Transport properties in a hydrogen-bonded chain model including dipole-dipole interactions

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Abstract. The proton mobility and transport of energy in hydrogen-bonded chains is an interesting problem because they play a crucial role in the interpretation of certain biological processes. We propose a physical model which consists basically of two one-dimensional harmonically coupled sublattices corresponding to the oxygens and protons, respectively. Our study starts with an improved form of the Antonchenko–Davydov–Zolotaryuk (ADZ) model in which the dipole–dipole interactions due to the proton motion are introduced. These interactions may affect the response of the nonlinear excitations propagating along the chain. We look for a solution for which the motion of oxygen ions can be neglected. We find a Φ^5-type equation which admits nonlinear excitations of solitary-wave-type. In our mathematical approximation we find different classes of solution for the analytical description of the proton motion. The expressions and the corresponding necessary conditions for the existence of these solutions are given. We present numerical simulations for certain cases and examine the potential involved in the system. The introduction of the dipole interaction produces an influence on the electric field of the system which means that the proton motion is also affected, making the proton conductivity much easier. Finally, possible further extensions of the work are discussed.

1. Introduction: presentation of the physical background

The transport of protons in hydrogen-bonded systems, particularly in ice, remains a very interesting but also a long-standing problem. The introduction of new ideas from nonlinear physics [1, 2] has provided the possibility of various approximations. The study becomes even more important because of the close connection with the problem of proton transport across biological membranes—something which could explain the fundamental properties of life [3, 4].

Since the work of Bernal and Fowler [5] it has been recognized that the anomalously high mobility of protons in water cannot be explained by standard theories and that the hydrogen bonds can be modelled by a double-minimum potential. Now it is generally accepted that, in ice as well as in water, protons are transferred by jumps from one water molecule to another along hydrogen bonds and a migration of hydroxonium and hydroxyl ionic defects [6] takes place. However, there are still many questions to be answered as the detailed structures of the defects and the mechanism of their mobility are not yet well understood. As the soliton concept has been discussed extensively for the case of transport in biological macromolecules, it could be a possible mechanism in some of these processes [7, 8].

In the case of studies of the proton transfer processes in ice lattices it is usual to consider one-dimensional chains, called Bernal–Fowler filaments [5]. The geometry of these lines is
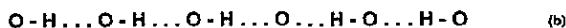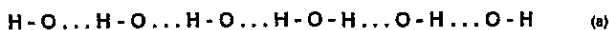
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H - O ... H - O ... H - O ... H - O - H ... O - H ... O - H   (a)

O - H ... O - H ... O - H ... O ... H - O ... H - O   (b)

Figure 1. Positive (a) and negative (b) charged ionic defects in the H-bonded chain (side groups are not shown).

not crucial and they can be considered as quasi-one-dimensional chains. In the normal state of the chain each proton is connected to an oxygen atom by a covalent bond on the one hand and a hydrogen bond on the other. It is accepted that the proton potential energy curve has the form of a double well with two minima corresponding to the two equilibrium states of a proton between two neighbouring oxygen atoms. A proton can be transferred either in the form of ionic defects or in the form of orientational (bonding or Bjerrum) defects (figures 1 and 2).
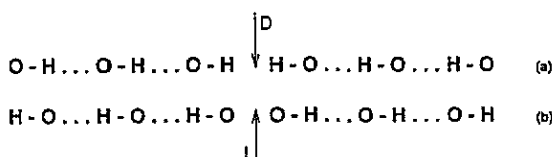
O - H ... O - H ... O - H $\overset{\textstyle\big| D}{\textstyle\big\Downarrow}$ H - O ... H - O ... H - O   (a)

H - O ... H - O ... H - O $\overset{\textstyle\big\Uparrow}{\textstyle\big| L}$ O - H ... O - H ... O - H   (b)

Figure 2. We present (a) positive (D) and (b) negative (L) orientational defects (these Bjerrum faults, as the violation of one of Bernal–Fowler rules, demand the presence of one and only one bonded proton ice-like structure.

At the beginning, charge transfer occurs at the expense of successive proton displacements between neighbouring oxygen atoms, i.e. the passage of an ionic defect. The position of the proton in the hydrogen bond is determined by a double-well potential as previously discussed (figure 3(a)). The proton displacement is controlled by the protonic elastic interaction induced in the model.
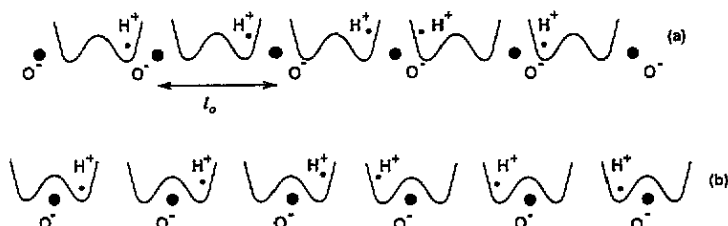

Figure 3. A double-well proton potential model of a positive ionic defect (a) and of a positive orientational defect (b).

When a proton approaches a molecule occupying a boundary of the chain it may form a covalent bond with the oxygen atom of the molecule and then the original proton moves to a neighbouring molecule. When this process is repeated, we have transport of protons along the chain. The chain then changes its state and the transport of protons is not possible in the same direction. This can be done only when a reorientation of OH groups takes

place by the second defect mechanism, known as Bjerrum faults in ice. To allow proton transport, it is necessary to return all the molecules to their initial positions. The motion of an orientational defect involves simple successive rotations of OH groups starting at one end of the chain and finishing at the other. Owing to these rotations we have the creation of a pair of D and L defects moving to different ends, and this can take place in any internal part of the chain. A sequence of rotations of all the molecules in a filament returns the chain to its original state. It follows that the motion of another proton can occur only after the passage of a Bjerrum defect. In figure 3 we present a potential model of a positive bonding defect.

The resultant proton current has two mutually related continuous components. The passage of a proton along a chain corresponds to the transport of 0.64 of the proton charge, while the remaining fraction, of 0.36, is carried by a Bjerrum defect [9]. This model of transport was proposed by Sokolov [10]. The theory of motion of Bjerrum defects has been described in [11, 12]. The transport of protons in the form of solitons was firstly considered in [1] and [13]. Antonchenko *et al* [1] have found, in their model, analytic solutions in the continuum approximation only for particular solitary wave velocities. Further work [2, 14] has given solutions for a far greater range of velocities and has also given remarkable results about the stability of these solutions. The problem was further pursued in a number of papers [15–18] in which a variety of theoretical extensions have been achieved. Other works have given a satisfactory number of numerical results [19] which contribute to the validity of the ADZ model. This model was really a successful attempt to approximate and explain mechanisms which occur in the atomic scale study.

The aim of this work is to examine the influences of dipole–dipole interactions on protonic conductivity in H-bonded chains. Simultaneously, we propose an analytical study of the nonlinear dynamics of the proton motion. In our study we consider an improved one-dimensional lattice model based on the ADZ model [1, 20] for H-bonded chains.

The emphasis is especially placed on the contributions of the dipole interactions due to the proton motion. The existence of electric dipoles along the chain can exert a strong influence on the system response and the proton conductivity can be enhanced. Since the discrete system is not always convenient for algebraic manipulations, we are faced with the continuum approximation of the microscopic model. This kind of approximation leads us to a Φ^6 equation which admits various localized solutions according to several selections and conditions. We conclude that ionic and orientational defects remain of the same importance as in previous works [2, 6] in order to explain protonic conductivity. Our study could also be extended in other related domains, but this will be the aim of future works.

The paper is organised as follows. In section 2 we construct the model which is based on the ADZ model. We introduce an appropriate bonding scheme in which the dipole interactions are of great importance. Then in section 3 we present the Hamiltonian of the system and obtain the equations of motion for a particular form of the dipole moment. The study is then limited to the case for which the heavy-ion sublattice is supposed to be fixed. Section 4 deals with the continuum approximation of the discrete system, which finally leads us to an equation of Φ^6 type, describing the proton motion. In section 5 we show different types of localized solution. Numerical simulations corresponding to the solutions are given and discussed in section 6. An analytical study of the system potential is examined in section 7. Section 8 discusses the results, and possible further extensions of the work are evoked.

2. Construction of the model

The model for an H-bonded chain, similar to that introduced by Antonchenko *et al* [1], consists of two interacting sublattices of harmonically coupled protons (mass m) and heavy ions (hydroxyl groups for ice or complex negative ions of mass M), as shown in figure 4.
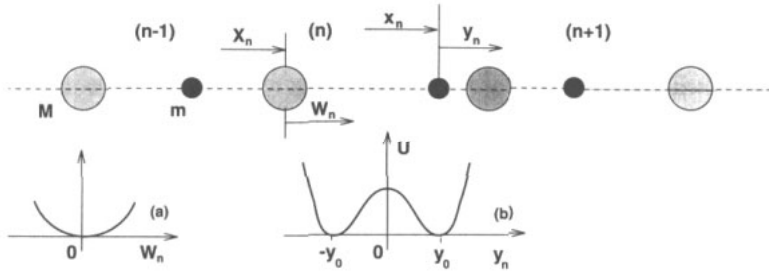

Figure 4. The one-dimensional lattice model for a hydrogen-bonded diatomic chain. We distinguish: (a) the harmonic potential for the heavy ions and (b) the double-well potential for protons.

This model can give an idea of the Bernal–Fowler filaments in ice [5]. It also represents more complex biological macromolecules in membranes [3, 4]. Each proton lies between a pair of heavy ions usually referred to as 'oxygens'. The proton is connected by a covalent and hydrogen bond with the two neighbouring oxygens. It is possible for a proton to jump from a position closer to one of the oxygens to a position closer to the next one. The proton overcomes the potential barrier. Next, the covalent and the hydrogen bond exchange their positions. The basic idea of the ADZ model is that the coupling between oxygen atoms and protons can provide a mechanism [14] which changes the potential barrier that protons have to overcome to jump from one molecule to another one, and facilitates the proton motion.

The bonding scheme that we use, consists of an harmonic oxygen–oxygen and hydrogen–hydrogen coupling, a nonlinear onsite potential and a nonlinear hydrogen–oxygen interaction. The proton experiences a double-well potential [21, 22] which can be chosen in the form

$$U(y_n) = \epsilon_0\left(1 - y_n^2/y_0^2\right)^2. \tag{1}$$

Because of the introduction of the onsite potential, we can expect topological excitations for the protons. In this paper we do not insist on the origin of the above potential, but it is assumed that the detailed interaction mechanism results in such a potential.

We give a schematic representation in figure 4. We note that in equation (1) y_n denotes the displacement of the nth proton with respect to the centre of the oxygen pair. ϵ_0 represents the height of the potential barrier and y_0 is the distance between the potential minima. We also note that in the chain, a local redistribution of charges is observed, as a result of the proton motion. A compression of the proton subsystem gives an extra positive charge while a rarefaction can provide an extra negative charge. For this reason, both ions can be connected with the motion of a certain type of domain wall [1].

The existence of electric dipoles in the chain, because of the electric charges, leads us to account for the mutual interaction between the dipoles. Protons belonging to a given chain are correlated with each other through the dipole interaction of O–H dipoles, which

provides a dominant contribution to the proton effective potential. In the general case, if we consider two successive dipoles, the interaction energy is defined by the expression

$$V_{int} = -\frac{2\mu_1\mu_2}{R_{12}^3} \tag{2a}$$

where μ_1 and μ_2 are the magnitudes of these dipoles and R_{12} is the distance between their centres of mass. The dipoles can be considered as a point, i.e. the length of each dipole is considerably less than R_{12}. This kind of assumption if fulfilled for a system of two OH oscillators arranged as in an ice or water network. If we note P_n, P_{n+1} the dipole moments of the nth and $(n+1)$th cells and r the distance between them, we can obtain an expression similar to equation $(2a)$ which describes the dipole energy and it is written as follows

$$V_{int} = \sum_n \frac{1}{2\pi\epsilon_{00}} \left[\frac{P_n P_{n+1}}{r^3} - 3\frac{(P_n r)(P_{n+1} r)}{r^5} \right] \tag{2b}$$

where ϵ_{00} is the dielectric constant in vacuum. Previous works [11, 12] and [23–25] have dealt with the problem of the dipole interactions. Along with previous works [19], we begin with a discrete model because it has already been found that, when reasonable parameter values are considered, the solutions are rather narrow.

3. The equations of the model

The total Hamiltonian of the system consists of four terms

$$H_{tot} = H_p + H_o + H_{int} + H_{dd}. \tag{3}$$

The proton part of the Hamiltonian is given as

$$H_p = \sum_n \left[\tfrac{1}{2}m\dot{y}_n^2 + U(y_n) + \tfrac{1}{2}m\omega_1^2(y_{n+1} - y_n)^2 \right]. \tag{4}$$

The first of the terms denotes the kinetic energy of the protons, the second term is the double-well potential while the third term represents the harmonic coupling with characteristic frequency ω_1 between neighbouring protons. The Hamiltonian of the basic sublattice of the heavy ions can be written as

$$H_o = \sum_n \left[\tfrac{1}{2}M\dot{w}_n^2 + \tfrac{1}{2}M\Omega_0^2 w_n^2 + \tfrac{1}{2}M\Omega_1^2(w_{n+1} - w_n)^2 \right]. \tag{5}$$

In the oxygen part of the Hamiltonian we consider only the relative displacement w_n between the two oxygens in a pair, because the variation of the O–O distance modifies the potential strength undergone by the protons. The first term denotes the kinetic energy of the oxygens, the second term represents the coupling between oxygens of the same cell, while the third term stands for the harmonic coupling between neighbouring oxygen pairs and takes into account the dispersion. (In the original ADZ model only optical vibrations were considered whereas in other works [19] acoustic vibrations were also included.) In our study Ω_0 and Ω_1 are characteristic frequencies of the optical modes.

The Hamiltonian H_{int} represents the coupling between proton displacements and heavy-ion displacements. This term takes into account the fact that, because of the proton displacement, the distance between the neighbour oxygen atoms can change. In other words

we can have a lowering of the double potential barrier due to the oxygen displacements that is due to the variation of the O–O distance. In the ADZ model we write

$$H_{int} = \sum_n \delta w_n \left(y_n^2 - y_0^2 \right). \tag{6}$$

Analytical solutions have been obtained [26] with a slight generalization of H_{int} by changing the $(y_n^2 - y_0^2)$ term into a general function $W(y_n)$. In equation (6), δ measures the strength of the coupling between the two sublattices and determines the amplitude of the distortion in the oxygen sublattice. In so far as the parameters of the model such as the harmonic lattice frequencies ω_1, Ω_1, Ω_0, the coupling constant δ, the barrier energy ϵ_0 and the width y_0 of the potential are concerned, we note that some values have already been proposed in a previous paper [19], but the question still remains open as there is always the possibility of improving the validity of the obtained results.

The Hamiltonian H_{dd} is derived from the dipole interactions. We note that the double-well potential considers, by its nature, the dipole–dipole interactions in the case where we study the equilibrium state of the system. This kind of interaction becomes valuable when the protons move along the H-bonded chain. Otherwise, when they stay at their equilibrium positions the dipole–dipole interaction is well described by the double-well potential acting on protons.

It is known that water molecules have a permanently constant dipole moment. The dipole–dipole energy is a function of the distance r and the angle between the dipole vector and the distance vector r [27]. In the present case, it is assumed that the distance r between neighbouring dipoles does not depend on the lattice displacement and all vectors of the dipole moment P_n are aligned. We can easily calculate the expression for H_{dd} and it becomes

$$H_{dd} = \overline{\beta} \sum_n P_n P_{n+1}. \tag{7}$$

($\overline{\beta}$ is a constant which may account for the environment of the chain). The dipole moment induced by the proton motion is zero when proton is at either position of the oxygen or when it is in the middle of the distance joining the oxygen pair where the interactions are opposite. In figure 5 we present this law for the dipole schematically. We consider r to be the O–H distance, while the O–O distance is denoted as R. The dipole moment of a water molecule [28] is zero at $(r/R) = 0$ and at $(r/R) = \pm 1$ because the water molecules would have become neon atoms. At $(r/R) = \frac{1}{2}$ the hydrogen atoms are midway between the oxygen atoms, the dipole moment is also zero and it changes sign as r/R passes through 0, $\frac{1}{2}$ and 1.
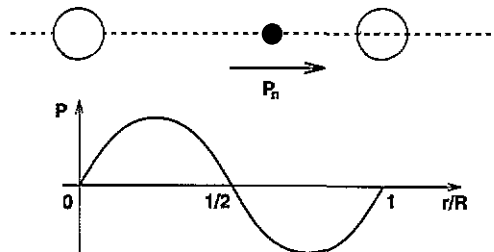

Figure 5. The microscopic electric dipole as a function of the proton position with respect to the nearest heavy ion positions.

The simplest form for the dipole moment P to approximate the structure of the curve in figure 5 can be given by a polynomial of the third degree

$$P_n = \bar{\alpha}(x_n - X_n)(x_n - X_{n+1})\left[x_n - \tfrac{1}{2}(X_n + X_{n+1})\right] \tag{8}$$

where $\bar{\alpha}$ is a constant. The absolute positions x_n and X_n are shown in figure 4 and we have

$$x_n = nl_0 + \tfrac{1}{2}l_0 + y_n \qquad X_n = nl_0 + w_n \qquad X_{n+1} = (n+1)l_0 + w_{n+1}. \tag{9}$$

We note that l_0 is the lattice spacing (it is about 5 Å, a value often met in real hydrogen-bonded systems).

From the Hamiltonian (3) and after simple calculations we find the motion equations of the system which form a set of coupled nonlinear differential-difference equations as below

$$\frac{d^2 y_n}{dt^2} = \omega_1^2(y_{n+1} - 2y_n + y_{n-1}) + (4\epsilon_0/my_0^2)\left(1 - y_n^2/y_0^2\right)2y_n - (2\delta/m)w_n y_n$$

$$\qquad - \bar{\beta}\frac{\partial P_n}{\partial y_n}(P_{n+1} + P_{n-1}) \tag{10a}$$

$$\frac{d^2 w_n}{dt^2} = \Omega_1^2(w_{n+1} - 2w_n + w_{n-1}) - \Omega_0^2 w_n - (\delta/M)\left(y_n^2 - y_0^2\right) - \bar{\beta}\frac{\partial P_n}{\partial w_n}(P_{n+1} + P_{n-1})$$

$$\qquad - \bar{\beta}\frac{\partial P_{n-1}}{\partial w_n}(P_n + P_{n-2}). \tag{10b}$$

These two equations cannot be solved analytically. For this reason any attempt of further mathematical analysis becomes extremely difficult.

We study the case for which the heavy-ion sublattice can be considered as 'frozen'. This type of approximation is related to the inertia of the oxygen sublattice which cannot follow the fast proton motion especially for large velocities, and this suggests that solution involves only the proton displacement while oxygens stay at rest and do not practically participate in the motion.

We can assume that w is very small compared to y. In the atomic lattice, y is of the order of few Å and for this reason we suppose that w is almost zero. The above assumption leads us to consider only the Hamiltonians H_p and H_{dd}. It is convenient to rewrite the equations of motion in a dimensionless form. Then, we introduce the units E_0 for energy, t_0 for time and l_0 for length. This system of units is introduced in order to facilitate the numerical computations and to enable the comparison of the results with experiments. We can easily find the derived units $m_0 = E_0 t_0^2/l_0^2$ for mass and $f_0 = \epsilon_0/l_0$ for force. The next step is to introduce the dimensionless parameters $\tilde{m} = m/m_0$, $\epsilon = \epsilon_0/E_0\tilde{m}$ and $\chi_1 = -\bar{\beta}\bar{\alpha}^2 l_0^6/E_0\tilde{m}$. Then, the energies are expressed in eV, masses in atomic mass units (amu) and displacements in Å. This defines a time unit (tu) equal to 1.0217×10^{-14} s; the frequency unit (tu^{-1}) is 0.9787×10^{14} Hz which is of the order of the lattice vibration frequencies in solids; and the energy unit $E_0 = 1.24 \times 10^{-4}$ eV. The parameters involved in the model are $l_0 = 5$ Å, $m = 1$(amu) and $M = 17$(amu) (hydroxyl group), $\epsilon_0 = 2$ eV and $y_0 = 1$ Å [14, 19, 21, 22]. The parameters are consistent with the values met in real hydrogen-bonded systems (for instance, ice). We set $u_n = y_n/l_0$, $u_0 = y_0/l_0$, $\tilde{H} = H/ml_0^2$, $c_0 = l_0/t_0$ and $G = 4\epsilon_0/ml_0^2$. With these new units, the Hamiltonian of the proton lattice can be written as

$$\tilde{H} = \sum_n \left[\tfrac{1}{2}\dot{u}_n^2 + \tfrac{1}{2}\omega_1^2(u_{n+1} - u_n)^2 + \tfrac{1}{4}G_0 u_0^2\left(1 - u_n^2/u_0^2\right) - \chi P_n P_{n+1}\right] \tag{11}$$

where the electric dipole is merely given by

$$P_n = u_n\left(u_n^2 - \tfrac{1}{4}\right). \tag{12}$$

Now, the equations of the discrete system describing the proton motion are reduced to

$$\ddot{u}_n = \omega_1^2\left(u_{n+1} - 2u_n + u_{n-1}\right) + G_0 u_n\left(1 - u_n^2/u_0^2\right) + \chi\left(3u_n^2 - \tfrac{1}{4}\right)\left[u_{n+1}\left(u_{n+1}^2 - \tfrac{1}{4}\right)\right.$$

$$\left. + u_{n-1}\left(u_{n-1}^2 - \tfrac{1}{4}\right)\right] \tag{13}$$

with $G_0 = 4\epsilon_0/l_0^2 u_0^2$ and $\chi = \chi_1 E_0/m l_0^2$.

4. The continuum approximation

The set of nonlinear differential equations for a discrete system is not manageable. Therefore, the next step to the somewhat rough simplification consists in considering the continuum approximation. We assume that the displacements are slowly varying over the lattice spacing. In the approximation, only terms up to the second-order are retained and the contribution of higher-order terms is not significant. Moreover, terms of the form $u(u_x)^2$ are neglected because this is the contribution of a nonlinear term involving the space variation of the displacement. The equation of the proton motion can be written as

$$u_{tt} - \left[1 + \chi\left(3u^2 - \tfrac{1}{4}\right)^2\right]u_{xx} - \alpha_1 u + \beta_1 u^3 - \gamma_2 u^5 = 0 \tag{14}$$

where we have set

$$\alpha_1 = G_0 + \chi/8 \qquad \beta_1 = G_0/u_0^2 + 2\chi \qquad \gamma_1 = 6\chi. \tag{15}$$

We note that all three parameters α_1, β_1 and γ_1 depend on χ, which is also present in the factor of u_{xx}. Because of this last remark, further investigation becomes extremely difficult. Thus we try to simplify the procedure by proposing the following hypothesis: we can set $1 + \chi(3u^2 - \tfrac{1}{4}) = \tilde{C}_0$ as a function of u. This function has two minima. If we consider a certain value of χ we can find the mean value $\langle \tilde{C}_0 \rangle$ and then we set $\langle \tilde{C}_0 \rangle$ as the coefficient of u_{xx}. This rough approximation has significance when there is no great difference between the greatest and the lowest values of the function. This occurs if the coefficient χ is considered as small enough such that $|\chi| \ll 1$. We now set $\langle \tilde{C}_0 \rangle = \omega^2$ and the equation for study takes on the form

$$u_{tt} - \omega^2 u_{xx} - \alpha_1 u + \beta_1 u^3 - \gamma_1 u^5 = 0. \tag{16}$$

We consider the following variable changes $u = \alpha U$, $t = \gamma T$, $x = \beta X$ with $\alpha = \sqrt{\beta_1/\gamma_1}$, $\gamma = \sqrt{\gamma_1}/\beta_1$, $\beta = \omega\sqrt{\gamma_1}/\beta_1$ (it must be that $\gamma_1 > 0$, $\beta_1 > 0$). It is also set that $A = \alpha_1\gamma^2$. At last, the equation becomes

$$U_{TT} - U_{XX} = AU - U^3 + U^5. \tag{17}$$

We are interested in localized solutions with a constant profile, moving at a characteristic velocity v, that is, solutions $U = U(\xi)$ where $\xi = X - vT$ is a shifted coordinate. We can now obtain an ordinary differential equation for the single variable ξ. We do not dwell on the algebraic manipulations to find out the different classes of solutions.

5. Different types of localized solutions

The equation of the proton motion presents a symmetry, so when U is a solution then $(-U)$ is also a solution. We set $U_1 = U(\xi \to -\infty)$ and $U_2 = U(\xi \to +\infty)$. We distinguish between types of solutions as we try to approach U_2 beginning from U_1, or the inverse.

(a) For the solution of type I (pulse) we have $U_1 = U_2 = 0$. The corresponding mathematical expression is

$$U = \pm \frac{U_m}{[1 + P \sinh^2(\Omega \xi /2)]^{1/2}} \tag{18}$$

where $U_m^2 = \pm 4A/(\sqrt{1 - A/A_0} \pm 1)$ and $P = 2\sqrt{1 - A/A_0}/(\sqrt{1 - A/A_0} \pm 1)$. The $(+)$ sign corresponds to supersonic waves ($|v| > 1$) and for this case we have also the condition $0 < A < A_0$. The $(-)$ sign corresponds to subsonic waves ($|v| < 1$) and for this case it must be necessarily considered $A < 0$. In both cases we have $A_0 = 3/16$ and $\Omega^2 = 4A/(v^2 - 1)$.

(b) The solution of type III represents a kink. In this case we have two opposite non-zero values ($U_1 = U_0$, $U_2 = -U_0$) and the expression is given by

$$U = \frac{\pm U_0 \tanh z}{[1 + P(1 - \tanh^2 z)]^{1/2}}. \tag{19}$$

Where we have defined $z = \frac{1}{2}\Omega\xi$, $P = U_0^2/(2U_0^2 - \frac{3}{2})$, $\Omega^2 = 4U_0^2(U_0^2 - \frac{1}{2})/(v^2 - 1)$. The definition for U_0 is given by $(U_0^{\pm})^2 = (1 \pm \sqrt{1 - 4A})/2$, as in the solution of type I, the $(+)$ sign corresponds to supersonic waves (it must be additionally $A < \frac{3}{16}$ and $A \neq 0$), and the $(-)$ sign corresponds to subsonic waves (it must be $A < \frac{1}{4}$ with $A \neq 0$ and $A \neq \frac{15}{64}$).

(c) For a solution of the type IV, we have $U_1 = U_2 \neq 0$. After calculations, we arrive at

$$U = \pm \frac{U_0}{[(P + 1) \tanh^2 z - P]^{1/2}}. \tag{20}$$

In this case we put $P = U_0^2/(2U_0^2 - \frac{3}{2})$, $\Omega^2 = 4U_0^2(U_0^2 - \frac{1}{2})/(v^2 - 1)$. The constant value U_0 is now defined by $(U_0^{\pm})^2 = (1 \pm \sqrt{1 - 4A})/2$. Once more, the $(+)$ sign corresponds to supersonic waves which can be defined when we consider $\frac{3}{16} < A < \frac{1}{4}$. The $(-)$ sign corresponds to subsonic waves. Now we must consider $A < \frac{1}{4}$ with $A \neq 0$, $A \neq \frac{15}{64}$.

(d) Finally, a particular case (type II) occurs, when $A = \frac{3}{16}$ and the solution represents a kink describing a transition from the state $U_1 \neq 0$ to the state $U_2 = 0$. This solution, which exists only in the case of a supersonic wave ($|v| > 1$) takes the form

$$U = \pm \frac{1}{[k_1 \exp(\pm\Omega\xi) + \frac{4}{3}]^{1/2}} \tag{21}$$

with $\Omega = \frac{1}{2}\sqrt{3/(v^2 - 1)}$ and k_1 is an arbitrary constant.

In table 1 we have gathered the possible types of solutions according to the range of A variation.

6. Numerical simulations

In this section we examine the dynamical behaviour of the solutions found in the previous part. It is important to study the stability of these solutions as well as the validity of the continuum approximation. We propose a numerical scheme by directly considering the

Table 1. Different types of solutions according to the variation of A. We present the existence of a certain type of solution.

| A Solutions	$A \geqslant \frac{1}{4}$	$\frac{1}{4} > A > \frac{3}{16}$	$A = \frac{3}{16}$	$\frac{3}{16} > A > 0$	$0 > A$
Type I supersonic				Solution exists	
Type I subsonic					Solution exists
Type II only supersonic			Solution exists		
Type III supersonic				Solution exists	Solution exists
Type III subsonic		Solution exists if $A \neq \frac{15}{64}$		Solution exists	Solution exists
Type IV supersonic		Solution exists			
Type IV subsonic		Solution exists if $A \neq \frac{15}{64}$		Solution exists	Solution exists
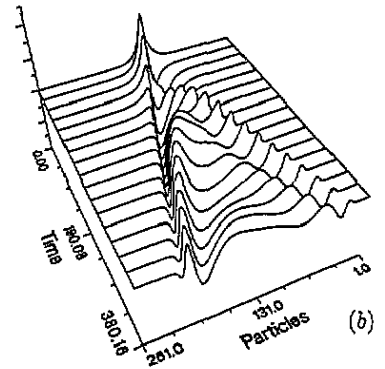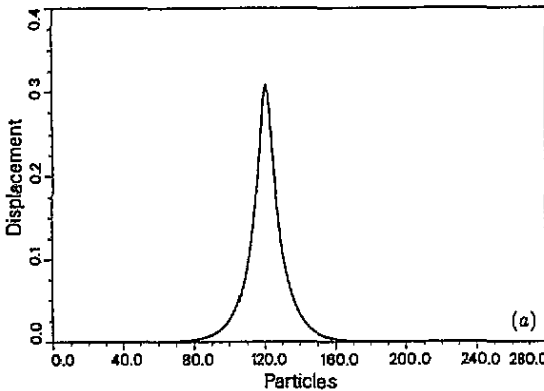
Figure 6. (*a*) A solution of type I (pulse). We present the subsonic case for $v = 0.1$. (*b*) Numerical simulation of the proton displacement.

equations of motion (13) of the discrete system, when the heavy ions are frozen. The resolution is realized by means of a Runge–Kutta method of the fourth order. We suppose that the conditions at lattice ends are periodic or pseudo-periodic (solutions of types II and III). The initial conditions for the displacements and the velocities of each lattice particle are given by the analytical expression of each type of solution (I, II, III, IV).

In figure 6(*a*) we present a solution of type I, corresponding to a subsonic pulse. The selected parameters are $\omega_1^2 = 0.065$, $G_0 = 0.00042$, $u_0 = 0.365$ and $\chi = 0.018$. The phase velocity is $v = 0.1$. The width of this pulse contains about 30 particles which means that the continuum limit is satisfied. In figure 6(*b*) we present the evolution of the excitation. After a short lapse of time, this pulse splits into two other pulses (a positive and negative
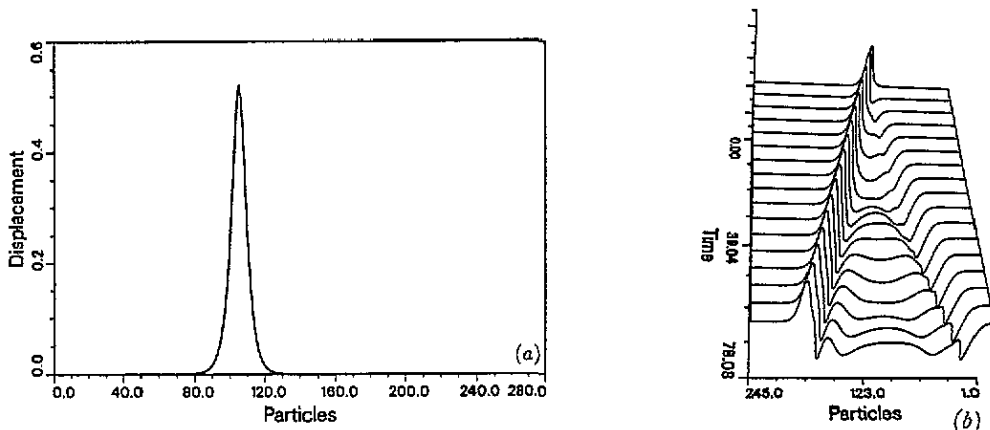
Figure 7. (a) Solution of the pulse-type I (supersonic case $\nu = 1.12$). (b) Time evolution of the solution.

one) travelling in the opposite directions. We can remark that the amplitudes of these pulses evolve as time elapses. The type I subsonic solution is found to be unstable.

The supersonic case is illustrated in figure 7(a). The observed pulse is more narrow (compared to the previous subsonic pulse), it contains about 20 particles. The parameters for the simulation are $\omega_1 = 1.0$, $G_0 = 0.0025$, $u_0 = 0.365$ and $\chi = 0.008$. The phase velocity is $v = 1.12$. We present the dynamical evolution of this pulse in figure 7(b). The observed behaviour is entirely different from that of the subsonic case. We again have a pulse which is propagating to the left and its amplitude remains quasi-constant. Simultaneously we observe a secondary negative pulse travelling in the opposite direction. The supersonic solution is also unstable.
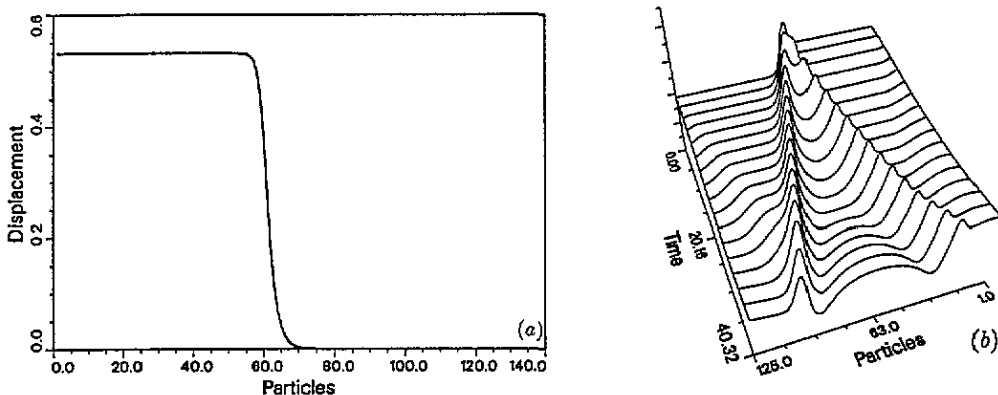

Figure 8. (a) A solution of type II which possesses a profile similar to a kink. (b) Time evolution of the solution.

In figure 8(a) we give a schematic representation of the solution of type II. This particular solution corresponds to a transition from the state $u = 0$ to the state $u = \sqrt{3}/2$ for the proton displacements (equation (21)). The parameters are $\omega_1 = 1.0$, $G_0 = 0.0016$, $u_0 = 0.365$ and the coefficient of the dipole–dipole interaction is obtained by considering $A_1 = \frac{3}{16}$ which

corresponds to $\chi = 0.3425$. Only the supersonic case is shown with $v = 1.10$. This solution contains about five particles. The evolution time is given in figure 8(b). It is obvious that the profile is unstable. After the appearance of a hump in the extension of the wave front, this solution splits into two other pulses propagating in opposite directions; the pulse on the left is greater than the pulse on the right. There is a remarkable similarity between the evolution corresponding to this case and that of type I. This is evident since the solution of type II is, in fact, a limiting case of the solution of type I, when $A_1 \rightarrow \frac{3}{16}$.
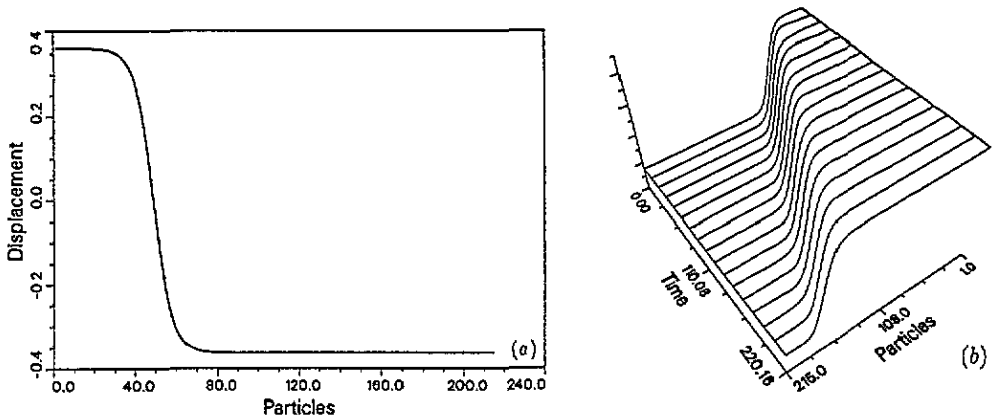

Figure 9. (a) A stable kink solution of type III. (b) Numerical simulation of the proton motion.

In figure 9(a) we present the kink solution of type III (equation (19)), corresponding to a proton transition from the well $u = -u_0$ to the well $u = +u_0$. The selected parameters are $\omega_1 = 1.0$, $G_0 = 0.0025$, $u_0 = 0.365$, $\chi = 0.008$ and the phase velocity is $v = 0.45$ (for the subsonic case). The kink contains at least 20 particles, which means that the continuum approximation is valid. We illustrate the dynamic behaviour of the solution in figure 9(b). The kink is remarkably stable and it favours the coherent motion of protons. The supersonic case is qualitatively identical to the subsonic one.
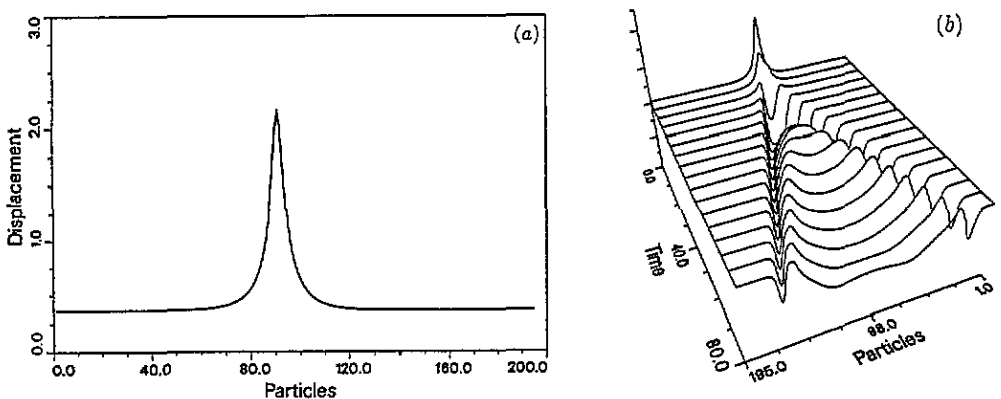

Figure 10. (a) A solution of type IV (subsonic case $v = 0.12$). (b) Numerical simulation of the model for the subsonic excitation of the type IV.

The solution of type IV is given in figure 10(a) (subsonic case). We have considered the parameters $\omega_1 = 1.0$, $G_0 = 0.0012$, $u_0 = 0.365$, $\chi = 0.5$ and the phase velocity is $v = 0.12$. The evolution is shown in figure 10(b) where the amplitude is reduced and the pulse is finally reversed. Then the initial pulse is divided into two other pulses of equal amplitudes propagating in opposite directions. This solution is unstable.
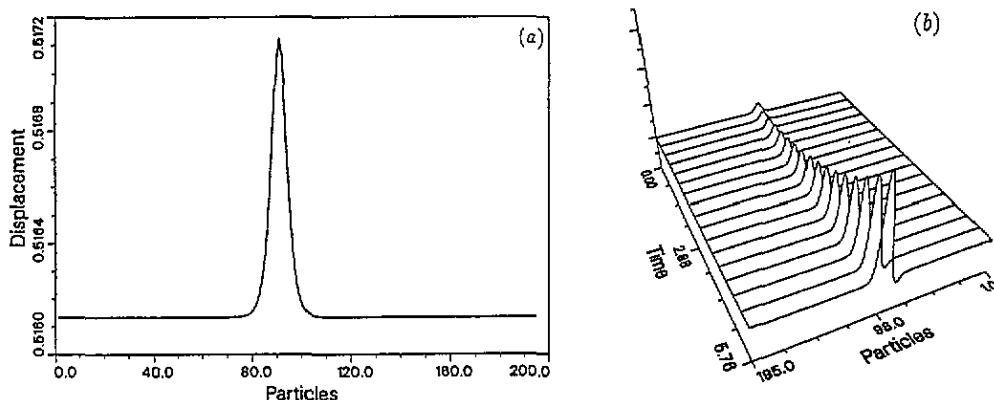

Figure 11. (a) A solution of type IV (supersonic case $v = 1.5$). (b) Numerical simulation of the proton motion corresponding to the supersonic solution of type IV.

Finally, the supersonic case corresponding to a solution of type IV (for a phase velocity $v = 1.5$) is presented in figure 11(a). We have set $\omega_1 = 1.0$, $G_0 = 0.0012$, $u_0 = 0.365$ and $\chi = 0.5$. The initial condition is slightly different from that of the subsonic case, but in both cases the width of the pulse is about 20 particles. We can observe that the form of the solution does not practically change. However, the amplitude increases gradually and after a finite time the solution collapses. It is evident that there exists a 'strong' instability.

After the above remarks it becomes obvious that only the kink solution of type III is stable. This is the reason why this kink can guarantee that a hopping mechanism of proton transport across the barrier of the Φ^2 potential is valid. The movement of protons characterized by the stable kink solution can be interpreted as the propagation of an ionic defect in the H-bonded chain.

7. Study of the potential of the system

It can be noted that equation (17) can be derived from the following Hamiltonian

$$H = \int \left[\tfrac{1}{2}U_T^2 + \tfrac{1}{2}U_X^2 + \psi(U) \right] \mathrm{d}x \tag{22}$$

where the potential ψ is defined by

$$\psi(U) = \tfrac{1}{2}AU^2 - \tfrac{1}{4}U^4 + \tfrac{1}{6}U^6. \tag{23}$$

The first term in the Hamiltonian (22) denotes the kinetic energy, the second term holds for the linear interaction (elastic) and the third part is the potential of Φ^5-type. On looking for solutions with a constant profile and moving at constant phase velocity v, that is, a function
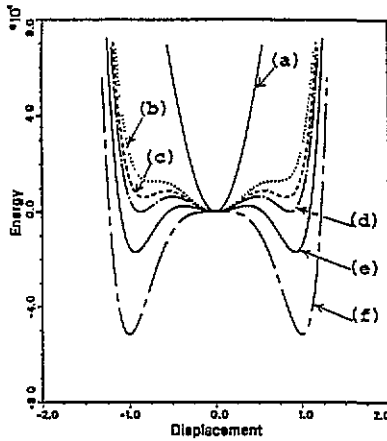
Figure 12. The potential ψ as a function of the proton displacement U for different values of A: (a) $A > \frac{1}{4}$, (b) $A = \frac{1}{4}$, (c) $\frac{3}{16} < A < \frac{1}{4}$, (d) $A = \frac{3}{16}$, (e) $0 < A < \frac{3}{16}$ and (f) $A < 0$.

of the variable $\xi = X - vT$, the Hamiltonian formulation yields the first integral of the motion

$$\frac{1}{2}\left(v^2 - 1\right)\left(U_\xi\right)^2 = \psi(U) - \psi_0 \tag{24}$$

where ψ_0 is a constant of integration. Now, it is clear that the properties of the potential (23) play an important role in the existence and stability of the localized solutions described in section 6. The potential (23) is sketched in figure 12 according to the values of A.

Then, several cases can be distinguished.

(i) For $A > \frac{1}{4}$ there is only one minimum of ψ at $U = 0$ (curve (a) in figure 12) and no localized solution exists.

(ii) For A such that $\frac{3}{16} < A < \frac{1}{4}$, (curve (c)) the potential possesses two symmetric metastable minima and two maxima while at $U = 0$ we have the stable minimum. For this case, supersonic solutions of type IV can exist with $\psi_0 = \min \psi(U) \neq 0$.

(iii) A particular case occurs for $A = \frac{3}{16}$ and the potential (23) possesses three equivalent stable minima at $U = \pm\sqrt{3}/2$ and $U = 0$ (curve (d)). A solution of type II exists for this situation which represents the transition from the minimum at $U = 0$ to that at $U = \sqrt{3}/2$ (or $U = -\sqrt{3}/2$). Moreover, only supersonic waves with $\psi_0 = 0$ are solutions.

(iv) When $0 < A < \frac{3}{16}$, the potential has two non-zero stable minima whereas the minimum at $U = 0$ is metastable (curve (e)). The choice $\psi_0 = 0$ leads to a pulse-like supersonic solution of type I. For $\psi_0 = \min \psi(U) \neq 0$, we have a kink solution of type III, both are supersonic waves. Subsonic solutions of type IV can exist by taking $\psi_0 = \max \psi(U) \neq 0$.

(v) Finally, for $A < 0$, the potential is similar to a symmetric double-well potential with two symmetric stable minima at a non-zero value of U (curve (f)). If $\psi_0 = 0$, we have a subsonic solution of type I (pulse-like solution) and of type III (kink).

This discussion can be compared to the result summarized in table 1. Roughly speaking, the stability of the solutions is ascertained if $\lim_{\xi \to \pm\infty} U = U_0$ is the global minimum of the potential $\psi(U)$. This occurs only for kink solutions of type III. Nevertheless, a detailed analysis based on the Lyapunov method will be in order to check the stability of every solutions [29, 30].

A depends on χ ($A = \alpha_1 \gamma_1 / \beta_1^2$ and see equation (15)) and it determines the dipole–dipole interaction. If we consider the case of ice, we can choose values for the different parameters involved in the model which are consistent with the recent literature on the subject [19, 28]. For a good choice of the parameters [19], χ can be estimated about 0.3. The barrier for the effective potential can be calculated

$$\Delta \psi = \tfrac{1}{24}\big[(1 - 6A) + (1 - 4A)^{3/2}\big] \tag{25}$$

for $A < \tfrac{1}{4}$. In a first approximation where χ/G_0 is rather small and going back to the expression of A in terms of the microscopic parameters, an estimate of the potential barrier can be written as

$$\Delta \psi \simeq \tfrac{1}{4}\Big(G_0 u_0^2\Big)\Big[1 - 36\chi u_0^2\Big]. \tag{26}$$

Note that, if χ is neglected, we recover the barrier of the double-well potential. It is also clear that the role of the dipole interaction is to lower the potential barrier and proton motion is therefore favoured.

8. Discussion

This paper is a first report on the effects of the dipole–dipole interaction on the proton motion. This type of interaction produces an influence on the electric field of the system and the proton conductivity can become easier. In the framework of our model we have focused our attention on the dynamics of the proton sublattice. The negative ion sublattice as well as the rest of the atomic environment has been considered 'frozen' and their influence on the dynamics of the protons is therefore neglected. In real systems, protons interact with their neighbours via dipole–dipole interactions which have been described in a crude approximation, by the simple nearest-neighbour harmonic interactions. In our model we have introduced an additional dipole interaction term in the Hamiltonian of the system. This has been done in order to approach the response of the system due to the contribution of these significant interactions. Thus, the proton transfer is materialized through the formation and migration of lattice defects, represented by topological solitonic excitations.

The description of the ionic and orientational defects associated with the protonic conductivity remains of the same importance as in Φ^4 case [14]. The coupling between the protons and the heavy ions in H-bonded chains has a strong influence on the dynamics of the ionic defects in the system. In the present analytical approach we have determined several possibilities for the solution describing the proton motion according to the values of parameters, since the resulting equation possesses stable, unstable and metastable steady states. The existence of a Φ^6 equation gives the possibility of a variety of solutions in a greater range than in previous studies [1, 2, 14–17, 19]. This potential approaches the initial form only for certain values of χ, which is connected with the dipole interaction. Otherwise we may obtain different forms (as in figure 12) with five critical points, corresponding to a more complex transition from the one state to the other.

We have found different types of solutions for the proton displacement. For each of them we have presented a direct relation with the effective potential of the system. The height of the effective potential barrier can be estimated to be ∼2 eV or ∼0.43 eV if we use two different sets of values for the parameters [19]. For the actual values chosen for the numerical simulations, the height of the potential barriers that protons have to overcome in order to jump from one molecule to the other can be found to be decreased due to the consideration of the dipole interactions.

The problem of the continuum approximation can still be investigated, as there are other possible cases which can be studied in more detail.

Another important point consists of considering, in a future work, a different, probably sinusoidal form of the dipole moment [28], rather than the polynomial form of the third degree. The initial model can be extended and enriched by the introduction of an external electric field applied on the protons (something which has been achieved in technical applications). Previous work has been done [14, 16] for constant and variable fields in time without the consideration of dipole interaction. As the real system is three-dimensional, it is clear that the one-dimensional model provides a simplified description of the system. For this reason we can introduce damping to explain the transfer of energy to extra degrees of freedom.

A further step is to consider a rotational motion of the dipoles, especially if we deal with nonlinear atomic chains. It would also be interesting to examine how the response is modified by the introduction of second-nearest-neighbour interactions and more. From our first results it is found that there are remarkably interesting mechanisms which could probably explain some of the most fascinating phenomena occuring at the microscopic scale.

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