LA-UR 91-2882

LA-UR--91-2882

DE92 000306

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SUBMITTED TO: The Proceedings of the NATO ARW Conference "Collective Proton Transport in Hydrogen Bonded Systems" held in Crete, Greece, May, 1991

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FORM NO 836 R4
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Proceedings of the NATO ARW " Collective proton transport in Hydrogen Bonded Systems "
Heraklion, Crete, Greece, May 1991

# THERMAL GENERATION AND MOBILITY OF CHARGE CARRIERS IN COLLECTIVE PROTON TRANSPORT IN HYDROGEN-BONDED CHAINS.

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## I. INTRODUCTION

The transport of protons in hydrogen-bonded systems is a long standing problem which has not yet obtained a satisfactorily theoretical description. Although this problem was examined first for ice, it is relevant in many systems and in particular in biology for the transport along proteins or for proton conductance across membranes, an essential process in cell life. This broad relevance makes the study of proton conduction very appealing. Since the original work of Bernal and fowler on ice[1], the idea that the transport occurs through chains of hydrogen bonds has been well accepted. Such "proton wires" were invoked by Nagle and Morowitz[2] for proton transport across membranes proteins and more recently across lipid bilayers[3]. In this report, we assume the existence of such an hydrogen-bonded chain and discuss its consequences on the dynamics of the charge carriers. We show that this assumption leads naturally to the idea of soliton transport and we put a special emphasis on the role of the coupling between the protons and heavy ions motions. The model is presented in section II. In section III we show how the coupling affects strongly the dynamics of the charge carriers and in section IV we discuss the role it plays in the thermal generation of carriers. The work presented in section III has been performed in 1986 and 87 with St Pnevmatikos and N. Flytzanis[4] and was then completed in collaboration with D. Hochstrasser and H. Büttner[5]. Therefore the results presented in this part are not new but we think that they are appropriate in the context of this multidisciplinary workshop because they provide a rather complete (and tractable) example of the soliton picture for proton conduction. Section IV discusses the thermal generation of the charge carriers when the coupling between the protons and heavy ions dynamics is taken into account. The results presented in this part are very recent and will deserve further analysis but they already show that the coupling can assist the formation of the charge carriers.

Since the results presented here consider only the ionic defects along a pre-existing hydrogen bonded chain they give a partial view of the proton transport mechanism. However, since the coupling between the motion of the carriers and the dynamics of the underlying lattice generates a very characteristic response, we hope that these

results might suggest some experimental test of the soliton picture for proton transport.

## II. The Antonchenko-Davydov-Zolotariuk model.

Since the original work of Bernal and Fowler[1], it is now accepted that, in ice as well as in water, protons are transferred by jumps from one water molecule to another along hydrogen bonds (fig. 1 a). According to this mechanism the charge carriers are $H_3O^+$ and $OH^-$ ionic defects. However the motion of these defects is not sufficient to explain a permanent proton conductivity since, after one defect as passed, the chain is left in a state that cannot carry charge in the same direction again.

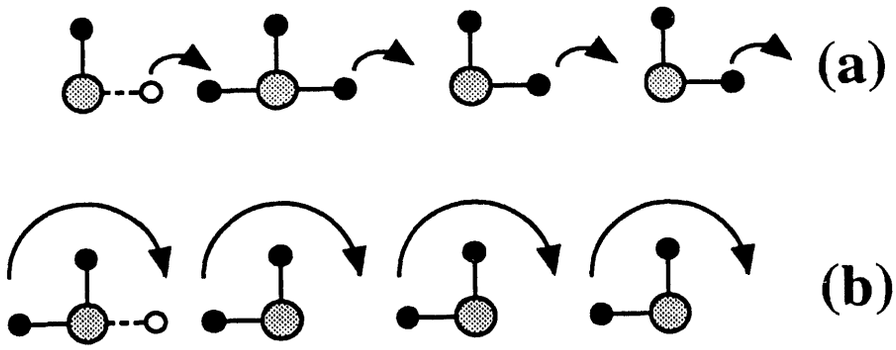


Figure 1: (a) Schematic picture of proton transport according to the Bernal Fowler mechanism. The figure presents the case of an $H_3O^+$ ionic defect. (b) Motion of a Bjerrum defect across an hydrogen bonded chain. The defect restores the chain in a state that can again carry charge according to the Bernal Fowler mechanism.

The chain has to be restored to its original state by another type of defect which rotates the water molecules, the so-called Bjerrum defects[6] (fig 1 b). In 1978 Nagle and Morowitz[2] extended the ideas of Bernal and Fowler and Bjerrum to membrane proteins, showing the great biological importance of proton transport across an hydrogen-bonded chain. However, in their model, the dynamics of the charge carriers was not described quantitatively. The first model describing this dynamics was proposed by Antonchenko-Davydov-Zolotariuk[7]. It combined a well known soliton model, the $\phi^4$ model[8], and the dynamics of the heavy ions. This ADZ model only describes the $H_3O^+$ and $OH^-$ ionic defects. Other models were introduced later to combine the ionic and Bjerrum defects in a single description[9], or to introduce other degrees of freedom of the heavy ions not included in the original ADZ model[5,10]. However, although this is not generally mentionned, these extended models are dependent on the actual crystal geometry while the ADZ model can be introduced by general arguments independent of the geometry of the chain. Moreover the ADZ model is easily tractable analytically and describes the essential features of the hydrogen bonded chain. This is why, in this report, we have chosen to restrict our discussion to this particular model.

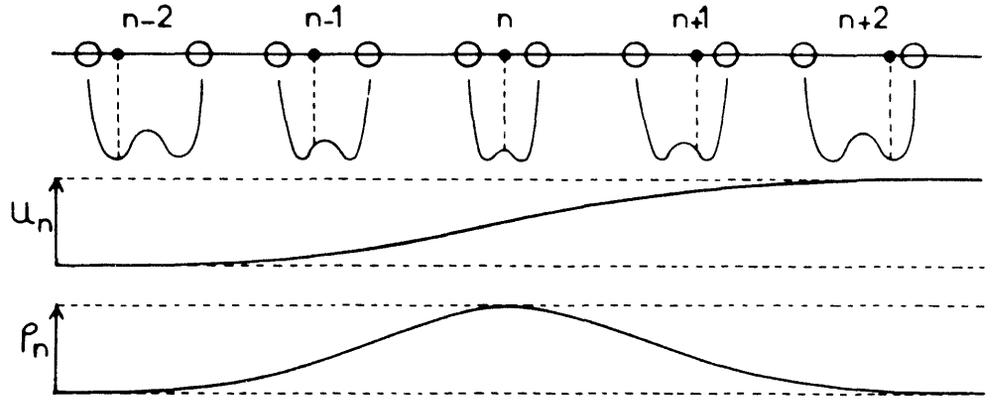


Figure 2: Picture of the Antonchenko-Davydov-Zolotariuk model showing the chain with the proton potentials, and a example of the solution of the equations of motion.

A schematic drawing of the ADZ model is shown in fig. 2. It consists of a chain of protons and heavy ions (which are henceforth called "oxygens" although they can be $OH^-$ or more complicated entities depending on the system). A classical description of the dynamics of this chain could in principle be derived from the hypersurface of potential energy as it can be obtained from ab-initio calculations. However, this potential energy depends on all the variables in the system and cannot be used as such to obtain a model which is analytically tractable. The main idea of all the soliton models is to select in the potential energy the part which is relevant for proton transport and split it into several components relative to the proton sublattice, the oxygen sublattice, and the coupling between the two sublattices. The different terms can be justified if we consider a simple prototype hydrogen-bonded system, the proton-bound water dimer[11] $(H_2O\ H\cdots OH_2)^+$. This system can be characterized by two parameters, the distance $X$ between the oxygens and the position $u$ of the bonding proton (note that, by choosing only these parameters which are the most relevant parameters for the bonding-proton dynamics, we have already greatly simplified the expression of the potential energy of the system). Ab-initio calculations show that, when $X$ has its equilibrium value, there are two energetically degenerate positions for the bonding-proton, close to one oxygen or close to the other. If $X$ is maintained fixed, the transfer of the proton between the two sites requires to overcome a potential energy barrier between the sites so that the potential energy for the proton has the shape of a double well. But if $X$ is allowed to vary, the proton transfer is accompanied by a reduction in the oxygens distance which lowers significantly the potential energy barrier. In some compounds the barrier can even vanish completely[12]. This effect is described in the ADZ model by writting the potential energy of the proton as the sum of a double well potential depending only on the proton position $u$, and an interaction term that depends both on $u$ and the distance of the two adjacent oxygens. The model must also take into account the existence of a stable equilibrium distance $a$ between neighboring oxygens by adding a term in the potential energy which, for simplicity, is chosen as a harmonic potential for the variable $\rho = a - X$. Moreover the hypersurface of potential energy couples any variable in the chain to any other. It is reasonable to assume that the shortest inter-

actions are the dominant ones. The interactions between adjacent atoms are already described by the terms mentionned above. The ADZ model considers in addition the interactions between neighboring protons and between neighboring oxygen pairs. The hamiltonian of the chain is written as

$$H = H_P + H_O + H_{int} \,, \tag{1}$$

The proton part is

$$H_P = \sum_n \frac{1}{2} m \left( \frac{du_n}{dt} \right)^2 + U(u_n) + \frac{1}{2} m \omega_1^2 (u_{n+1} - u_n)^2$$

where the index $n$ designates the unit cells and $m$ is the proton mass. The first term is the kinetic energy term, $U(u_n)$ is the double well potential obtained for fixed $X$ in the ab-inito calculations. It is written as

$$U(u_n) = \epsilon_0 (1 - u_n^2/u_0^2)^2 \,, \tag{2}$$

and the last term represents the harmonic coupling with characteristic frequency $\omega_1$ between neighboring proton. In the double well expression $U(u_n)$, $\epsilon_0$ is the height of the potential barrier between the two equilibrium sites situated at the positions $u = \pm u_0$.

The oxygen part is

$$H_O = \sum_n \frac{1}{2} M \left( \frac{d\rho_n}{dt} \right)^2 + \frac{1}{2} M \Omega_0^2 \rho_n^2 + \frac{1}{2} M \Omega_1^2 (\rho_{n+1} - \rho_n)^2 \,. \tag{3}$$

$M$ is the oxygen mass, $\Omega_0$ is the frequency of the optical mode corresponding to the oscillations of the distance between adjacent oxygens and $\Omega_1$ characterizes the coupling between neighboring oxygen pairs.

The interaction part is

$$H_{int} = \sum_n \chi \rho_n (u_n^2 - u_0^2) \,, \tag{4}$$

where $\chi$ measures the strength of the coupling between the proton and hydrogen sublattices. The expression of the interaction potential in the ADZ model is interesting because it is both physically relevant and mathematically convenient. It describes correctly the interaction because if $\rho_n$ increases (*i.e.* the distance between two adjacent oxygens decreases), the addition of the interaction potential to $U(u_n)$ generates a double well potential with a lower barrier and closer minima. Moreover, the specific form of $H_{int}$ gives equations of motions which, in some cases, reduce to the well known $\phi^4$ model and are thus solvable.

The comparison between the results of the ab-initio calculations and the ADZ model shows that this model provides a rather natural description of the hydrogen-bonded chain. It includes indeed some approximations since the hypersurface of potential energy has been severely simplified and because some degrees of freedom of the oxygens are ignored since an oxygen pair is described by a single variable $\rho_n$. The model does not include an overall translation of the pair, *i.e.* the acoustic modes of the oxygen sublattice. But, as the main change in the distance between adjacent oxygens is caused by a local optical motion, the approximation is reasonable.

## III. Mobility of the charge carriers in the ADZ model.

The mobility of the carriers can be determined by investigating the dynamics of the ADZ model. We show in this section that its equations of motion have two solitonlike solutions which correspond to the $H_3O^+$ and $OH^-$ ionic defects and we discuss the dynamics of these solutions.

The hamiltonian (1) generates a set of coupled differential equations for the $u_n$ and $\rho_n$ that cannot be solved analytically, but, if the nearest neighbor couplings between protons and between oxygen pairs are strong enough, one can use a continuum approximation which replaces a set of functions $u_n(t)$ by the two-variable function $u(x,t)$, and similarly for the $\rho_n(t)$ which are replaced by $\rho(x,t)$. Within this approximation, the original set of coupled differential equations is replaced by two coupled PDE's

$$u_{tt} - c_0^2 u_{xx} - \frac{4\epsilon_0}{m u_0^2} u \left(1 - \frac{u^2}{u_0^2}\right) + \frac{2\chi}{m}\rho u = 0 \,, \tag{5}$$

$$\rho_{tt} - v_0^2 \rho_{xx} + \Omega_0^2 \rho + \frac{\chi}{M}(u^2 - u_0^2) = 0 \,, \tag{6}$$

where $x = na$ is the continuous space variable, $c_0 = a\omega_1$ is the sound speed in the proton sublattice, and $v_0 = a\Omega_1$ is a parameter which characterizes the dispersion of the oxygens optical mode. A charge carrier moving at speed $v$ is described by a permanent profile solution, *i.e.* a solution which depends only on $\xi = (x - vt)/a$. The equations of motion are therefore reduced to

$$\frac{1}{a^2}(c_0^2 - v^2) u_{\xi\xi} + \frac{4\epsilon_0}{m u_0^2} u \left(1 - \frac{u^2}{u_0^2}\right) - \frac{2\chi}{m}\rho u = 0 \,, \tag{7}$$

$$\frac{1}{a^2}(v^2 - v_0^2)\rho_{\xi\xi} + \Omega_0^2 \rho + \frac{\chi}{M}(u^2 - u_0^2) = 0 \,. \tag{8}$$

Analytical solutions of this set of coupled equations are only known in some particular cases. If the coupling between the two sublattices vanishes ($\chi = 0$), Eq. (7) reduces to the $\phi^4$ equation[8] which has kinklike permanent profile solutions, while equation (8) is simply linear. In the presence of the coupling, an exact analytical solution can only be obtained for the particular speed $v = v_0$ because, in this case, Eq. (8) gives an expression of $\rho$ as a function of $u$. Introducing this expression in Eq. (7), we get

$$\frac{1}{a^2}(c_0^2 - v^2) u_{\xi\xi} + \frac{4}{m u_0^2}\left(\epsilon_0 - \frac{\chi^2 u_0^4}{2\Omega_0^2 M}\right) u \left(1 - \frac{u^2}{u_0^2}\right) = 0 \,, \tag{9}$$

which is again the standard $\phi^4$ equation with a renormalized barrier $\epsilon$ between the two proton sites

$$\epsilon = \epsilon_0 - \frac{\chi^2 u_0^4}{2\Omega_0^2 M} \,. \tag{10}$$

The simplicity of this equation is due to the special form chosen for the interaction

term in the hamiltonian. Equation (9) has kinklike solutions

$$u = \pm u_0 \tanh(\xi/L) \,, \tag{11}$$

where $L$ measures the kink width and is given by

$$\frac{1}{L^2} = \frac{2}{m\omega_1^2 u_0^2}\left(\epsilon_0 - \frac{\chi^2 u_0^4}{2\Omega_0^2 M}\right)\frac{1}{1 - v^2/c_0^2} \,. \tag{12}$$

The corresponding solution in the oxygen sublattice has a bell shape

$$\rho = \rho_0 \mathrm{sech}^2(\xi/L) \quad \text{with} \quad \rho_0 = \chi u_0^2/M\Omega_0^2 \,. \tag{13}$$

This solution is shown in fig. 2 with the plus sign for $u$. The figure shows that the kink in $u$ generates a local reduction in the proton density, which amounts to creating a negatively charged carrier in the chain. This solution corresponds to the $OH^-$ defect in the Bernal Fowler picture. The other solution with a minus sign in $u$ increases the local proton density and it corresponds to the $H_3O^+$ defect. Both are accompanied by a local reduction in the distance between adjacent oxygens which is associated to a decrease in the effective barrier for the protons. The kink solutions of the $\phi^4$ model are not solitons in the strict sense because they don't survive collisions with simply a phase shift. However they are stable solitonlike structures which propagate with a constant shape and speed. Therefore this particular solution for $v = v_0$ suggests that the coupling between the two sublattices assists the proton transport because it makes the jump from one position to the other easier by lowering locally the potential energy barrier. However the investigation of the dynamics of the model for other velocities shows that this is not always the case.

For $v \neq v_0$, an exact analytical solution cannot be obtained and we have to rely on numerical methods. A scheme using an effective hamiltonian has been recently designed to find permanent profile solutions moving at any speed[10], but we can also take advantage of the exceptional stability of the solitonlike solutions we are looking for to use the system itself as an equation solver. The idea is to run a molecular dynamics simulation in which a static solution obtained by energy minimization is forced to move at the desired speed by an external force. A small damping is added to absorb the radiations emitted while the static solution is accelerated. When a steady state is achieved, the external force and damping are gradually removed. This procedure shows that the two velocity domains $v \leq v_0$ and $v > v_0$ are fundamentally different.

(i) for $v \leq v_0$, a permanent profile solution exists and when the external force and damping are removed, it propagates freely at constant speed. An approximate analytical description of this solution can be derived because the shape of the kink in the proton sublattice is only weakly modified by the coupling with the oxygens. Therefore it is well approximated by the solution of Eq. (9) with $v < v_0$ although this equation does not treat Eq. (8) exactly in this case. Then the displacements in the oxygen sublattice are obtained by solving Eq. (8) with a known $u$ solution, *i.e.* by treating the oxygen motions as if they were forced by a given proton kink. The amplitude of the oxygen pulse obtained by this approach is in good agreement with the numerical results.

(ii) for $v > v_0$, there are no permanent profile solutions. The numerical simulations show that, as the kink in the proton sublattice propagates, instead of being accompanied by a localized solution in the oxygen sublattice, it radiates waves in this sublattice. The same approximate analytical treatment as for $v \leq v_0$ shows that Eq. (8) forced by a kink in $u$ moving at velocity $v > v_0$ has no localized solution. The radiation in the oxygen sublattice corresponds to a transfer of energy from the proton kink so that a proton kink launched at a speed $v > v_0$ slows down until its speed reaches $v_0$ where the radiation stops.

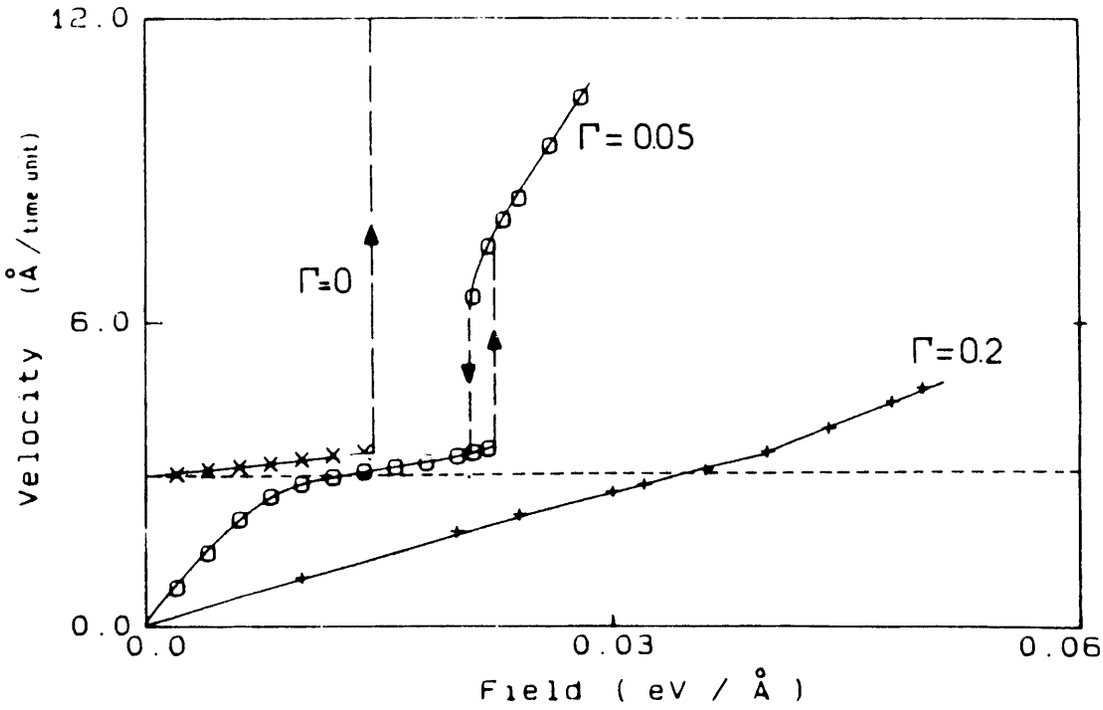


Figure 3: Velocity of the proton kink driven by an external field as a function of the field strength for several values of the damping coeffiecient $\Gamma$. The horizontal dotted line indicates the velocity $v_0$. Note the hysteresis phenomena for $\Gamma = 0.05\ 10^{14}\ s^{-1}$.

Therefore, whereas for $v \leq v_0$ the coupling between the two sublattices is assisting the motion of the charge carriers, for $v > v_0$ it has an opposite effect. This generates a strong nonlinearity in the mobility of the carriers when they are submitted to an external field. We have determined this mobility by carrying numerical simulations in the presence of an external field. When it drives the ionic defect, the field feeds energy in the system. In a three-dimensional system part of this energy is distributed among many degrees of freedom which are not included in the one-dimensional ADZ model. This energy transfer has been approximately modelled by adding a phenomenological damping term in the equations of motion. Figure 3 shows the equilibrium velocity $v_f$ of the proton kink as a function of the applied field $F$ for different values of the damping coefficient $\Gamma$.

Without damping ($\Gamma = 0$) there is an abrupt discontinuity in $v_f$ when $F$ reaches a critical value $F_c$. For $F < F_c$, the velocity of the solitary wave is always larger than $v_0$ and increases very slowly with $F$ (plateau in fig. 3). For $F > F_c$, $v_f$ jumps to a value close to $c_0$ where it is limited by discreteness effects which cause radiation in the proton sublattice[13]. In the presence of damping this abrupt discontinuity is smoothed out but, for intermediate damping, some hysteresis is found in the charge carrier mobility when $F$ is increased to a value larger than the critical value and then decreased. Consequently the numerical results show a very strong nonlinear response of the charge carriers to an external field. This behavior is due to the coupling between the two sublattices and can be understood if one considers the balance between the energy transmitted to the carriers by the external field and the energy they radiate in the oxygen sublattice when their speed exceeds $v_0$[4]. In the absence of damping, the proton kink does not lose any energy as long as its velocity is smaller than $v_0$ and thus any small $F$ drives it to a velocity above $v_0$ where the radiation can compensate the energy input due to $F$. But an analytical calculation shows that the radiated energy exhibits a maximum for a speed slightly higher than $v_0$. At very high speed, the heavy oxygens atoms cannot follow the fast proton motion and the energy transferred to the oxygens decreases. The existence of this maximum in the radiated energy explains the existence of a critical field $F_c$. For $F > F_c$, the radiation cannot balance the energy input, hence the jump to very high carrier speed. In the presence of damping, the balance has to take into account the energy loss due to damping. The plateau is reduced and there is now a limited equilibrium speed when $F$ exceeds $F_c$. A complete analysis shows that the hysteresis observed numerically can be understood within the same framework[4]. Consequently the mobility of the charge carriers in the ADZ model is controlled by the coupling between the charge carriers and the host lattice which results in a strongly nonlinear response.

## IV. Thermal generation of charge carriers.

The analysis of conductivity experiments in hydrogen-bonded systems generally assume that the number of ionic defects is fixed. At low temperature some of them are trapped by defects or inhomogeneities and they are gradually released when temperature increases. One may ask however if the thermal *creation* of ionic defects is possible. This section examines this question. As for the mobility of the carriers, we show that the coupling between the proton and the oxygen sublattice has a strong influence.

The first step to determine whether thermal creation is possible is to compute the energy of an ionic defect. This is the energy of the solitonlike solutions determined previously and, for $v = v_0$ it is given by

$$E(v_0) = \frac{8}{3\sqrt{2}} \frac{\sqrt{m}}{\sqrt{1 - v_0^2/c_0^2}} \frac{c_0}{a} u_0 \sqrt{\epsilon}(1 + C) , \tag{14}$$

with

$$C = \frac{4}{5} \frac{v_0^2}{c_0^2} \frac{\chi^2 u_0^2}{m M \Omega_0^2} . \tag{15}$$

The coupling between the two sublattices appears in two places in this formula.

Table I. Energies $E$ of ionic defects for different parameter sets.

| $\epsilon_0$ | $u_0$ | $\omega_1$ | $\Omega_0$ | $v_0/c_0$ | $\chi$ | $\epsilon$ | $C$ | $E$ |
|---|---|---|---|---|---|---|---|---|
| 2.0 eV | 1 Å | 2.21 | 0.184 | 0.192 | 0.1 | 1.99 eV | $4\ 10^{-3}$ | 16.1 eV |
| 0.1 eV | 0.8 Å | 1.0 | 0.570 | 0.1 | 0.1 | 0.996 eV | $2\ 10^{-5}$ | 0.48 eV |
| 0.18 eV | 0.8 Å | 1.0 | 0.570 | 0.1 | 1.5 | 0.987 eV | $6\ 10^{-3}$ | 0.48 eV |

First it shows up in the term $\sqrt{\epsilon}$ because, in the absence of coupling one would get $\epsilon_0$ instead of $\epsilon$. Since the effective barrier $\epsilon$ is lowered by the interaction as indicated by Eq. (10), the coupling contributes to *reduce* the creation energy of a defect. Second the coupling is responsible for the correction term $C$ in Eq. (14). This term represents the energy which exists in the oxygen sublattice due to the local distorsion that accompanies the proton kink. This extra energy contributes to *increase* the creation energy of a defect. Table I lists the energy of an ionic defect for three different parameter sets.

The choice of appropriate parameters for the model is delicate because some of them are not directly accessible to experiments. The first set was introduced by Spatschek, Laedke and Zolotariuk[14] and used later by ourselves[4] and more recently by Nylund and Tsironis[15] for a comparison between model results and experiments. This set gives a defect energy which is extremely high (16 eV) end is certainly not correct. The two other sets have been chosen in order to give equal energies for the defects with weak ($\chi = 0.1$) or strong ($\chi = 1.5$) coupling between the sublattices. The values of $\epsilon_0$ have been chosen to be consistent with the ab-initio results[11] and also with a very extensive analysis of a large number of hydrogen bonded compounds performed by Sokolov et al.[12]. The value of $\omega_1$ has been chosen so that the characteristic width of a defect, *i.e.* its spatial extent $L$, is if the order of two lattice spacings. The frequency $\Omega_0$ of the oxygens optical mode has been set to 300 $cm^{-1}$. The parameter $v_0$ is the most difficult to chose because it is related to the dispersion of this optical mode which is not accessible by a spectroscopy experiment. We have chosen to impose $v_0/c_0 = 0.1$ but it would be interesting to refine this value either by comparison with the results of ab-initio calculations on a system involving at least two oxygen pairs so that the coupling between them can be obtained, or by using dispersion curves determined by neutron diffraction. The coupling constant $\chi$ is also a parameter which is not well known, which is why we have considered two cases, $\chi = 0.1$ and $\chi = 1.5$ corresponding respectively to weak and strong coupling. In the weak coupling case, table I shows that $\epsilon$ is very close to $\epsilon_0$ and the correction $C$ is very small. In the strong coupling case $\epsilon \approx 0.5\,\epsilon_0$, while the correction term remains rather small. The global effect is a significant reduction of the energy of the defect.

However, even if the model parameters are not perfectly known, the energy of an ionic defect is of the order of 0.5 eV so that its thermal creation around room temperature is extremely unlikely unless some particular mechanism can intervene to localize thermal energy in the chain. In a nonlinear system like the hydrogen-bonded chain such a mechanism exists; it is the *modulational instability* of a plane

wave. Before attempting to study it for the coupled lattices of the ADZ model, let us discuss the idea on a simple case with only the proton sublattice. We start from the equation of motion (5) with $\chi = 0$, *i.e.*

$$u_{tt} - c_0^2 u_{xx} - \frac{4\epsilon_0}{m u_0^2} u \left(1 - \frac{u^2}{u_0^2}\right) = 0 \,, \tag{16}$$

In order to study the build-up of large amplitude solutions we expand around the equilibrium position $u_0$ using a multiple scale expansion which goes beyond a simple linear expansion

$$u = u_0 + \varepsilon u_1(T_0, T_1, T_2, \ldots, X_0, X_1, X_2, \ldots) + \varepsilon^2 u_2(T_0, T_1, T_2, \ldots, X_0, X_1, X_2, \ldots) \,, \tag{17}$$

with $T_0 = t$; $T_1 = \varepsilon t$ is a slow time which will describe the slow evolution of the solution, $T_2 = \varepsilon^2 t$, and in a similar manner $X_0 = x$, $X_1 = \varepsilon x$, etc. At order $\varepsilon$ one gets an evolution equation for $u_1$ which gives

$$u_1 = A(X_1, T_2) e^{i(kx - \omega t)} + CC \,, \tag{18}$$

where $\omega$ and $k$ are related by the linear dispersion relation of the lattice. In the small amplitude limit, $u_1$ would simply correspond to the phonon modes of the lattice. But if nonlinearity is taken into account, the higher order terms give a nonlinear Schrödinger equation (NLS equation) for $A$,

$$i \frac{\partial A}{\partial T_2} + P \frac{\partial^2 A}{\partial X_1^2} + Q |A|^2 A = 0 \,, \tag{19}$$

with $P = (c_0^2 - v_g^2)/2\omega$, $v_g = c_0^2 k/\omega$, and $Q = 24\,\epsilon_0/\omega u_0^4$ . This equation has an exact space-independent solution $A = A_0 \exp(iQA_0^2 T_2)$ which corresponds to a plane wave solution in $u_1$. However this solution in which the energy is evenly distributed over the chain is unstable. Looking for a perturbed solution $A = [A_0 + A_1(X_1, t_2)] \exp(iQA_0^2 T_2)$, one finds that, if $PQ > 0$, which is the case for the equation that we consider here, the perturbation tends to grow and generates a spontaneous modulation of the wave. A more complete analysis shows that the plane wave tends to break-up into solitary waves, or breather solutions of the NLS equation, in which the energy is concentrated. The same mechanism is also true for the thermal fluctuations. When their amplitude is sufficient to excite the nonlinearities in the system, an energy localization occurs and promotes the formation of kink-antikink pairs.

This mechanism is well known for an equation like (16), but the case of the ADZ model of the hydrogen-bonded chain is more complicated because we must consider the two coupled equations (5) and (6). Nevertheless the same energy localization mechanism exists and it is even made more efficient by the coupling between the two sublattices[16]. A multiple scale expansion performed on the variables $u$ and $\rho$ yields at first order

$$u_1 = A_+(X_1, T_2) e^{i(\omega_+ t - kx)} + A_-(X_1, T_2) e^{i(\omega_- t - kx)} + CC \tag{20}$$

$$\rho_1 = B_+(X_1, T_2) e^{i(\omega_+ t - kx)} + B_-(X_1, T_2) e^{i(\omega_- t - kx)} + CC \tag{21}$$

where the two sets of terms arise from the existence of two branches in the dispersion curve of the diatomic chain, with frequencies $\omega_+$ and $\omega_-$. Each sublattice sees its

own dispersion curve and a "shadow" of the dispersion curve of the other sublattice due to the coupling. For instance, the component of amplitude $A_-$ in the proton sublattice is the "shadow" of the component $B_-$ in the oxygen sublattice. Therefore $A_-$ is related to $B_-$ and similarly $B_+$ can be expressed as a function of $A_+$ so that the only independent factors are $A_+$ and $B_-$. They are solutions of a set of coupled NLS equations

$$i\frac{\partial A_+}{\partial T_2} + P_1\frac{\partial^2 A_+}{\partial X_1^2} + Q_{11}|A_+|^2 A_+ + Q_{12}|B_-|^2 A_+ = 0 \tag{22}$$

$$i\frac{\partial B_-}{\partial T_2} + P_2\frac{\partial^2 B_-}{\partial X_1^2} + Q_{22}|B_-|^2 B_- + Q_{21}|A_+|^2 B_- = 0 \tag{23}$$

The coefficients $P_1, P_2, Q_{ij}$ have lengthy expressions in terms of the model parameters but they can be obtained analytically[16]. Similar systems of coupled NLS equations have been obtained previously for birefringent fibers[17] or coupled lasers beams in aplasma[18,19]. One general feature of these coupled NLS is that modulational instability is more likely to occur, and the growth rate of the instability is larger than for a single NLS. This is also true for the equations derived above for the hydrogen-bonded chain. Instead of the single condition $P\,Q > 0$ for a single NLS, there are now several sufficient instability conditions for the exact plane wave solution

$$A_+ = A_0 \exp[i(Q_{11} A_0^2 T_2 + Q_{12} B_0^2 T_2)] \tag{24}$$

$$B_- = B_0 \exp[i(Q_{21} A_0^2 T_2 + Q_{22} B_0^2 T_2)]\,. \tag{25}$$

The first one

$$P_1\,Q_{11}\,A_0^2 + P_2\,Q_{22}\,B_0^2 > 0 \tag{26}$$

is simply the generalization of the instability condition of a single NLS equation. The others have complicated expression, but the net result is that, with the model parameters listed in table I, the instability is always present.

Figure 4 shows the result of a numerical simulation performed with the second parameter set of table I (weak coupling case). In this simulation using molecular dynamics at constrained temperature, a chain containing 256 protons is slowly heated. At low temperature the protons were all on the same side of the double well ($u_n \approx +u_0$) so that the chain had no ionic defect. The black areas which corresponds to domains in which the protons have moved to the opposite position $-u_0$ show that ionic defects have been formed at high temperature.

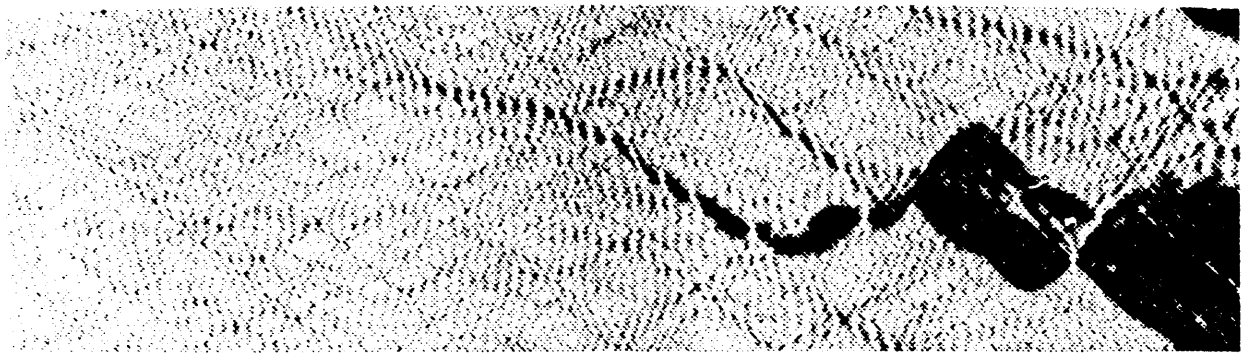

Figure 4: Thermal generation of a pair of ionic defects in the ADZ model. The figure shows the positions of the protons in the chain with a gray scale. Light grey corresponds to protons around the position $+u_0$ and black corresponds to protons around the position $-u_0$. The chain extends along the vertical axis. The temperature extends along the horizontal axis. In this experiment the system was heated with a linear temperature ramp so that the horizontal axis is also proportional to time. An ionic defect appears on this figure as an interface between a clear and a dark region.

The tendency for energy localization appears clearly because the large amplitude motions start in a small region of the chain. In this region one can notice that the formation of a large domain in which the protons have switched well is preceeded by a sequence of alternating balck and white regions which grow bigger and bigger. These dots correspond to large amplitude oscillations of the protons in a small domain of the chain. A few protons move toward $-u_0$ giving rise to a dark dot, then come back to their original position then move toward $-u_0$ again. This type of motion is typical of a breather mode of the NLS equation. As the temperature is raised, the amplitude of the breather increases while its frequency decreases until it freezes, giving rise to a kink-antikink pair. This type of oscillatory precursor motions before a pair of ionic defects are formed shows that the NLS description, hence the modulational instability mechanism, is the appropriate description of the thermal generation of ionic defects in the hydrogen bonded chain. However, in spite of the enhancement of the energy localization due to the coupling between the proton and oxygen sublattices, the thermal generation of the carriers still requires a high temperature. In the simulation shown in fig. 4, the temperature varies from 500K to 1500K and the formation of a pair of ionic defects is observed around 1200K. Since the energy of the two defects is 0.96 eV (corresponding to T=11,130K if we set $k_B T = 0.96$ eV) the energy localization is responsible a substantial decrease in the generation temperature. Nevertheless, in spite of the enhancement due to the coupling between the two sublattices, the thermal generation of ionic defects around room temperature can be expected to be a rare event.

## V. Conclusion.

The analysis of the different terms of the potential energy of the ADZ model has shown that they provide an approximate description of the hypersurface of potential

energy of an hydrogen-bonded chain. Therefore, if one accepts the idea that protons are transported along such a chain, the model leads naturally to solitonlike solutions. These solutions provide a general description of the two types of ionic defects: very narrow solutions correspond to independent proton jumps while broader ones describe a collective proton transport. Only the broad solutions can be expected to have solitonlike properties because, if the kink width is only of the order of the lattice spacing, discreteness effects trap it[13]. This soliton picture could also be obtained with a simpler model assuming that the heavy ions are fixed. However ab-initio calculations or the analysis of vibrational proton frequencies in a large number of hydrogen bonded systems[12] show that the proton motion is accompanied by a rather large distorsion of the heavy ion sublattice. This distorsion is included in the ADZ model and we have shown that it has a very stong influence, both on the mobility and on the thermal generation of ionic charge carriers. Due to energy exchanges between the protons and heavy ions a nonlinear mobility is found. This characteristic behavior could provide an experimental test of the validity of the model. We have also shown that the distorsion of the heavy ion sublattice enhances the modulational instability that can localize the energy and promote the thermal generation of ionic defects. However, even with this enhancement, the thermal generation of defects at room temperature remains a rare event.

The ADZ model is still a fairly simple description of a hydrogen bonded system and it can be improved to describe the Bjerrum defects[9], include acoustic modes for the oxygens[5] or even include anharmonic interaction between the protons to describe the difference in energy between the $H_3O^+$ and $OH_-$ ions. However, the most urgent research to carry in this domain is the determination of appropriate parameters for the model. They are essential to allow a comparison between theory and experiments and to decide whether the soliton picture is closer to reality than independent proton jumps. Good model parameters could probably be provided by ab-initio calculations on systems big enough to include the dynamics of the heavy ions and to test the degree of cooperativity in the proton motions.

## ACKNOWLEDGEMENTS

Part of this work has been supported by the EEC Science program under contract . The present paper has been written during the stay of two of us (M.P. and R.B.) at the Center for Nonlinear Studies of the Los Alamos National Laboratory. We thank the Center for its hospitality.

The work presented here has been initiated by a collaboration with Stephanos Pnevmatikos and would not have been done without him. We would like to stress here once more the very important role he played in popularizing the soliton concept in several domains of physics and in bringing together researchers with various interests. He was also a great friend who will be always remembered.

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10/29/91