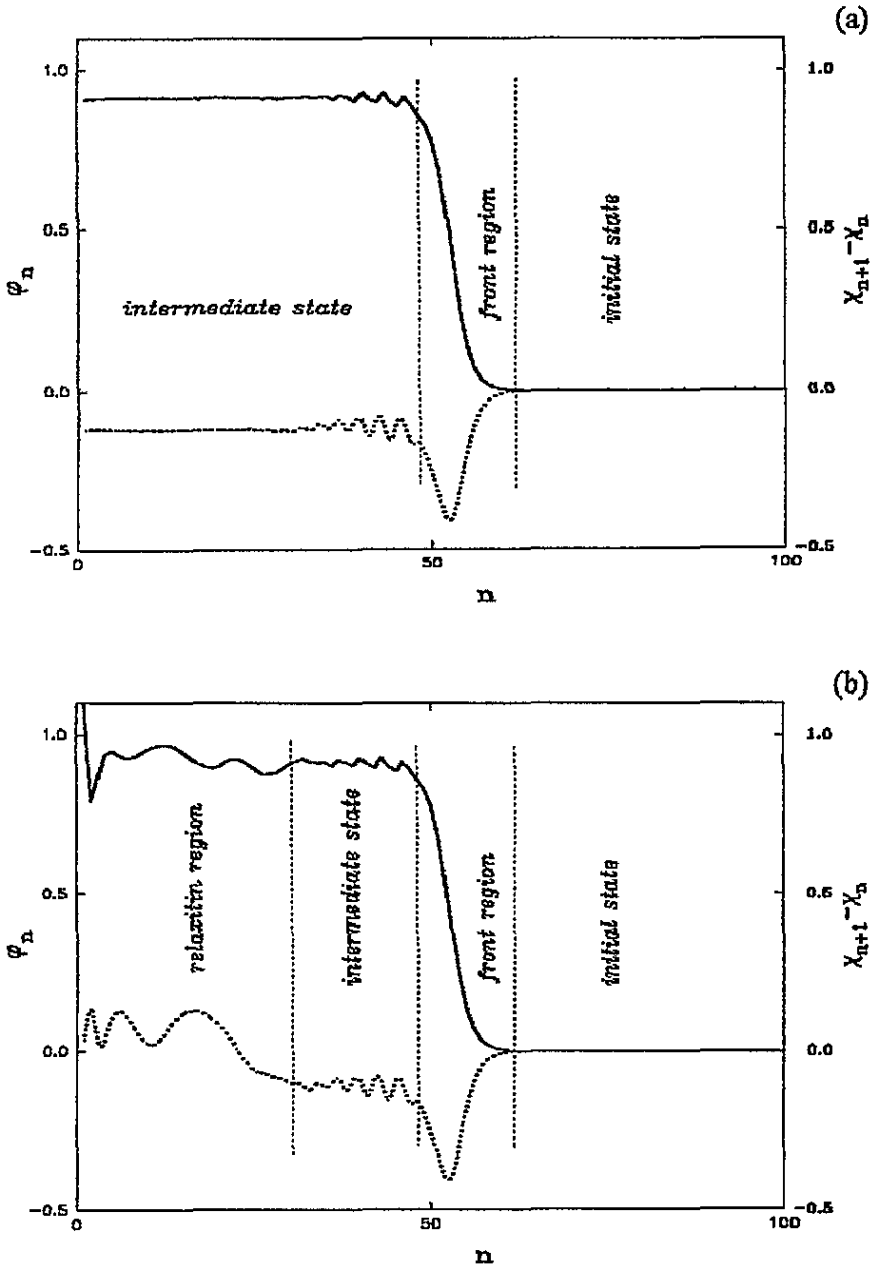
Figure 8. Fine structure of the reaction kink in the case of (a) 'infinite' and (b) finite chains: ——, reaction coordinate; – – –, lattice deformation.

of the kink lifetime.

The second region consists of molecules in the intermediate state, and the numerical solution is close to the analytical solution at the initial stage of kink movement. It is only the small radiation that disturbs this quasi-stationary region during the process.

Finally, the third region is associated with relaxation to the final state. Starting from

the edge of the chain this region then propagates into the second (intermediate-state) region and catches the front up after it stops. As the energy of the intermediate state is higher than the energy of the final state, relaxed molecules are vibrationally excited.

As far as the lifetime of the reaction kink is concerned, it may be divided into three stages. The first starts at the moment of kink initiation and is characterized by a small retardation of the reaction front. The region consisting of relaxed molecules if formed during this period also. The second stage is characterized by appreciable retardation of the reaction front and essential energy redistribution between the frontal and 'intermediate' regions. This process is accompanied by a considerable decrease in height of the soliton connected with the reaction coordinate velocity φ_t. Finally, the last stage of the kink life starts at the moment that the front stops and completes the sharp phase boundary formation (figures 6 and 7). During this time, one can observe the initial extension of the width of the front and its subsequent contraction.
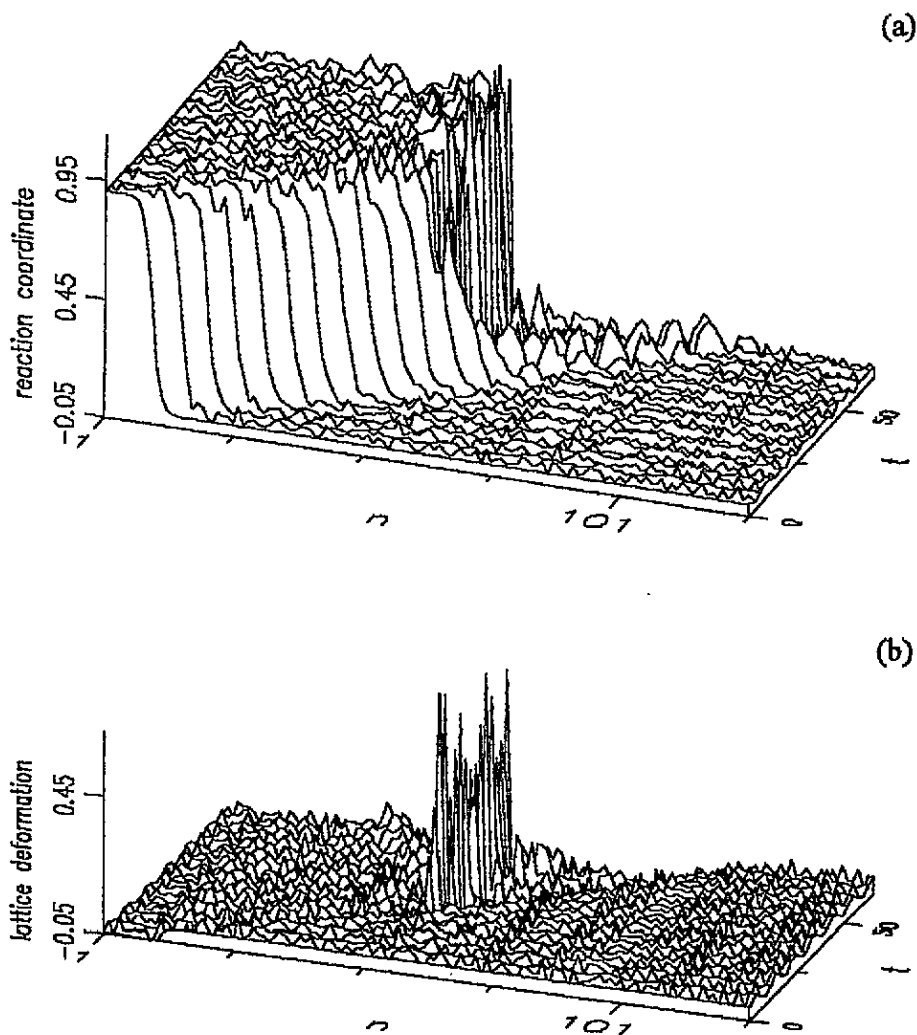

Figure 9. The same as figure 6 at a non-zero initial temperature (about 0.02 of the barrier energy).

Special calculations have shown convincingly the small effect of the finite temperature (in a wide region) on the frontal region and the velocity of its propagation (figure 9). All these results show that the kink motion with a finite lifetime in BENDSs is indeed an elementary event of a new type in the process of structural transition or chemical reaction. Its spatial promotion spans a large part of the lattice in contrast with the local elementary event. The activation energy for such a cooperative elementary event corresponds to the natural kink energy. So we have really a very efficient solitonic elementary mechanism of the structural transition at the atomic level. Let us recall that this may coexist with homogeneous progress at the macroscopic level.

Very significant problems relating to the initiation conditions of topological solitons of a new type and comparison of two very distinct elementary mechanisms of structural transition (cooperative and local) will be the subject of further detailed investigations.

4. Conclusion

Analysis of analytical and computer simulation data allows one to conclude that, under certain conditions, a new cooperative elementary mechanism of structural transitions and chemical reactions exists which is different significantly from the local overcoming of the energy barrier. This mechanism is connected with unactivated motion of a topological soliton of new type. The latter realizes the cooperative transition from an initial equilibrium state to an intermediate dynamic state. Then in a finite lattice such a state relaxes to the final state well beyond the front region but the most significant features of the elementary event are determined by soliton motion. Small initiation energies and large lifetimes of solitons may lead under certain conditions to the formation of a macroscopic front. If the initiation energy is not sufficiently small, the propagation of the structural transition is homogeneous at a macroscopic level. In any case the presence of solitons can accelerate the transition significantly. Besides structural transitions in the bistable molecular crystal the solitonic mechanism may be significant in such processes as detonation in solids (here the absolutely stable energy minimum is shifted to infinity), conformational transitions in macromolecules (DNA), proton transfer in complex lattices with hydrogen bonds in the presence of external fields, and the fracture of polymer chains.

Appendix 1.

By assuming that the lattice constant is equal to unity and measuring the reaction coordinate and lattice deformation in lattice constants, one can obtain the relations between the interatomic force rigidities and the parameters of the dynamic equations:

$$M_t = M + m \qquad \mu = Mm/M_t \tag{A1.1}$$

$$V_0^2 = (a + K + k)/M_t \tag{A1.2}$$

$$\nu V_1^2 = \left[a - \left(K\frac{m}{M} + k\frac{M}{m}\right)\right] \Big/ M_t \qquad (A1.3)$$

$$\alpha = a \qquad (A1.4)$$

$$\beta = \frac{a}{2}\frac{M-m}{M_t} + k\frac{M}{M_t} - K\frac{m}{M_t} \qquad (A1.5)$$

$$\gamma = \alpha/6 \qquad (A1.6)$$

$$\omega^2 = a/\mu \qquad (A1.7)$$

$$h = V_0^2/12. \qquad (A1.8)$$

The factor ν introduced in equation (A1.3) may be $+1$ or -1 corresponding to negative or positive inclinations of the optical branch of the dispersion law [9].

To obtain the analytically solved model, one can use the following form of the potential function $U(\varphi)$:

$$U(\varphi) = U_0\left(\frac{\varphi^2}{2} + \lambda\frac{\varphi^3}{3} + \kappa\frac{\varphi^4}{4}\right). \qquad (A1.9)$$

To investigate the static homogeneous state of system under consideration let us write the potential energy in the form

$$\Pi(\varepsilon, \varphi) = M_t\left(\frac{V_0^2}{2}\varepsilon^2 - \alpha\varepsilon\varphi + \frac{\mu}{M_t}\frac{\omega^2}{2}\varphi^2\right) + U(\varphi) \qquad (A1.10)$$

where $\varepsilon = \chi_{j+1} - \chi_j$ = constant is the homogeneous lattice deformation and $\varphi = \varphi_j$ = constant is the corresponding reaction coordinate. A relationship between the coordinates ε and φ can be obtained from the first of the equilibrium equations:

$$\partial\Pi/\partial\varepsilon = M_t(V_0^2\varepsilon - \alpha\varphi) = 0. \qquad (A1.11)$$

The stationary values of the reaction coordinate are the solutions of the second equation of equilibrium which is written in the following form:

$$\frac{\partial\Pi}{\partial\varphi} = M_t\left(\frac{\mu}{M_t}\omega^2 - \frac{\alpha^2}{V_0^2}\right)\varphi + U(\varphi) = 0. \qquad (A1.12)$$

For the specific form of the potential $U(\varphi)$ that we deal with, one can obtain the equilibrium position in a clear form. The magnitude of the reaction coordinate in the initial state is

$$\varphi_{\text{in}} = 0. \qquad (A1.13)$$

The reaction coordinate in the final state is

$$\varphi_{\text{fin}} = -\frac{\lambda}{3\kappa}\left(1 + \sqrt{D}\right). \qquad (A1.14)$$

The reaction coordinate at the top of barrier, corresponding to the unstable equilibrium position is

$$\varphi_{\text{bar}} = -\frac{\lambda}{3\kappa}\left(1 - \sqrt{D}\right). \tag{A1.15}$$

Here

$$D = 1 - 4\frac{\kappa(u_0 + \omega^2\mu/M_t - \alpha^2/V_0^2)}{u_0\lambda^2} \tag{A1.16}$$

and $u_0 = U_0/M_t$.

We can evaluate the expression under the square root from the requirement that the initial state must be stable:

$$0 < 4\frac{\kappa(u_0 + \omega^2\mu/M_t - \alpha^2/V_0^2)}{u_0\lambda^2} < 1. \tag{A1.17}$$

So we can see that $-\lambda/2\kappa < \varphi_{\text{fin}} < -\lambda/\kappa$ and $0 < \varphi_{\text{bar}} < -\lambda/2\kappa$. For the exothermic processes the initial potential energy is larger than the final energy: $\Pi(0,0) > \Pi(\varepsilon_{\text{fin}}, \varphi_{\text{fin}})$. From this requirement and the inequality (A1.17) we obtain

$$-2\lambda/3\kappa < \varphi_{\text{fin}} < -\lambda/3\kappa \tag{A1.18}$$

$$0 < \varphi_{\text{bar}} < -\lambda/3\kappa. \tag{A1.19}$$

Appendix 2.

Further one can find a value of the 'intermediate' reaction coordinate φ_k as a solution of equations (8) and (9) for the potential $U(\varphi)$ mentioned above (see appendix 1):

$$\varphi_k = -2\lambda/3\kappa.$$

Thus the relationships between the equilibrium and 'intermediate' reaction coordinates follow from equations (A1.18) and (A1.19):

$$\frac{2}{3} < \varphi_k/\varphi_{\text{fin}} < 1 \tag{A2.1}$$

$$\varphi_k/\varphi_{\text{bar}} > 2. \tag{A2.2}$$

The corresponding relation for the lattice deformation is

$$\frac{2}{3}\frac{u_0(1 - 2\lambda^2/9\kappa) + \omega^2}{\alpha^2} > \frac{\chi_\zeta^{(k)}}{\varepsilon_{\text{fin}}} > \frac{u_0(1 - 2\lambda^2/9\kappa) + \omega^2}{\alpha^2}. \tag{A2.3}$$

For the various values of potential parameters, one can obtain the asymptotic lattice deformation, which may differ significantly from the equilibrium value.

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