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Mobility and conductivity of ionic and bonded defects in hydrogen-bonded chains with nonlinear interactions

A.S. Tchakoutio Nguetcho[1,2,a], P.B. Ndjoko[1], and T.C. Kofane[1,3]

[1] Laboratoire de Mécanique, Département de Physique, Faculté des Sciences, Université de Yaoundé I, B.P. 812, Yaoundé, Cameroun
[2] International Chair of Mathematical Physics and Applications ICMPA-UNESCO Chair, 072 BP50, Cotonou, Université d'Abomey-Calavi, Benin
[3] The Abdus Salam International Centre for Theoretical Physics, P.O. Box 586 Strada Costiera, II-34014 Trieste, Italy

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Abstract. The proton conductivity and the mobility arising from motions of the ionic and bonded defects, in hydrogen-bonded molecular systems are investigated by means of the quantum mechanical method. Our two component model goes beyond the usual classical harmonic interaction by inclusion of a quartic interaction potential between the nearest-neighbor protons. Among the rich variety of soliton patterns obtained in this model, we focus our attention to compact kink (kinkon) solutions to calculate analytically, the mobility of the kinkon-antikinkon pair and the specific electrical-conductivity of the protons transfer in the hydrogen-bonded systems under an externally applied electrical-field through the dynamic equation of the kinkon-antikinkon pair. For ice, the mobility and the electrical conductivity of the proton transfer obtained are about 5.307×10^{-7} $\mathrm{m^2\,V^{-1}\,s^{-1}}$ and 6.11×10^{-4} $\Omega^{-1}\,\mathrm{m^{-1}}$, respectively. The results obtained are in qualitative agreement with experimental data.

PACS. 62.30.+d Mechanical and elastic waves; Vibrations – 63.20.-e Phonons in crystal lattices – 05.45.Yv Solitons – 63.20.Ry Anharmonic lattice modes

1 Introduction

One-dimensional chain of hydrogen bonds has attracted a lot of attention since it provides a simple model for many problems in physics, chemistry and biology [1–21]. One problem which has received much theoretical interest is the proton transport that takes place through the hydrogen bonds. This interest grew out of the complete lack of success in attempts to built models that can explain simultaneously the ionic and Bjerrum formation and propagation using well-known soliton properties [16,22,23].

Early studies of properties of the one-dimensional atomic [18,20] and diatomic chains of protons and heavy ions led to the proposal, which is further discussed in reference [12], that the proton dynamics is strongly influenced by anharmonic lattice vibrations. For example, it has been shown that for certain choices of the boundary conditions and conditions requiring the presence of linear and nonlinear dispersion terms, the protons exhibit a richer dynamics that cannot be produced with only linear couplings. In addition, the continuum limit of this model [12] shows soliton patterns of compact support such as peak, drop, bell, cups, shock, kink, bubble and loop structures. In the framework of this approach, it has also been shown that when anharmonic interactions of phonons are taken into account, the width and energy of soliton patterns are in qualitative agreement with experimental data [12,18,20]. In these studies, however, attention has been focused to the classical behavior of these excitations without discussing the relevance of quantum effects in the structure of solitons with compact support. Of course, a more realistic treatment of such defect configurations and their properties should also take into consideration quantum effects. Up to now, quantum effects of protons transfer in quasi-one-dimensional hydrogen-bonded systems have been reported [8,24–30]. However, to our knowledge, only the work by Kevrekidis et al. [31] studied the quantization of solitons with compact support, and provides a motivation for extra theoretical and experimental effort. Explicit expressions for both the mobility and the conductivity of the kinkon-antikinkon pair in hydrogen-bonded molecular systems using the quantum-mechanical method are of interest and we evaluate these physical parameters for ice crystal.

In this paper, we are going to focus on molecular systems which are long periodic chains of hydrogen bonds forming channels for the proton transport. In particular, we present theoretical calculations which

[a] e-mail: nguetchoserge@yahoo.fr

concern the mobility of the kinkon-antikinkon pair and the specific electrical-conductivity of the protons transfer in the hydrogen-bonded chains under an externally applied electrical field through the dynamic equation of the kinkon-antikinkon pair solutions. The paper is organized as follows. In Section 2, the quantum model Hamiltonian is introduced and the corresponding equations of motion are derived. In Section 3, the mathematical analysis of the model equations and their kink solutions with compact support are considered. We also compute the mobility and the conductivity of the kinkon-antikinkon pair solutions in the presence of an externally applied electrical-field. In Section 4, we compare the obtained results with the experimental data and finally, the last section contains a summary and conclusions.

2 The model and equations of motion

Due to the fact that we here consider the molecular crystals to be at a finite temperature, and which can be in contact with a thermal reservoir at temperature of $T \neq 0$ K, it is necessary to take account of the anharmonic vibrations of the molecular chains in the systems when compared with the case where we do not take into account the temperature effect [12,39,40]. Therefore, the total one-dimensional hydrogen-bonded Hamiltonian describing the collective excitation state resulting from the structural deformation and localized fluctuation in such a case should be represented as [12,39]:

$$H = H_p + H_o + H_{int}, \tag{1}$$

where the Hamiltonian of the proton sublattice is:

$$H_p = \sum_n \left[\frac{1}{2m}p_n^2 + V(u_n) + \frac{1}{2}mC_0^2(u_{n+1}-u_n)^2\right] + \sum_n \left[\frac{1}{4}mC_a(u_{n+1}-u_n)^4\right]. \tag{2}$$

In a real system, the proton-proton interaction near the equilibrium positions is expected to be very weak. Therefore the value of (mC_0^2) must be small. However, when a proton moves far away from one equilibrium position and approaches the other one, the electronic structure of the oxygen atom changes dramatically. In order to reflect this situation, we introduce an additional anharmonic interaction, which, in our calculation, is expressed by a fourth-order term. This nonlinear short-range potential is assumed to be polynomial in order that its form can correspond to the small amplitude expansion of a more realistic potential such as a Toda, Lennard-Jones or Morse lattice potential [40]. C_0 is the characteristic velocity and C_a the anharmonic coupling parameter between neighboring protons. u_n denotes the displacement of the n^{th} proton with respect to the center of the heavy-ion pair, $p_n = m\frac{du_n}{dt}$ is the momentum, and the term $V(u_n)$ is the symmetric double-well substrate potential:

$$V(u_n) = V_0 V_{\text{sub}}(u_n), \tag{3}$$

where

$$V_{\text{sub}}(u_n) = \left(1 - \frac{u_n^2}{u_0^2}\right)^2. \tag{4}$$

V_0 denotes 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.

For the motion of the heavy ion, we assume an harmonic oscillator with low frequency acoustic-vibration, on account of the large mass associated to a large number of atoms or atomic groups. Thus, the Hamiltonian of the heavy-ion sublattice is [8,12,14]:

$$H_o = \sum_n \left[\frac{1}{2M}P_n^2 + \frac{1}{2}Mv_0^2(y_{n+1}-y_n)^2\right] \tag{5}$$

where y_n and $P_n = M\frac{dy_n}{dt}$ are the displacement of the heavy ion from its equilibrium position and its conjugate momentum, respectively. The last term of equation (5) describes an harmonic coupling between neighboring heavy ions pairs.

The last contribution to the total Hamiltonian H arises from the dynamical interaction between the two sublattices and describes the modulation of the double well potential caused by the variation of the distance between the heavy ions that surround the proton. Its physical meaning is the lowering of the potential barrier due to the oxygen displacements. This energy can be measured experimentally or estimated from approximated theoretical expressions [12,14,32,33]. The shape that we use takes into account the interactions between the relative movements of atoms in two chains. It can also describe interactions between donors and acceptors [13]. In the discrete lines of Josephson transmission, it describes the inductive coupling [14]. The interacting Hamiltonian is given by:

$$H_{int} = \sum_n \chi(y_{n+1}-y_n)\left(u_0^2 - u_n^2\right), \tag{6}$$

where χ measures the strength of the coupling between the two interacting sublattices and determines the amplitude of the distortion in the heavy ion sublattice. We also justified this form of the interacting Hamiltonian by the fact that, the interaction between the oscillators and molecular lattice exists because of the local fluctuation and deformation of structure in this system.

As it is well-known [8], the vibration frequency of the proton is quite high relative to the heavy ion due to its small mass and strong interaction. Thus, we generalize our model into quantum-mechanical case to study the quantum-mechanical properties. Naturally, we make the transformation:

$$u_n = \sqrt{\frac{\hbar}{2m\omega_0}}\left(a_n + a_n^+\right), \tag{7a}$$

$$p_n = \sqrt{\frac{\hbar m\omega_0}{2}}(-i)\left(a_n - a_n^+\right), \tag{7b}$$

where a_n^+ and a_n are the creation and annihilation operator of the proton, respectively and $i = \sqrt{-1}$. The total

Hamiltonian (1) becomes:

$$
\begin{aligned}
H = \sum_n \Bigg\{ & \hbar\omega_0 a_n^+ a_n + \frac{\hbar\omega_0}{4}\left[\left(a_{n+1}+a_{n+1}^+\right)^2\right. \\
& \left.-2\left(a_{n+1}+a_{n+1}^+\right)\left(a_n+a_n^+\right)\right] \\
& +V_0\left[1-\frac{\hbar}{m\omega_0 u_0^2}\left(a_n+a_n^+\right)^2+\frac{\hbar^2}{4m^2\omega_0^2u_0^4}\left(a_n+a_n^+\right)^4\right] \\
& +\frac{1}{16}\frac{C_a\hbar^2}{m\omega_0^2}\left[\left(a_{n+1}+a_{n+1}^+\right)-\left(a_n+a_n^+\right)\right]^4 \\
& +\frac{1}{2}M\left(\frac{dy_n}{dt}\right)^2+\frac{Mv_0^2}{2}\left(y_{n+1}+y_n\right)^2 \\
& +\chi\left(y_{n+1}+y_n\right)u_0^2 \\
& -\frac{\hbar}{2m\omega_0}\chi\left(y_{n+1}+y_n\right)\left(a_n+a_n^+\right)^2\Bigg\}. \qquad (8)
\end{aligned}
$$

The creation and annihilation operators of particles act on the lattice sites and they can be obtained in the Heisenberg picture using equation (8):

$$i\hbar\frac{\partial}{\partial t}a_n = [a_n, H] \qquad (9a)$$

$$i\hbar\frac{\partial}{\partial t}a_n^+ = \left[a_n^+, H\right]. \qquad (9b)$$

In order to solve the system (9a) and (9b), and as far the solitary excitations induced by the collective excitations for the protons and phonons, arising from the localized fluctuation of the protons and deformation of structure of the heavy ionic sublattice are concerned, a physically acceptable candidate for quantum states should be represented by the following quasi-coherent state [8]: from equation (8), we see that the motion of the proton is a nonlinear problem. In such a system, features of the proton are changed when compared with the bare proton. Thus the collective excitations for the protons and phonon, arising from the localized fluctuation of the protons and deformation of structure of the heavy ionic sublattice, have coherence. The wave function describing the collective excitations in the systems should be represented by the following quasi-coherent state:

$$|\Phi(t)\rangle = |\varphi(t)\rangle\,|\beta(t)\rangle \qquad (10)$$

with

$$|\varphi(t)\rangle = \frac{1}{\eta}\left(1+\sum_n \varphi_n(t)\,a_n^+\right)|0\rangle_{pr}, \qquad (11a)$$

$$|\beta(t)\rangle = e^{\frac{1}{i\hbar}\left[\sum_n\left[\theta_n(t)P_n-\pi_n(t)y_n\right]\right]}|0\rangle_{ph}, \qquad (11b)$$

where $|0\rangle_{pr}$ and $|0\rangle_{ph}$ are the ground states of the proton and the phonon, respectively. The terms $\theta_n(t) = \langle\Phi\,|y_n|\,\Phi\rangle$, and $\pi_n(t) = \langle\Phi\,|P_n|\,\Phi\rangle$ are three sets of unknown functions. η is a normalization constant and is taken equal to unity for the convenience of calculation. The present wave function of the proton, $|\varphi(t)\rangle$ is not an excitation state of a single particle, but rather a coherent state, or more accurately, a quasi-coherent state.

$$
\begin{aligned}
|\varphi\rangle &\sim \frac{1}{\eta}e^{\left[\sum_n \varphi_n(t)a_n^+\right]}|0\rangle_{pr} \\
&= \frac{1}{\eta}e^{\left[\sum_n\left[\varphi_n(t)a_n^+-\varphi_n^*(t)a_n\right]\right]}|0\rangle_{pr}. \qquad (12)
\end{aligned}
$$

Equation(12) is a standard coherent state. We retain only the two terms of the expansion of a standard coherent state, which mathematically can be justified in the case of small $\varphi_n(t)$, which can be viewed as an effective truncation of a standard coherent state. Therefore we refer to $|\varphi(t)\rangle$ in $|\Phi(t)\rangle$ as quasi-coherent state. However, it is not an eigenstate of a number operator $\hat{N} = \sum_n a_n^+ a_n$, since

$$\hat{N}\,|\varphi(t)\rangle = \left(\sum_n \varphi(t)_n a_n^+\right)|0\rangle_{pr} = |\varphi(t)\rangle - |0\rangle_{pr}. \qquad (13)$$

Therefore, the $|\varphi(t)\rangle$ represents a coherent superposition of the proton state with one quantum and the ground state of the proton. However, in this state the number of quanta are determinate, instead of commensurable, likely in the standard coherent state. To find out how many quanta this state contains, we have to compute the expectation value of the number operator $\hat{N}$ in this state and sum over the sites. The average number of quanta for this state is

$$
\begin{aligned}
N &= \langle\varphi(t)\,\left|\hat{N}\right|\,\varphi(t)\rangle \\
&= \sum_n \langle\varphi(t)\,\left|a_n^+ a_n\right|\,\varphi(t)\rangle \\
&= \sum_n |\varphi_n(t)|^2 = 1 \qquad (14)
\end{aligned}
$$

where we utilize the following relation

$$\sum_n |\varphi_n(t)|^2 = 1. \qquad (15)$$

Therefore, the above wavefunction of the proton is a quasi-coherent state containing one quantum. Thus, $|\Phi\rangle$ not only exhibits coherent features of collective excitations of the protons and phonons caused by the nonlinear interaction generated by proton-phonon interaction, but can make the numbers of protons maintain conservation in the Hamiltonian equation (8). The expectation value of the coordinate and the conjugate momentum are given by

$$\theta_n(t) = \langle\Phi(t)\,|y_n|\,\Phi(t)\rangle \qquad (16a)$$

$$\pi_n(t) = \langle\Phi(t)\,|P_n|\,\Phi(t)\rangle. \qquad (16b)$$

By considering the formulas of the expectation values of the Heisenberg equations operators θ_n and P_n, in the state $|\Phi(t)\rangle$ which contains coherent features of collective excitations of the protons and phonons caused by the nonlinear interaction generated by the proton-phonon interaction and makes the numbers of protons maintain conservation in the Hamiltonian equation (8), the equations

of motion satisfied by θ_n and φ_n are written as

$$M\frac{d^2\theta_n}{dt^2} = Mv_0^2\left(\theta_{n+1}+\theta_{n-1}-2\theta_n\right) - \frac{2\hbar}{m\omega_0}\chi\left(|\varphi_n|^2-|\varphi_{n-1}|^2\right), \quad (17)$$

$$-\frac{d^2\varphi_n}{dt^2} = 4\omega_0^2\varphi_n - 2\omega_0^2\left(\varphi_{n+1}+\varphi_{n-1}\right) - \frac{8V_0}{mu_0^2}\varphi_n - \frac{4\chi}{m}\left(\theta_{n+1}-\theta_n\right)\varphi_n + \frac{16V_0\hbar}{m^2\omega_0^2u_0^2}|\varphi_n|^2\varphi_n + \frac{4C_a\hbar}{m\omega_0}\left[\left(\varphi_n-\varphi_{n-1}\right)^3-\left(\varphi_{n+1}-\varphi_n\right)^3\right]. \quad (18)$$

The system of equations (17) and (18) constitutes coupled nonlinear differential-difference equations, of which, exact analytical solutions are unobtainable. These equations, however, can be treated analytically when we are interested in smooth waves or waves with long wavelengths compared with the lattice constant. We adopt a continuum approximation ($na = x$), in which the discrete fields $\varphi_n(t)$ and $\theta_n(t)$ are substituted by the corresponding continuous fields $\varphi(x,t)$ and $\theta(x,t)$. Thus, equations (17) and (18) can be represented by

$$\frac{\partial^2\varphi}{\partial t^2} = 2a^2\omega_0^2\left(\frac{\partial^2\varphi}{\partial x^2}\right) + \frac{12a^4C_a\hbar}{m\omega_0}\frac{\partial^2\varphi}{\partial x^2}\left(\frac{\partial\varphi}{\partial x}\right)^2 + \frac{4a\chi}{m}\varphi\left(\frac{\partial\theta}{\partial x}\right) - \frac{16V_0\hbar}{m^2\omega_0u_0^4}\varphi^3 + \frac{8V_0}{mu_0^2}\varphi \quad (19)$$

$$\frac{\partial^2\theta}{\partial t^2} = a^2v_0^2\left(\frac{\partial^2\theta}{dx^2}\right) - \frac{4a\hbar\chi}{Mm\omega_0}\varphi\left(\frac{\partial\varphi}{\partial x}\right) \quad (20)$$

where a is the lattice constant.

3 Kinkon excitations

In order to find, travelling waves at a constant velocity v, the partial differential equations (19) and (20) can be reduced to ordinary differential equations in the dimensionless variable s by the substitution: $s = \frac{x-vt}{a}$. Thus, equation (20) is integrated once to give

$$\frac{d\theta}{ds} = \frac{2\chi}{Mv_0^2\left(1-V_2^2\right)}\left(\frac{\hbar}{m\omega_0}\right)\varphi^2 + K_1. \quad (21)$$

Substituting equation (21) into equation (19) leads to

$$\left(V_1^2-1\right)\frac{d^2\varphi}{ds^2} = C_{nl}\left(\frac{d\varphi}{ds}\right)^2\frac{d^2\varphi}{ds^2} - g|\varphi|^2\varphi + \varepsilon\varphi, \quad (22)$$

where $V_1 = \frac{v}{a\sqrt{2}\omega_0}$ and $V_2 = \frac{v}{av_0}$ are the scaled soliton velocities of protons and heavy-ions, respectively. K_1 is an integral constant. C_{nl} is the parameter that controls the strength of the nonlinear coupling and is related to the anharmonic coupling coefficient C_a by the relation $C_{nl} = \frac{6C_a}{\omega_0^2}\left(\frac{\hbar}{m\omega_0}\right)$. $\chi_1 = \frac{\chi}{mC_0^2}$ and $\chi_2 = \frac{\chi}{Mv_0^2}$ are the parameters that control the strength of the coupling between the two interacting sublattices. g and ε are the shape parameters of the effective potentials which are defined by

$$g = \left[\frac{16V_0}{mu_0^4C_0^2} - \frac{8\chi_1\chi_2}{\left(1-V_2^2\right)}\right]\left(\frac{\hbar}{m\omega_0}\right) \quad (23a)$$

$$\varepsilon = \frac{8V_0}{mC_0^2u_0^2} - 4A\chi_1 \quad (23b)$$

respectively, with $A = -K_1$.

The first integral of equation (22) is

$$z^4 - 2z_0^2z^2 = \alpha\left(\varphi^2-\varphi_0^2\right)^2 - \frac{\varepsilon^2}{gC_{nl}} + K_2 \quad (24)$$

where $z = \frac{d\varphi}{ds}$, $z_0 = \sqrt{\frac{V_1^2-1}{C_{nl}}}$, $\alpha = \frac{g}{C_{nl}}$, $\varphi_0 = \sqrt{\frac{\varepsilon}{g}}$ and K_2, the constant of integration determined from the boundary conditions [12]. Equation (24) admits different kinds of excitations [12] among which, are kink excitations with compact support (kinkon). These kinkons are the localized structure of permanent profile and which explains the dynamics and transfer of proton in the hydrogen bonds systems and satisfy the classical boundary conditions [12,20]

$$\frac{d\varphi}{ds} \longrightarrow 0, \quad \varphi \longrightarrow \varphi_0, \quad \text{as} \quad s \longrightarrow \pm\infty$$
$$\frac{d\theta}{ds} \longrightarrow 0, \quad \text{as} \quad s \longrightarrow \pm\infty, \quad (25)$$

under the condition

$$0 = \left[\frac{16V_0}{mu_0^4C_0^2} - \frac{8\chi_1\chi_2}{\left(1-V_2^2\right)}\right]\left(V_1^2-1\right)^2 + \frac{12C_a}{C_0^2}\left[\frac{8V_0}{mC_0^2u_0^2} - 4A\chi_1\right]^2 \quad (26)$$

where $A = -K_1 = \frac{2\chi}{Mv_0^2\left(1-V_2^2\right)}\left(\frac{\hbar}{m\omega_0}\right)\varphi_0^2$.

Within these conditions, the implicit solution is given by:

$$\pm\frac{\sqrt{2}z_0}{\varphi_0}\left(s_{ltn}-s_0\right) = \arcsin\left(\frac{l}{\sqrt{2}}\frac{\varphi}{\varphi_0}\right) + \ln\left[t\sqrt{1-\frac{1}{2}\left(\frac{\varphi}{\varphi_0}\right)^2} + \frac{n}{\sqrt{2}}\frac{\varphi}{\varphi_0}\right] \quad (27)$$

where ln is the Neperian logarithm, $l = \pm1$, $t = \pm1$, $n = \pm1$, these symbols simply indicate the sign of each denoted term on the right-hand side of equations (27), and s_0 is defined by the chosen initial condition.

For the boundary condition

$$\varphi \to -\varphi_0 \quad \text{while} \quad s \to -\infty \quad \text{and,}$$
$$\varphi \to -\varphi_0 \quad \text{while} \quad s \to \infty, \quad (28)$$

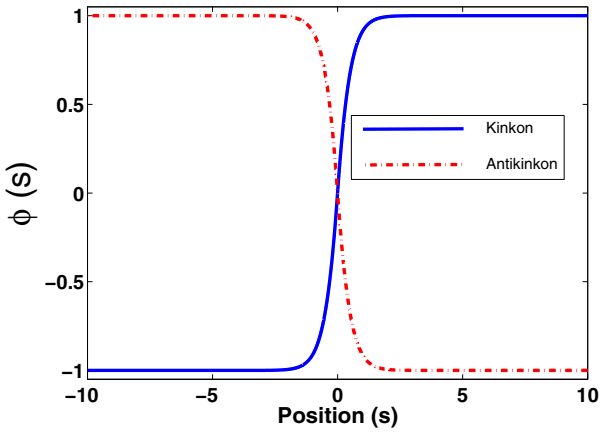

Fig. 1. Representation of the field of soliton solutions φ (for the proton) as a function of the position s, corresponding to the waveforms of kinkon structure according to equations (27) for $s_0 = 0$, $z_0 = 2$, and $\varphi_0 = 1$.

kinkons are given by

$$\begin{array}{llll} \dfrac{\sqrt{2}z_0}{\varphi_0}s_{+++} & \texttt{if} & \dfrac{\sqrt{2}z_0}{\varphi_0}s \in \,]-\infty, 0]\,, & \text{and} \\ -\dfrac{\sqrt{2}z_0}{\varphi_0}s_{-+-} & \text{if} & \dfrac{\sqrt{2}z_0}{\varphi_0}s \in [0, \infty[& \end{array} \tag{29}$$

and plotted in Figure 1.

Next, we evaluate the dynamical quantities such as the energy and momentum of the kinkon. The total energy which is transferred by a kinkon is expressed as

$$E = E_p + E_o + E_{int}. \tag{30}$$

To find this total kinkon energy, we can use the Hamiltonian H_p, H_o, and H_{int} in the continuum limit, respectively. Then, we obtain

$$E = \frac{\hbar v^2}{a\omega_0 V_1^2}\int_{-\infty}^{+\infty}\left[\frac{1}{2}\left(\frac{\partial\varphi}{\partial t}\right)^2 + \frac{1}{2}\left(\frac{\partial\varphi}{\partial x}\right)^2 - \frac{\varepsilon}{4a^2}\left(1-\frac{\varphi^2}{\varphi_0^2}\right)^2 + \frac{a^2 C_{nl}}{4}\left(\frac{\partial\varphi}{\partial x}\right)^4\right]dx, \tag{31}$$

whose integration gives

$$E = \frac{\hbar v^2\varphi_0}{a\omega_0 V_1^2}\left[\frac{\pi\sqrt{2}}{8}\left(1+v^2\right)\frac{\varepsilon}{\sqrt{\left(1-V_1^2\right)g}} - \frac{1}{32}\left(\sqrt{2}\left(6+\pi\right)\sqrt{g} + \sqrt{2}\left(\pi-2\right)\varepsilon\sqrt{\varepsilon}\right)\sqrt{\left(1-V_1^2\right)}\right]. \tag{32}$$

The kinkon describes the motion of the proton over the barrier of the double well potential in intrabond by a mechanism of jumping from one molecule to another (see Fig. 2). Thus the ionic defect occurred in the system. This proton kinkon are accompanied by the compression or

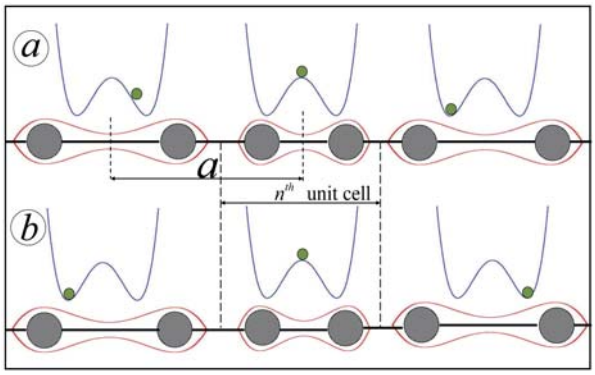

Fig. 2. Schematic representation of a soliton (an extended ionic defect) with both components. (a): a kinkon and, (b): an antikinkon in the proton sublattice and a localized compression of the heavy-ion sublattice.

rarefaction of the heavy ion sublattice around the protonic defect. Theses solitons with the plus sign in equation (27) represents a localized reduction in the proton density (expansion of the proton sublattice), arising from the motion of the kinkon soliton which amounts to creating a negatively charged carrier and extended ionic defect moving with the velocity v less than the speed of sound C_0. Therefore the soliton solution correspond to the OH^- ionic defect that appear in the Bernal Fowler picture. The other soliton solution with minus sign in $\varphi(x,t)$ in equation (27) represents the compression of the protonic sublattice and the increase of the localized proton density which amounts to creating a positively charged carrier and an extended ionic defect. Therefore it corresponds to the H_3O^+ ionic defect. Hence the solutions in equation (27) represent the proton transfer in the ionic defects in the intrabonds accompanied by a localized deformation of the heavy ionic sublattice. Contrary to the kink soliton in hydrogen bonded chain, or in other real physical systems which can be modelled by our system, the solutions obtained involves about a few number of protons only. Therefore, the present model seems to be more realistic and applicable to a system which consist of a small number of hydrogen bonds. Amongst others, it was shown by Tchofo et al. [37] that, despite the fact that the lattice discreteness of the system has some harmful effects on the dynamics of compactons such as the existence of the Peierls-Nabarro potential which provides pinning sites for compactons or a linear coupling which gives rise to a phonon band which enters in direct resonance with the internal modes of the compactons, causing radiation of energy away from the compactons, these types of solutions have an extraordinary capacity to execute a stable ballistic propagation in the system. These limiting factors are also strongly reduced for $mC_0^2 \simeq 0$ and $mC_a \gg 1$. In addition, the existence of a Goldstone mode in this parameter region makes possible a stable ballistic propagation for compactons. It was also shown by Xia et al. [38]. In their study of the propagation and collision of the compacton-like kinks in the system of an anharmonic discrete lattice with a double well one-site potential by direct algebraic method and numerical experiments that, the localisation

of the compactons is related to the nonlinear coupling parameter (C_a) the potential barrier height V_0 of the double well potential, the velocity of the propagation of the compacton as determined by the linear coupling parameter (mC_0^2), the nonlinear term (mC_a) and the localisation parameter. They also show by numerical experiments that appropriate (C_0) is suitable for a stable propagation of compacton.

On the other hand, we can also calculate the total field momentum of the kinkon(k)-antikinkon(ak) pair by

$$P = \frac{1}{a}\int_{-\infty}^{+\infty} \frac{\hbar}{\omega_0}\frac{\partial\varphi}{\partial x}\frac{\partial\varphi}{\partial t}dx + \frac{1}{a}\int_{-\infty}^{+\infty} M\frac{\partial\theta}{\partial x}\frac{\partial\theta}{\partial t}dx, \quad (33)$$

which corresponds to the usual relation between P and V for a moving kinkon-antikinkon

$$P = P_k + P_{ak} = M_{sol}V \quad (34)$$

with

$$M_{sol} = m_k^* + m_{ak}^*, \quad (35)$$

where

$$m_k^* = \frac{\pi\sqrt{2}\hbar\varepsilon^{\frac{3}{2}}}{4a^2\omega_0 g\left(1-V_1^2\right)^{\frac{1}{2}}}, \quad (36a)$$

$$m_{ak}^* = \frac{\sqrt{2}\left(6+\pi\right)\hbar^2\chi^2\varepsilon^{\frac{3}{2}}\left(1-V_1^2\right)^{\frac{1}{2}}}{2a^2Mv_0^4m^2\omega_0^2g^2\left(1-V_2^2\right)^2}, \quad (36b)$$

are effective masses of the kinkon and antikinkon, respectively, obtained after a suitable combination of the equations (21), (27) and (33). P_k and P_{ak} which may be rewritten as

$$P_k = -\frac{\hbar}{\omega_0}\frac{v}{a^2}\int_{-\varphi_0}^{+\varphi_0}\left(\frac{\partial\varphi}{\partial s}\right)d\varphi, \quad (37a)$$

$$P_{akk} = -\frac{Mv}{a^2}\int_{-\varphi_0}^{+\varphi_0}\left(\frac{\partial\theta}{\partial s}\right)^2\left(\frac{\partial\varphi}{\partial s}\right)^{-1}d\varphi, \quad (37b)$$

are the momentums of the kinkon and antikinkon, respectively.

4 Mobility and conductivity

Next, we discuss the physical properties such as the mobility and conductivity of the proton in hydrogen-bonded systems. Since the chain is neutral in the absence of any kind of defect in the normal case, with the occurrence of the solitons, arising from the displacement of the proton and distortion of the heavy ionic sublattice in the systems, a charge ($q = q_I + q_B$) deviating from the regular protonic charge distribution occurs and thus, the solitons are charged. q_I and q_B are the charge portions of ionic and bonded defects, respectively. If the hydrogen-bonded system is subjected to an applied external field, we have to incorporate the energy gained by the system. The responses of the protons and heavy ions to the force are different [9,36] and we denote the effects of the proton and the ion sublattices by different fields F_1 and F_2, respectively.

Among others, in real solids, the interaction between moving particles and other degrees of freedom of the lattice gives rise to a mechanism for the energy loss. This mechanism can be formally modeled by phenomenological damping coefficient λ_1 for the proton and λ_2 for the heavy ions.

Namely, the equations of motion (19) and (20) are replaced by the following equations

$$\frac{\partial^2\varphi}{\partial t^2} = f_1\left(\varphi,\theta\right) - \lambda_1\frac{\partial\varphi}{\partial t} - \sqrt{\frac{m\omega_0}{\hbar}}\frac{F_1}{m} \quad (38a)$$

$$\frac{\partial^2\theta}{\partial t^2} = \frac{f_2\left(\varphi,\theta\right)}{M} - \lambda_2\frac{\partial\theta}{\partial t} - \frac{F_2}{M} \quad (38b)$$

where the functions f_1 and f_2 are defined by the relations:

$$f_1 = 2a^2\omega_0^2\left(\frac{\partial^2\varphi}{\partial x^2}\right) + \frac{12a^4C_a\hbar}{m\omega_0}\frac{\partial^2\varphi}{\partial x^2}\left(\frac{\partial\varphi}{\partial x}\right)^2 + \frac{4a\chi}{m}\varphi\left(\frac{\partial\theta}{\partial x}\right) - \frac{16V_0\hbar}{m^2\omega_0u_0^4}\varphi^3 + \frac{8V_0}{mu_0^2}\varphi \quad (39)$$

$$f_2 = Ma^2v_0^2\left(\frac{\partial^2\theta}{\partial x^2}\right) - \frac{4a\hbar\chi}{m\omega_0}\varphi\left(\frac{\partial\varphi}{\partial x}\right) \quad (40)$$

respectively.

The linear mobility $\mu = \frac{\langle v\rangle}{F}$, which describes the steady-state mean atomic velocity $\langle v\rangle$ in response to the dc driving force F in the limit $F \to 0$, was considered in a number of works (e.g. see [34] and references cited therein). In general, the mobility μ should depend on F. As has been discussed, the total external potential $V_{tot}(\varphi) = V_{sub}(\varphi) - F\varphi$ is a corrugated plane, with an average slope determined by the external force F, where $V_{sub}(\varphi)$ is a periodic substrate (one-site) potential.

The external field and damping are considered small so that they lead only to a little change in the velocity of the kinkon-antikinkon pair, but does not alter its waveform. We also assume that, the forces F_1 and F_2 are only functions of the time and considering further the boundary conditions satisfied by $\varphi(x,t)$ and $\theta(x,t)$, then we can obtain the following equation from equations (33) and (38):

$$\frac{dv}{dt} + \gamma v = \frac{8a^2g^{\frac{1}{2}}}{\pi\sqrt{2}\varepsilon}\left(1-V_1^2\right)\left(m + \frac{2\left(6+\pi\right)\chi^2\left(1-V_1^2\right)}{\pi Mv_0^4g\left(1-V_2^2\right)^2\left(\frac{m\omega_0}{\hbar}\right)}\right)^{-1}F \quad (41)$$

with

$$\gamma = \frac{m\lambda_1 + \frac{2(6+\pi)\chi^2\left(1-V_1^2\right)}{\pi Mv_0^4g\left(1-V_2^2\right)^2\left(\frac{m\omega_0}{\hbar}\right)}\lambda_2}{m + \frac{2(6+\pi)\chi^2\left(1-V_1^2\right)}{\pi Mv_0^4g\left(1-V_2^2\right)^2\left(\frac{m\omega_0}{\hbar}\right)}} + \frac{1}{M_{sol}}\frac{dM_{sol}}{dt}$$

$$F = F_1 + B\left(\frac{m\omega_0}{\hbar}\right)^{\frac{1}{2}}F_2$$

$$B = \frac{\sqrt{2}\left(4+\pi\right)\chi\left(1-V_1^2\right)^{\frac{1}{2}}}{8Mv_0^2\left(1-V_2^2\right)g^{\frac{1}{2}}\left(\frac{m\omega_0}{\hbar}\right)}.$$

Since it was shown that the velocity of the kinkon-antikinkon pair is smaller than the sound speeds of the two sublattices, i.e., $V_1 \ll 1$, $V_2 \ll 1$ [35,36], then $g, \varphi_0, \varepsilon$ and γ are independent of time and equation (41) becomes

$$\frac{dv}{dt} + \gamma_0 v = \frac{8a^2 g_0^{\frac{1}{2}}}{\pi\sqrt{2}\varepsilon_0}\left(m + \frac{2\left(6+\pi\right)\chi^2}{\pi M v_0^4 g_0 \left(\frac{m\omega_0}{\hbar}\right)}\right)^{-1} F \tag{42}$$

with

$$g_0 = \left[\frac{16V_0}{mu_0^4 C_0^2} - 8\chi_1\chi_2\right]\left(\frac{\hbar}{m\omega_0}\right)$$

$$\varepsilon_0 = \frac{8V_0}{mC_0^2 u_0^2} - 4A_0\chi_1$$

$$\gamma_0 = \frac{m\lambda_1 + \frac{2(6+\pi)\chi^2}{\pi M v_0^4 g_0\left(\frac{m\omega_0}{\hbar}\right)}\lambda_2}{m + \frac{2(6+\pi)\chi^2}{\pi M v_0^4 g_0\left(\frac{m\omega_0}{\hbar}\right)}}$$

$$B_0 = \frac{\sqrt{2}\left(4+\pi\right)\chi}{8Mv_0^2 g_0^{\frac{1}{2}}\left(\frac{m\omega_0}{\hbar}\right)}.$$

The electric field force F and the electric field E are related through the equation [8]

$$F = q^* E = \left(q_k + B_0\sqrt{\frac{m\omega_0}{\hbar}}q_{ak}\right)E, \tag{43}$$

where q_k and q_{ak} are just the effective charges of the kinkon and antikinkon, respectively. The differential equation equation (42) leads to the expression of the kinkon-antikinkon pair velocity:

$$v\left(t\right) = v\left(0\right)e^{-\gamma_0 t} + \frac{8a^2 g_0^{\frac{1}{2}}}{\pi\sqrt{2}\varepsilon_0}\left[m\lambda_1 + \frac{2\left(6+\pi\right)\chi^2}{\pi M v_0^4 g_0\left(\frac{m\omega_0}{\hbar}\right)}\lambda_2\right]^{-1} q^* E\left(1 - e^{-\gamma_0 t}\right), \tag{44}$$

where $v\left(0\right)$ is the initial speed of the kinkon-antikinkon pair.

When $t \to \infty$, the system is in a steady state and the ultimate velocity of the kinkon-antikinkon pair yields

$$v\left(t\to\infty\right) = \frac{8a^2 g_0^{\frac{1}{2}}}{\pi\sqrt{2}\varepsilon_0}\left[m\lambda_1 + \frac{2\left(6+\pi\right)\chi^2}{\pi M v_0^4 g_0\left(\frac{m\omega_0}{\hbar}\right)}\lambda_2\right]^{-1} q^* E. \tag{45}$$

In such a state, a steady current can occur.

If we define the mobility of the $H_3 0^+$ ion as

$$v = \mu E, \tag{46}$$

where v is given by (45), the $H_3 0^+$ ion mobility is equal to

$$\mu = \frac{8a^2 g_0^{\frac{1}{2}}}{\pi\sqrt{2}\varepsilon_0}\frac{q_k + B_0\left(\frac{m\omega_0}{\hbar}\right)^{\frac{1}{2}} q_{ak}}{m\lambda_1 + \frac{2(6+\pi)\chi^2}{\pi M v_0^4 g_0\left(\frac{m\omega_0}{\hbar}\right)}\lambda_2}\left(\frac{m\omega_0}{\hbar}\right). \tag{47}$$

If the density n_0 of the kinkon-antikinkon pair is small enough to neglect the interaction of the kinkons, then we obtain the expression for the conductivity caused by migration of ionic and Bjerrum defects:

$$\sigma = n_0 q^* \mu = n_0 \frac{8a^2 g_0^{\frac{1}{2}}}{\pi\sqrt{2}\varepsilon_0}\frac{\left[q_k + B_0\left(\frac{m\omega_0}{\hbar}\right)^{\frac{1}{2}} q_{ak}\right]^2}{m\lambda_1 + \frac{2(6+\pi)\chi^2}{\pi M v_0^4 g_0\left(\frac{m\omega_0}{\hbar}\right)}\lambda_2}\left(\frac{m\omega_0}{\hbar}\right) \tag{48}$$

where n_0 is proton numbers in an unit volume. Although the analytical expression of mobility and electric conductivity do not depend explicitly on the parameter of anharmonicity C_a, they remain nevertheless implicitly related to this one by the parameters ε and g by the relation (26).

5 Comparison with experiments

Now, we can calculate the mobility of the $H_3 0^+$ ion from equation (47) and compare it with experiments on ice crystals since experimental data on their mobility and on the other properties required for our calculations are well known. In ice, the $H_3 0^+$ ions also move by jumps of the excess proton from one water molecular to the neighboring molecule in the crystal. The figure describes also the ice structure because each oxygen atom in the ice is linked by hydrogen bonds to four other oxygen atoms in an almost tetrahedral configuration. Only two protons are close to one oxygen atom (besides ionic defect states). In the figure, we represent the Bernal-Fowler filament in the form of an infinite periodic chain of water molecules produced by means of hydrogen bonds [1]. In such chain, every water molecule uses one proton for formation of a hydrogen bond while the lateral proton forms with the oxygen atom the covalent bond and does not take part in the proton transfer along the chain.

For ice crystal, the values of the parameters, for the temperature $T = -10\ ^o\mathrm{C}$ are: $a = 2.76$ Å, $u_0 = 0.39$ Å, $C_0 = 1.1 \times 10^4\,\mathrm{ms}^{-1}$, $v_0 = 0.1\ C_0$, $m = m_p$, $M = 17m_p$, $\chi = 0.15$ eV Å^{-3}, [9,16–18,35,36], $\omega_0 = \frac{C_0}{\sqrt{2}}$, $\lambda_1 \sim (0.6 - 0.7) \times 10^4\ \mathrm{s}^{-1}$, $\lambda_2 \sim (9.1{-}13) \times 10^4\ \mathrm{s}^{-1}$, $q_1 = 0.68e$, $q_2 = 0.32e$, $n_0 = 10^{22}\ \mathrm{mol}^{-1}$ [8,9,16–19]. Using these data we find the mobility

$$\mu = 5.307 \times 10^{-7}\ \mathrm{m}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1},$$

and the conductivity

$$\sigma = 6.11 \times 10^{-4}\ \Omega^{-1}\,\mathrm{m}^{-1}.$$

In the years (1950), some authors [21] have shown that the mobility of the proton in the ice, is about $(0.05{-}0.1) \times 10^{-4}\ \mathrm{m}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$. Only, the experiments of Nagle et al. [17,19] have also shown that, this mobility is much smaller and they have explained the difference between the above two results by a possible consideration of the surface conduction of the protons by the other authors. The currently values recorded in the literature are

of the order of $(5-10) \times 10^{-7}\ \mathrm{m^2\,V^{-1}\,s^{-1}}$ [21]; however, those values remain always much higher than the mobility of the other ions (like Li^+ and F^-) in the ice. The value of the mobility, μ, which we have obtained is much smaller than the old one and is in agreement with the experimental values of the transfer of the protons in the crystal of ice [17,19,21,36].

6 Conclusion

In summary, we have presented a study of a nonlinear model for the motion of defects in quasi one-dimensional hydrogen-bonded systems with an anharmonic two sublattice model. We have used the so-called kink compacton (kinkon) to study the conductivity of the proton transfer in the hydrogen-bonded systems by quantum mechanical method. We found the mobility and the electrical-conductivity of the proton transfer under an externally applied electrical-field. The result obtained are in qualitative agreement with experimental data for ice.

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