Influence of heat bath and disorder in the sequence of amino acid masses on Davydov solitons

Influence of heat bath and disorder in the sequence of amino acid masses on Davydov solitons

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Abstract. The theory of Davydov solitons for the energy transport in proteins is briefly summarised, using for the dynamics of the solitons the quantum equations of motion. To obtain a more realistic model for the internal thermal motion of the protein lattice, a temperature of 300 K is considered. Since the 20 natural amino acids have different masses, disorder in the mass sequence is discussed. The soliton remains remarkably stable against thermal motions as well as against mass variation at one site. Also, a random sequence of masses destroys the soliton only for a very large deviation from the average mass.

1. Introduction

In the last few years it has been discovered that non-linearity in the forces occurring in physical systems plays a decisive role in the explanation of a large variety of phenomena. First of all it was found that a lattice bound only by linear forces, i.e. harmonic potentials, would have an infinite heat conductivity, and that only the introduction of non-linearity leads to a finite value of this quantity [1]. Perhaps the most interesting feature of non-linear dynamics is the existence of soliton solutions.

A soliton was first observed in the form of a non-dispersive localised wave packet in a channel [2]. (Since linear wave packets disperse rather quickly, solitary solutions are an exclusive feature of non-linear wave equations.) Since then, soliton concepts have been invoked for the explanation of many phenomena in physics and chemistry. In this paper we only want to mention some of them briefly. One type of equation exhibiting solitary solutions is the sine-Gordon equation. It has been applied e.g. to the dynamics of ferro- and antiferro-magnetic materials [3, 4] and rotations around carbon–carbon bonds in polyethylene [5].

A solitary solution may also be obtained for double-well potentials of the φ^4-type, and these have been used to treat e.g. phase changes [6, 7] and the dynamics of the sugar-phosphate backbone of DNA [8]. The spinless charge-transport in lightly doped alternating transpolyacetylene can be related to solitons in a φ^4-type potential that occur in a tight-binding or Hückel-type Hamiltonian of the π-electrons [9]. After a series of calculations have demonstrated the necessity of introduction of explicit electron–electron interactions into the model to obtain satisfactory agreement with certain experiments (see [10] and references therein), dynamical calculations have shown that in this

case also solitons exist [11]. Recently, a model invoking conformational solitons in nucleotide-base stacks for the explanation of long-range effects of carcinogens was formulated [12] and studied numerically [13]. The Davydov soliton discussed in this work was introduced to explain another biological problem, namely, that many biological processes are associated with an energy transfer through proteins. The energy is released by hydrolysis of adenosine triphosphate (ATP). The mechanism of this energy transport is not quite clear [14].

As an alternative to electronic mechanisms [14], it has also been supposed that the energy is stored as vibrational energy in the isolated C–O stretching mode of the proteins. However, in linear models an initially localised vibrational-energy quantum would be rapidly dispersed. On the other hand, if one, following Davydov's idea [15], takes into account the coupling between the C–O vibration and longitudinal sound waves in the lattice, non-linear terms appear in the equations of motion. Thus the creation of solitary waves in the system is possible. Since solitary waves are highly mobile and localised, because dispersive effects are counterbalanced by the non-linear ones, these waves would provide an efficient mechanism for storage and transport of energy in proteins. Direct experimental evidence for the existence of such solitons in proteins is (due to the enormous difficulties of such measurements in complex systems as proteins) still missing. However, in acetanilide crystals a substructure with chains of hydrogen bonds similar to proteins is present, and in low-temperature infrared and Raman spectra a new band in the energy region of the C–O stretching vibration appears. The only successful theory to date for the explanation of this band is based on a model similar to the Davydov soliton concept in proteins, while all other—more conventional—attempts have failed [16].

In this paper, we present quantum-molecular dynamical studies on solitons in an α-helix, applying Davydov's model. We consider coupling to a heat bath and aperiodicity in the sequence of masses in the chain. In § 2 the model is briefly discussed and a short review of previous work by other groups on the topic given. In § 3 the results we have obtained are discussed and finally in § 4 a short summary is given.

2. Method

For our studies we use the most simple form of the Hamiltonian for the Davydov system [15] since more sophisticated forms incorporating details of the helical structure of proteins lead, qualitatively, to the same results [17]:

$$H = \varepsilon_0 \sum_n b_n^+ \cdot b_n - J \sum_n b_n^+ \cdot (b_{n+1} + b_{n-1}) + \sum_n \frac{p_n^2}{2M_n}$$

$$+ \tfrac{1}{2} W \sum_n (q_n - q_{n-1})^2 + \chi \sum_n b_n^+ b_n (q_n - q_{n-1}). \tag{1}$$

In this Hamiltonian b_n^+ and b_n are the usual boson creation and annihilation operators respectively [18] for the amide I oscillators at site n (see figure 1). For their ground-state energy ε_0 and the dipole–dipole coupling constant of two neighbouring CO groups, $\varepsilon_0 = 0.205$ eV and $J = 9.67 \times 10^{-4}$ eV can be deduced from infrared spectra [19]. Second neighbours' interactions between CO oscillators are an order of magnitude smaller and can be neglected [17]. Between the lattice units a harmonic potential due to the C=O . . . H—N hydrogen bonds is assumed with a force constant W. p_n is the momentum
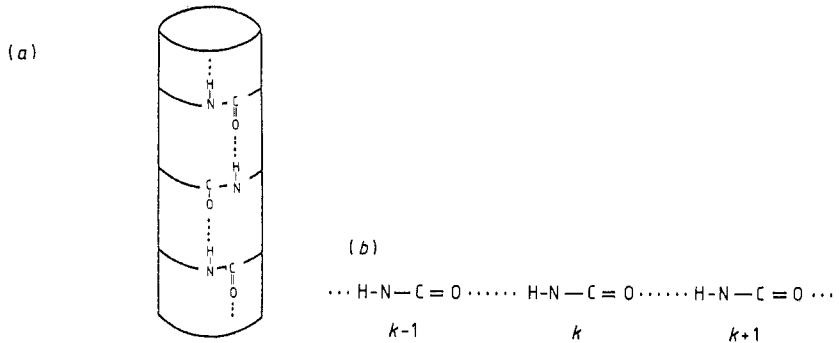
Figure 1. Sketch of the hydrogen-bonded system of energy transport in proteins (a) around the α-helix, (b) idealised.

and q_n the position operator of unit n. For the mass M_n of a unit, an average value of 114 amu (atomic mass units) is usually assumed, corresponding to myosine [17]. For W a value of 76 N m^{-1} is taken [20]. From infrared spectra it is known that the energy of the CO stretching vibration in hydrogen bonds is a function of the length of the hydrogen bond [21]. The experimental vibrational energy plotted against the length r of the hydrogen bonds for different systems shows a linear dependence

$$\varepsilon = \varepsilon_0 + \chi r. \tag{2}$$

The experimental value of χ is 6×10^{-11} N (see [19] and references therein). Previous *ab initio* calculations on formamide dimer lead to $\chi = 3$–5×10^{-11} N [22]. Our Hartree–Fock calculations on formamide dimer using a split-valence basis set with polarisation functions (p type on hydrogen, d type on heavy atoms) also resulted in $\chi \simeq 6 \times 10^{-11}$ N.

With the Hamiltonian described above the time-dependent Schrödinger equation

$$H|\psi\rangle = i\hbar(\partial/\partial t)|\psi\rangle \tag{3}$$

has to be solved approximately. In most of the previous studies performed on equation (3), the displaced oscillator state ansatz [15] of Davydov

$$|\Gamma\rangle = \sum_n a_n(t)b_n^+ \exp\left(-\frac{i}{\hbar}\sum_m (p_m q_m(t) - q_m p_m(t))\right)|0\rangle \tag{4}$$

was applied, where the coefficients $a_n(t)$ are complex numbers. In this ansatz $q_n(t)$ is the expectation value of the position operator, $p_n(t)$ that of the momentum operator of the lattice unit n, $|0\rangle$ is the vacuum state, and $|a_n(t)|^2$ is the probability of finding an amide I vibrational quantum at site n provided that $\Sigma_n|a_n|^2 = 1$.

However, in their recent work Brown and co-workers have shown [23, 24] that in the transportless case ($J = 0$) the ansatz (4) leads to the correct time evolution of $q_n(t)$ but to an incorrect value of the phonon energy. The more sophisticated second ansatz of Davydov [15] is even shown to lead to incorrect $q_n(t)$. Note that for $J = 0$ the Hamiltonian can be solved exactly [23].

Brown and co-workers [24] have derived a non-linear density-matrix equation of motion. However, this rather complicated theory was, at least to our knowledge, only applied in linearised form to a two-site system [25]. Using a time-dependent unitary transformation method on the Davydov Hamiltonian, Mechtly and Shaw [26] were able to derive equations of motion that are exact in the transportless limit ($J = 0$). Their

numerical simulations show results qualitatively similar to previous calculations [17] using ansatz (4). However, soliton formation starts at a higher threshold value of χ ($\chi_t \simeq 10 \times 10^{-11}$ N) than in simulations using ansatz (4) ($\chi_t \simeq 4 \times 10^{-11}$ N) [17]. We used $\chi = 9 \times 10^{-11}$ N.

If, therefore, one is mainly interested in the qualitative features of the soliton dynamics, it would seem to be justified to use ansatz (4), which also leads to equations of motion which are computationally much simpler. The equations of motion derived from ansatz (4) are

$$i\hbar\dot{a}_n = \varepsilon_0 a_n - J(a_{n+1} + a_{n-1}) + \chi(q_n - q_{n-1}) \tag{5a}$$

$$M_n\ddot{q}_n = W(q_{n+1} - 2q_n + q_{n-1}) + \chi(|a_{n+1}|^2 - |a_n|^2). \tag{5b}$$

These equations can be obtained by using the expectation value of H as a classical Hamiltonian function [15, 17] or also, as recently shown, by quantum mechanical methods [27].

Finally the total energy of the system is given by

$$E = \langle \Gamma | H | \Gamma \rangle$$

$$= \sum_k \left(\varepsilon_0 |a_k|^2 - J a_k^* (a_{k+1} + a_{k-1}) + \frac{p_k^2}{2M_k} \right.$$

$$\left. + \frac{W}{2} (q_k - q_{k-1})^2 + \chi(q_k - q_{k-1})|a_k|^2 \right). \tag{6}$$

For the numerical integration of equations (5), the second order equation (5b) was transformed to two coupled equations of first order in time. The complex equation (5a) was solved as a system of two coupled equations for the real and imaginary parts of a_k. We have used a system of 200 units, and thus a system of 800 coupled differential equations of first order in time had to be solved. This was achieved by a fourth order Runge–Kutta algorithm [28] using a time step Δt between 0.2 and $0.5(\bar{M}/W)^{1/2}$ ($\bar{M}$ is the average mass of 114 amu). The conservation of energy and norm of $|\varphi\rangle$ could be achieved within 1% of their initial values. It can be shown that for an exact solution of (5) the term $J a_k^* (a_{k+1} + a_{k-1})$ occurring in the energy expression (6) is a real quantity, as is required for the energy. Therefore its imaginary part can be used as a further test of the quality of the numerical simulation. With the above-mentioned time-step size, the imaginary part of this term was of the order of 10^{-37} N m in all simulations performed.

However, one should keep in mind that while (5) reproduces the correct $q_n(t)$ for $J = 0$ [23], the phonon energy is incorrect. Also, quantitative results obtained from (5) should be interpreted with care [26]. We are interested basically in two problems: First of all, *in vivo* proteins are coupled to a heat bath; and secondly, proteins are aperiodic polymers and therefore the use of an average mass $\bar{M} = 114$ amu instead of individual peptide masses M_n is an approximation.

Both problems together have been studied by Halding and Lomdahl [29] using classical molecular dyamics and a Lennard–Jones potential between the peptide units of an α-helix. This work [29] does not deal with Davydov solitons, but the pulses studied bear some similarity with the solitons studied in this paper. However, the work of Halding and Lomdahl [29] is an example of the application of a classical thermalisation scheme to a classically described lattice. They found that a clearly resolved pulse travels through a chain without mass variation for $T = 310$ K. In the case of mass variation they found that with decreasing excitation energy the ability of the pulse to carry energy

decreases. It would seem to be interesting to study effects of mass variation in the case of the quantum equations of motion (5) for Davydov solitons also.

In the case of thermal fluctuations there exists considerable discussion in the literature. Lomdahl and Kerr [30] and Lawrence and co-workers [31], using equations (5) augmented by energy-providing random forces and dissipation terms, found that at 300 K the Davydov soliton is destroyed. By contrast, Bolterauer [32] and other authors (see references 3–6 in [32]) found solitons to be stable at this temperature. In a recent paper Cruzeiro and co-workers [33] derived evolution equations from Davydov's original theory, using quantum mechanical methods. Their numerical applications also predicted the stability of Davydov solitons up to 310 K [33].

Bolterauer [32] argues that, in the case of applying a classical model for the heat bath as used in [30, 31] to a quantised lattice, not even the correct thermal equilibrium will be obtained. He shows explicitly that, in case of two coupled oscillators, if one is treated classically and the other with the aid of quantum mechanics, the thermal-excitation energy in the quantum oscillator will be greatly overestimated when compared to the exact quantum-mechanical solution of the problem. Bolterauer [32] discusses the fact that, if the soliton is faster than the relaxation of the heat bath, the system can be prepared in a phonon state corresponding to the thermal energy Nk_BT and, after excitation of the oscillator system, the heat bath may be switched off. Lomdahl and Kerr [30] also studied this case but, as Bolterauer [32] discusses, their classical thermalisation scheme should lead to an incorrect phonon state already existing before excitation. Bolterauer [32] discusses his model from an analytical point of view only, showing that the equations of motion obtained with a phonon state corresponding to $T = 0$ are the same as those derived for $T \neq 0$. Note that in [32] a state vector different from ansatz (4) is used, but it leads to the same equations of motion as does (4). The difference lies in the meaning of the parameters. It would seem to be interesting to perform direct numerical simulations using the heat-bath model discussed in [32] instead of the classical random-forces-dissipation model used in [30, 31].

3. Results and discussion

3.1. Influence of a heat bath

Since proteins are *in vivo* in contact with a heat bath of about 300 K, one has to decide whether or not the thermal motion of the lattice still permits soliton motion. For a CO vibrational energy of $\varepsilon_0 = 3.28 \times 10^{-20}$ N m and a temperature of 300 K, one obtains a Boltzmann factor of 3×10^{-4} i.e. in thermal equilibrium only three out of 10 000 oscillators are excited. Therefore one can safely assume that the heat bath primarily affects the soliton motion only via the lattice, which exhibits a quasi-continuum of vibrational states. However, through the coupling the heat bath also acts on the oscillator system. Prior to the soliton commencement the sytem is in equilibrium with the heat bath. The oscillator system is in its ground state, while the lattice is in thermal motion, which can be described as linear combination of its normal modes. With the soliton commencement a non-equilibrium state is created. One may now consider two extreme cases [32]: first, where the time the soliton needs to travel through the protein is small compared to the time the heat bath needs to re-establish equilibrium with the system; or, secondly, where the soliton velocity is small compared to the velocity of equilibration. Since the soliton velocity is high, we consider the first case to be more realistic.
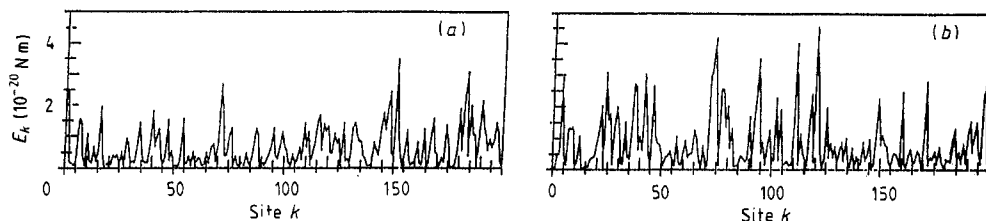
Figure 2. Local lattice energy E_k (in 10^{-20} N m) as function of site for different times t for the model system in contact with a heat bath: (a) $t = 0$; (b) $t = 60$ ps.
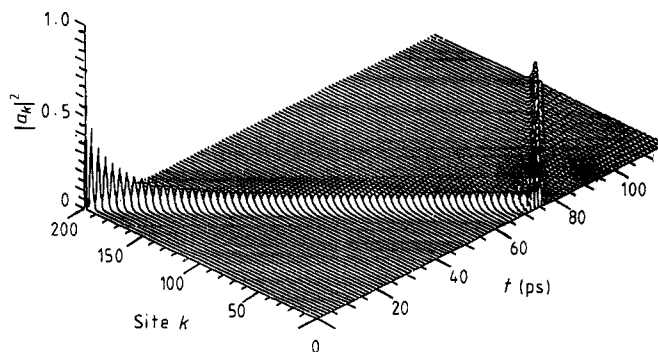

Figure 3. Evolution of $|a_k|^2$ (see text) as function of site and time for a Davydov soliton in contact with a heat bath of 300 K.

Prior to the soliton commencement ($t = 0$) we introduce an energy Nk_BT, where N is the number of sites and k_B Boltzmann's constant. With the help of a random number generator, the energy is distributed on the sites. If the soliton would interact with impurities bound to the protein or, for example, with hydrogen bonds to DNA, one could also introduce energy loss into the model. If the sites of these bonds are not determined exactly, one could, for example, remove a certain number of energy quanta in a random way. Next the equations of motion of the decoupled lattice are solved, i.e. the energy is distributed on all normal modes. Then at $t = 0$ the soliton is started. Figure 2(a) shows the local lattice energy in 10^{-20} N m at $t = 0$ and figure 2(b) at $t = 60$ ps. The lattice-energy fluctuations associated with the heat bath are larger by roughly three orders of magnitude than the local lattice energies associated with the soliton motion. Nevertheless, as figure 3 (where $|a_k|^2$ is shown for this case) indicates, the soliton moves through the chain completely undisturbed. Therefore, despite the large lattice-energy fluctuations due to the heat bath, the non-linear coupling between lattice and oscillators is still able to stabilise the soliton. This result agrees with the analytical considerations in [32] and also with the completely classical molecular-dynamical study of Halding and Lomdahl [29]. However, it disagrees with the conclusion derived from a classical thermalisation scheme [30, 31] for Davydov solitons, consistent with the arguments of Bolterauer [32].

3.2. Effects of disorder in the sequence of masses

In the simulations described so far, an average mass of $\bar{M} = 114$ amu was used for each site. However, a real protein is an aperiodic polymer where 200 different amino acids

occur with molecular weights between 75 amu (glycine) and 204 amu (tryptophane). This corresponds to a variation between $0.66\bar{M}$ and $1.79\bar{M}$. However, in our model only small elongations perpendicular to the protein backbone occur and therefore the influence of the different masses of the amino-acid residues should be much smaller than suggested by the interval given above.

To test the stability of the Davydov soliton against disorder in the sequence of masses in a first series of calculations, we have increased only the mass at site 100. All other masses have been kept equal to $\bar{M}$. Surprisingly enough, up to very large masses of $100\bar{M}$ (figure 4(a)) no visible perturbations occur in the soliton motion. While the motion of the soliton does not change much, a very small fraction of the sound energy is trapped at the impurity and the major fraction is scattered back. As figures 4(b–d) show, these fractions do not increase up to $M_{100} = 1000\bar{M}$. From these results one may conclude that an impurity at one site that may also be some other molecule bound to the protein at this site (like reactive centres as e.g. heme groups) does not disturb the soliton at all, unless it does not influence the coupling constant χ significantly.

In a second series of computer experiments we have introduced a random series of masses for the whole chain, $\alpha_k\bar{M}$, where the α were determined using a random-number generator with equal probability within a prescribed interval. In figure 5 four examples are shown; $(0.66 \leqslant \alpha_k \leqslant 1.79)$, $(0.66 \leqslant \alpha_k \leqslant 100)$, $(0.66 \leqslant \alpha_k \leqslant 200)$, and $(0.66 \leqslant \alpha_k \leqslant 250)$.

The aperiodicity due to the first two smaller intervals for α_k does not significantly affect the soliton motion. However, in the case of the two larger intervals, the vibrational energy disperses. The interval over which the soliton still moves unperturbed $(0.66 \leqslant \alpha_k \leqslant 100)$ is obviously larger than the variation of masses of the natural amino acids $(0.66 \leqslant \alpha_k \leqslant 1.79)$. However, we consider the effective perturbation of this mass variation on the soliton to be much smaller than the mass interval suggests. This is due to the fact that the amino acids in a protein do not move as free particles but are covalently bound in the direction of the main chain that is perpendicular to the direction of their movement in the Davydov model. Therefore, one can assume that the effective influence of mass variation in the side groups of the amino acids on Davydov solitons should be much smaller than the actual numbers for the masses suggest. So we conclude that the aperiodicity of natural proteins should not significantly affect the soliton formation and motion.

4. Conclusions

A heat bath of 300 K coupled to a protein, as is the case *in vivo*, under the assumption that the soliton travels fast when compared with the velocity of thermal equilibration, leads to no perturbation of the soliton motion whatsoever. An impurity in the middle of the chain, acting only through its mass, was shown to have no considerable influence on the soliton up to masses as high as $1000\bar{M}$. For comparison, the largest amino acid has only a mass of $1.79\bar{M}$. The more interesting case of a random sequence of masses has no influence in the case of an interval of $(0.66\bar{M} \leqslant M_k \leqslant 100\bar{M})$. For larger deviations the vibrational energy disperses rapidly. However, since the effective perturbations resulting from the natural mass deviations of amino acids should be smaller than the actual masses themselves, as discussed above, the approximation of an average mass throughout all sites seems to be justified.
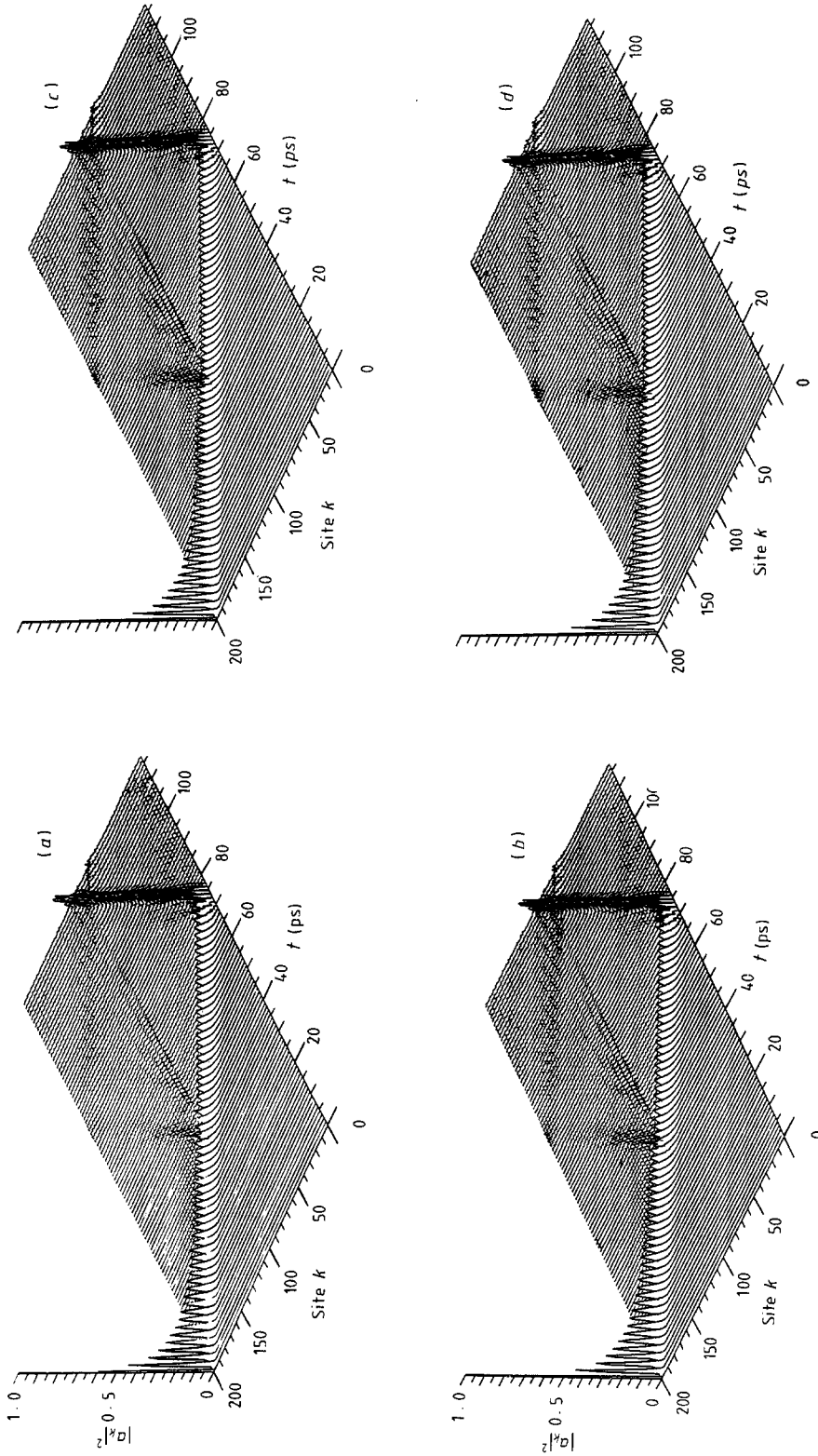
Figure 4. Evolution of $|\alpha_k|^2$ (see text) as function of site and time for a Davydov soliton in a chain with an impurity at site 100 for different impurity masses ($\bar{M} =$ 114 amu): (a) $100\bar{M}$; (b) $200\bar{M}$; (c) $500\bar{M}$; (d) $1000\bar{M}$.
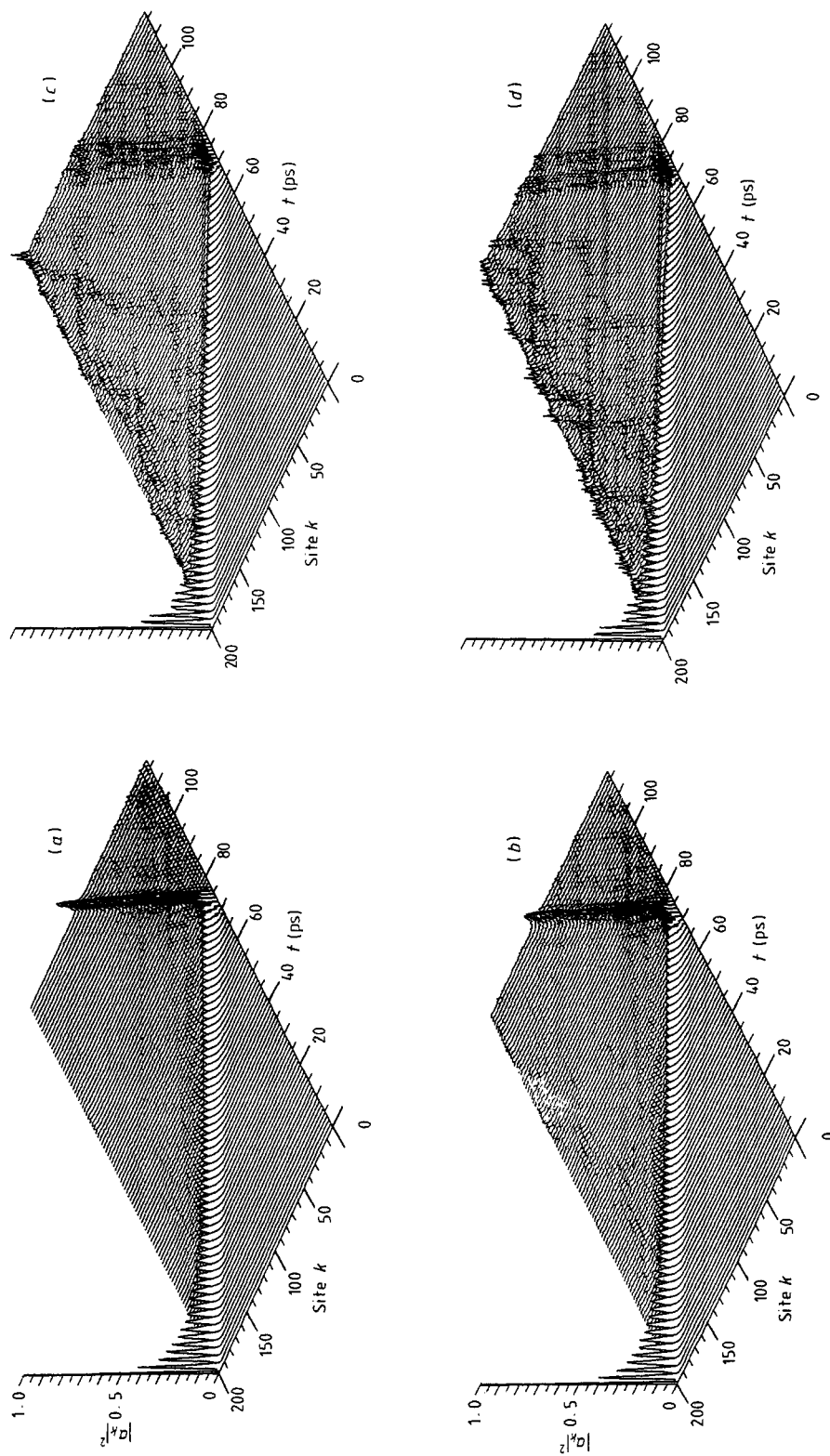
Figure 5. Evolution of $|a_k|^2$ (see text) as function of site and time for a Davydov soliton in a chain with a random mass sequence $\alpha_k M$ for different intervals of the α_k: (a) $0.66 \leqslant \alpha_k \leqslant 1.79$; (b) $0.66 \leqslant \alpha_k \leqslant 100$; (c) $0.66 \leqslant \alpha_k \leqslant 200$; (d) $0.66 \leqslant \alpha_k \leqslant 250$.

Acknowledgment

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