Soliton patterns and breakup thresholds in hydrogen-bonded chains

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Abstract. The dynamics of protons in hydrogen-bonded quasi one-dimensional networks are studied using a diatomic lattice model of protons and heavy ions including a $\phi^4$ on-site substrate potential. It is shown that the model with linear and nonlinear coupling of the quartic type between lattice sites for the protons admits a richer dynamics that cannot be produced with linear couplings alone. Depending on two types of physical boundary conditions, namely of the drop or condensate type, and on conditions requiring the presence of linear and nonlinear dispersion terms, soliton patterns of compact support, whether with a peak, drop, bell, cusp, shock, kink, bubble or loop structure, are obtained within a continuum approximation. Phase trajectories as well as analytical studies provide information on the disintegration of soliton patterns upon reaching some critical values of the lattice parameters. The total energies of soliton patterns are computed exactly in the continuum limit. We also show that when anharmonic interactions of the phonon are taken into account, the width and energy of soliton patterns are in qualitative agreement with experimental data.

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1 Introduction

Transport of protons in hydrogen-bonded systems is a topic of great research interest, aiming to describe nonlinear solitonic excitations which, according to the ideas of Antonchenko, Davydov and Zolotaryuk [1], would be related to the formation and propagation of ionic and Bjerrum defects. In fact these ideas have successfully been tested in a variety of organic as well as inorganic materials which form chains, networks and solids utilizing hydrogen-bonding mechanisms, such as for example ice and hydrogen halides which are the best known examples of inorganic hydrogen-bonded solids [2–4], whereas proteins, DNA, and other biological macromolecules are examples of organic hydrogen-bonded chains [5,6]. Protonic conductivity is usually associated with motion along a hydrogen-bonded chain of ionic (ionization) and Bjerrum (orientational or bonding) defects [4,7]. The former involve translational motions of the hydrogen-bonded protons, whereas the latter are results of rotations of the hydroxyl ions or some other hydroxyl groups. Transport of protons may begin either with the passage of an ionic defect or the passage of an orientational defect, but thereafter the motion of these defects must strictly alternate [5,6,8,9]. Furthermore, it has been demonstrated that many biological activities, such as photosynthesis, repair mechanisms of DNA after radiation damage, metabolism, signal transduction in cells, enzymatic processes, and respiration which are driven by electron transfer reactions [10,11], may proceed along a single pathway which, as the preferred channel for electron transfer reactions, can be established by a hydrogen-bonded strand within the secondary structure [12,13].

One of the questions that has been raised for the mechanism of proton conductivity concerns the roles played by the nonlinear on-site potential for the protons, leading to three possible scenarios: (1) the model usually consists of two interacting sublattices: one of harmonically coupled light ions (protons) with a doubly degenerate nonlinear on-site potential of the $\phi^4$ type and the other of harmonically coupled heavy ions. Theories differ in choosing the form of the interaction between the two sublattices. Usually, a nonlinear coupling between the two sublattices is considered [14,15], although there are models which consider a linear coupling [16,17]; (2) the doubly...
degenerate nonlinear on-site potential is of the double-Morse type. In fact, as shown by quantum chemistry calculations [18–20], a good approximation of the double-well potential can be constructed as the superposition of two symmetrically positioned ion-ion Morse potentials as well as an ion-ion coupling [21–29]; (3) the nonlinear on-site potential is of the double sine-Gordon type with nonlinear [30,31] and linear [32] couplings. In the first two cases, models are able to describe energy transport, dielectric polarization, and proton storage in hydrogen-bonded networks but they are unable to explain the protonic mass in such a system which is required in order to support the saturated protonic conductivity in ice and other hydrogen-bonded semiconductors [33]. In the last case, models can explain simultaneously the ionic and Bjerrum defects formation and propagation using well-known soliton properties [30–32,32]. Besides the nonlinear on-site potential for the protons, hydrogen-bonded models with phonon anharmonisms occur as well. Such a model was first introduced by adding higher-order terms such as the cubic and quartic anharmonicities to the harmonic potential [34–39]. Later, an exponential nonlinearity was considered, represented by, e.g., Morse, Toda or Lennard-Jones potentials [40–44].

As is well-known, the solitons existing in these models result from the balanced competition between dispersion and nonlinear effects. Recently, it has been shown that the inclusion of anharmonicities in the study of lattice models can produce qualitatively new effects. In particular, Rosenau and Hyman [45] found solutions of the solitonic type without infinite tails, termed solitons with compact support or compactons [46–51]. In other words, two adjacent compactons do not interact unless they come into contact in a way similar to the contact between hard spheres. It has been shown that the effects of lattice discreteness, and the presence of a linear coupling between lattice sites are detrimental to a stable ballistic propagation of the compacton, because of the particular structure of the small oscillation frequency spectrum of the compacton in which the lower frequency internal modes enter in direct resonance with phonon modes [48]. The existence of a localized breathing mode with compact support has been demonstrated [48]. A quantization condition on the value of the width parameter of the discrete compacton has been proposed [47].

The aim of this paper is to investigate the properties of the one-dimensional diatomic chain of protons and heavy ions, where the proton dynamics is influenced by anharmonic lattice vibrations. Except for the work by Kashimori et al. [37], our anharmonic treatment of the lattice vibrations goes beyond the usual harmonic approximations of two-sublattice soliton model of the hydrogen-bonded proton Hamiltonians [1,30,33]. In the model with quartic nonlinear proton-proton coupling to be discussed, conditions are considered that require the presence of nonlinear dispersion as well as linear dispersion. In this paper we show that soliton pattern mechanisms that require a nonlinear coupling of the protons in adjacent hydrogen bonds may exist if one properly chooses a class of physical boundary conditions. The obtained patterns are solitons of compact support, without infinite tails rather than the kinks with infinite tails in the coupled double-well model.

The paper is organized as follows. In Section 2, the model Hamiltonian of one-dimensional interacting two-sublattice model of anharmonically coupled protons and harmonically coupled heavy ions is presented. Using two types of physical boundary conditions, namely the “zero” or nonvanishing classes of boundary conditions, in the continuum limit two-component compacton-like solutions are obtained and their total energies are calculated. Analytic expressions for the dependence of the breakdown threshold value on the nonlinear parameter, on the constant coupling between the two sublattices, and on the velocity of the soliton patterns are derived. The last section contains a summary and conclusions.

2 The model and analytical results

2.1 The model

In the study of proton transfer processes in hydrogen-bonded systems, it is usual to consider one-dimensional chains, the so-called Bernal-Fowler filaments [1,2,27,52,53], which consist of two coupled sublattices \( \cdots X - H \cdots X - H \cdots X - H \cdots X - H \cdots \), where the hydrogen atom \( H \) (or proton \( H^+ \)) with mass \( m \) in each lattice unit is connected to its adjacent heavy ions or more generally hydroxyl groups \( X \) or \( X^- \) via either a covalent (−) or a hydrogen (⋯) bond of mass \( M \) \((m < M)\), forming a hydrogen bonded bridge \( X - H \cdots X \) [1,37]. The covalent and hydrogen bonds in a \( X - H \cdots X \) configuration are interchangeable, viz., the proton in the bond that links the two \( X \) ions together can tunnel between two equilibrium positions which are energetically approximately equivalent. In such a case, the two-dimensional intrabond proton potential is assumed to be a symmetric double-well function of a general form with two minima. This double well potential is also motivated physically by considering the simultaneous electromagnetic interaction of the two proton neighbour heavy ions (details on the structure of this potential are given in Refs. [54,55]). A typical example of such a potential for the proton in the hydrogen bond is the well-known double-well potential [1]:

\[
V(u_n) = V_0 V_{sub}(u_n),
\]

with

\[
V_{sub}(u_n) = \left(1 - \frac{u_n^2}{u_0^2}\right)^2,
\]

where \( u_n \) denotes the displacement of the \( n \)th proton with respect to the center of the heavy-ion pair, \( V_0 \) the potential barrier, and \( 2u_0 \) [the two minima \((\pm u_0, 0)\) correspond to the degenerate ground states of the chain] is the distance between the two minima of the double-well potential, as illustrated in Figure 1.