Nonlinear Proton Dynamics in Hydrogen-Bonded Networks

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Abstract

The role of the *cooperativity of hydrogen bonding* and of *dichotomously branching transfers of protons* has been studied on the basis of the *dynamical* square lattice model which can be considered as a direct two-dimensional generalization of the well-known Aubry-Krumhansl-Schrieffer kink-bearing model with the Bernal-Fowler ice rules imposed as a constraint. The extended positive (H_3O^+) and negative (OH^-) ionic defects are shown to be described by 2D topological solitons which appear to be singular at their centers.

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1. Introduction

As is well-known (see, e.g., the comprehensive book [1]), any of the ice crystals (I_h, I_c, etc.) forms a three-dimensional (3D) hexagonal network in which each oxygen atom is surrounded tetrahedrally by its four adjacent oxygen atoms. According to the so-called *Bernal-Fowler ice rules*, in this network each hydrogen atom (or proton) is situated on the line (*hydrogen bond* or bridge) joining each pair of oxygen atoms but is approximately 1 Å from one oxygen atom and 1.76 Å from the other, the arrangement of hydrogen atoms in the complete lattice being such that each oxygen atom has two hydrogen atoms attached to it at distance of about 1 Å, thereby forming a water molecule H_2O. An ice crystal which obeys these rules is referred to as an *ideal crystal* and there is a large number of such configurations estimated by Pauling [2] and Nagle [3] and calculated exactly by Lieb [4]. However, besides this ideal structure, there are also configurations with the ionic and orientational (Bjerrum) defects [1]. The structure of ice can be changed from one configuration to another either by translational displacements of protons along hydrogen bonds from one potential minimum to another one or by rotations of water molecules.

In this prezentation we generalize the 1D coupled double-well model introduced and studied by Aubry [5] and Krumhansl and Schrieffer [6] to the 2D network with the Bernal-Fowler ice rules as a *constraint*. In the framework of this model we can describe the ionic defects: positive H_3O^+ and negative OH^-. The creation and dynamics of these defects is associated with *translational* motions of protons along hydrogen bonds. Any translational displacement of a proton creates a charge redistribution of the electronic shells of the two surrounding oxygen atoms resulting in appearence of effective forces which displace the protons in the *six* adjacent bonds. Therefore, proton motion in a hydrogen bond is dynamically correlated *through oxygen atoms* by neighboring proton displacements, so that the proton dynamics should be described as a collective process. In the 3D realistic case the *interbond* interaction of the nearest-neighboring protons through each oxygen atom involves *four* protons, instead of *two* in the case of a hydrogen-bonded chain. So far the collective proton dynamics has extensively been studied only in the 1D case (see the recent review paper by Scott [7] and references therein).

Apart from the interbond interaction of the protons, there is an interaction of each proton with the two adjacent oxygen ions which depends on the proton position in the bond and the relative distance between these ions. This (nonlinear) interaction gives rise to the existence of an on-site potential of a symmetric double-well form with the top of the barrier situated at the midpoint of the hydrogen bridge.

2. Proton arrangements and interbond interactions

To describe all possible arrangements of protons on the four bonds around each oxygen atom, we introduce a tetragonal system with the 4-vector $\vec{z} = (z_1, z_2, z_3, z_4)$ describing the proton displacements from the bond midpoints. Let these displacements be *positive* if they are directed *from* the oxygen atom. They are assumed to have values ± 1 at the minima. Then all the *six* possible proton arrangements corresponding to any ideal configuration of ice can be written in the following vector form:

$$\vec{e}_1 = \left(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}\right) \ , \ \ \vec{e}_2 = -\vec{e}_1 \ , \ \ \vec{e}_3 = \left(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}\right) \ ,$$

$$\vec{e}_4 = -\vec{e}_3 \ , \ \ \vec{e}_5 = \left(\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}\right) \ , \ \ \vec{e}_6 = -\vec{e}_5 \ .$$

As for the ionic defects, there are *four* possible configurations for H_3O^+:

$$\vec{p}_1 = \left(\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}\right) \ , \ \ \vec{p}_2 = \left(-\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}\right) \ ,$$

$$\vec{p}_3 = \left(-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}\right) \ , \ \ \vec{p}_4 = \left(-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}\right) \ ,$$

and *four* configurations for OH^-: $\vec{n}_i = -\vec{p}_i$, $i = 1,2,3,4$. These are *point* defects when the interbond interaction is not considered. They become to be extended if the cooperativity of the hydrogen bonding is taken into account and even if it is very small, it crucially changes the proton dynamics as was shown previously in 1D case [8].

To define a four-proton interbond interaction we notice that in the 1D case the corresponding pair-proton interaction term is represented in the harmonic approximation by a symmetric quadratic form. Similarly, the 4-proton interaction can be expressed by the following symmetric (with respect to all the permutations of z_i's, $i = 1,2,3,4$) quadratic form: $A = A(\vec{z},\vec{z}) = z_1^2+z_2^2+z_3^2+z_4^2+2c(z_1z_2+z_1z_3+z_1z_4+z_2z_3+z_2z_4+z_3z_4)$ where the constant c can be determined by substituting the ground state vectors $\vec{e}_i$, $i = 1,...,6$, into this general expression and equating it zero. From the resulting linear equations we find $c = 1$. Therefore, the four-proton quadratic form with the Bernal-Fowler constraint has the unique representation: $A = (z_1 + z_2 + z_3 + z_4)^2$ which adequately reflects the tetragonal symmetry.

3. A 2D dynamical lattice model

Now we may "project" (or "shrink") the local tetragonal structure onto a plane and form a square lattice. Obviously, this transformation keeps the *local topology* of the 3D hexagonal and 2D square lattices and does not violate the fundamental Bernal-Fowler rules. Therefore such *localized* nonlinear excitations as extended ionic defects can be described , at least qualitatively, in the frame of the square model. Denote by x_{mn} the displacement of the proton from the midpoint in the horizontal bond between the lattice sites $(m-1,n)$ and (m,n) and by y_{mn} the proton displacement from the midpoint in the vertical bond between the sites $(m,n-1)$ and (m,n). We refer to these bonds as the (m,n)th x and y bond, respectively. At any site (m,n), all of the four displacements $x_{mn}, x_{m+1,n}, y_{mn}, y_{m,n+1}$ are involved into the interbond interaction through the (m,n)th oxygen atom. Using the representation for the form A, we put

$$z_1 = \phi_{m+1,n}\ ,\ z_2 = -\phi_{mn}\ ,\ z_3 = \psi_{m,n+1}\ ,\ z_4 = -\psi_{mn}\ ,$$

where $\phi_{mn} = x_{mn}/a$ and $\psi_{mn} = y_{mn}/a$ with a being the distance between the bond midpoint and one of the minima, and then write the total Hamiltonian as follows

$$H = \sum_{m,n} \left[\frac{1}{2}m_p\left(\dot{x}_{mn}^2 + \dot{y}_{mn}^2\right) + \frac{1}{2}\kappa(x_{m+1,n} - x_{mn} + y_{m,n+1} - y_{mn})^2 \right. \\ \left. + \varepsilon_0 V(\phi_{mn}) + \varepsilon_0 V(\psi_{mn})\right] \tag{1}$$

where m_p is the proton mass, the dots denote the differentiation with respect to time t, and κ is the proton-proton interbond interaction. A dimensionless double-well potential $V(\phi)$ has two zero-energy equilibrium positions at $\phi = \pm 1/2$ and it is normalized in such a way that $V(0) = 1$, then ε_0 is the height of the barrier.

The equations of motion which correspond to the Hamiltonian (1) and describe the dynamics of the 2D vector lattice field $\{x_{mn}(t), y_{mn}(t)\}$ in the *presence of a thermal bath* have the following form:

$$\begin{aligned} m_p\ddot{x}_{mn} &= \kappa(x_{m+1,n} - 2x_{mn} + x_{m-1,n} + y_{m,n+1} - y_{mn} - y_{m-1,n+1} + y_{m-1,n}) - \\ &- \varepsilon_0 dV/dx_{mn} - m_p\Gamma\dot{x}_{mn} + \xi_{1mn}, \end{aligned} \tag{2}$$

$$\begin{aligned} m_p\ddot{y}_{mn} &= \kappa(x_{m+1,n} - x_{mn} - x_{m+1,n-1} + x_{m,n-1} + y_{m,n+1} - 2y_{mn} + y_{m,n-1}) - \\ &- \varepsilon_0 dV/dy_{mn} - m_p\Gamma\dot{y}_{mn} + \xi_{2mn}. \end{aligned} \tag{3}$$

The normally distributed random forces $\xi_n(t)'$s describe the thermal bath with temperature $T > 0$ and they are defined by the covariance

$$\langle \xi_{\alpha mn}(t)\xi_{\alpha' m' n'}(t')\rangle = 2m_p\Gamma k_B T\delta(t-t')\delta_{\alpha\alpha'}\delta_{mm'}\delta_{nn'}$$

where $\Gamma = 1/t_r$ is the damping coefficient and t_r is the relaxation time.

4. Boundary conditions and Gauss' law

Now we specify the boundary conditions for the dynamical equations (2) and (3). Let G be an arbitrary (simply connected) lattice domain surrounded by a closed path ∂G which intersects each of x and y bonds at its midpoint. The domain G can be generalized to have a boundary consisting of a finite number of simply closed paths C_γ , $\gamma = 0, 1, \ldots, j$, where C_0 contains the paths C_1 , $\ldots, C_\gamma$ in its interior. If all of the protons located in the bonds, which are intersected by this path, are found in one of the ground states ($\pm 1/2$), then the following two cases may occur: each *boundary proton* lies either inside or outside the domain G. The contour ∂G is defined to be *positively oriented* if the boundary protons located to the right of it, turn out to belong to the interior of G. Counting all the boundary protons with an appropriate sign (+1 if a boundary proton is located inside G and –1 if it is outside G), we can find the total charge q of the ice domain G. The topological charge q is an integer and its unit corresponds to –0.64$|e|$ electric charge as determined experimentally [1]. Let N_{in} is a total number of boundary protons belonging to the interior of G and N_{out} a number of boundary protons outside G. Then by induction (including more defects by enlarging domain G) we can prove the following equation:

$$\frac{1}{2}(N_{in} - N_{out}) = \sum_{(m,n)\in\partial G} (\vec{u}_{mn} \cdot \vec{\sigma}_{mn}) = q \tag{4}$$

where the unit vector $\vec{\sigma}$ is normally oriented to ∂G at site (m, n) and directed outside domain G. In fact, this result has a *discrete* form of *Gauss' theorem*: the flux of the two-component field $\{\vec{u}_{mn}(t)\} = \{\phi_{mn}\ , \psi_{mn}\}$ through a closed contour ∂G of an ice lattice domain G gives the total topological charge of this domain. If q is positive (negative), it gives the number of *extra* negative (positive) defects inside G.

On the other hand, it is naturally to define the sum of local proton displacements in x and y bonds (2D discrete *divergence*) as *density of topological charge* ρ_{mn}, so that $\sum_{m,n}\rho_{mn} = q$. Then the equation

$$(\nabla\cdot\vec{u})_{mn} = (\phi_{m+1,n} - \phi_{mn} + \psi_{m,n+1} - \psi_{mn}) = \rho_{mn} \tag{5}$$

can be considered as a *discrete differential form* of Gauss' law.

5. A nonlinear proton potential and parameter values

The double-well potential can be constructed explicitly as the sum of two *pair* ion-proton potentials, e.g. the Morse potentials [9-11]. The resulting double-Morse potential has the form

$$V(\phi;\beta) = \left[\frac{\alpha - \cosh(\beta\phi)}{\alpha - 1}\right]^2\ ,\ \alpha = \cosh\frac{\beta}{2} > 1\ . \tag{6}$$

The limit $\beta \to 0$ gives the well-known ϕ^4–potential: $V(\phi;0) = (1-4\phi^2)^2$. In general, the parameters β and ε_0 can be fitted according to *ab initio* calculations as was done by Duan and Scheiner [10]. On the other hand, these parameters as well as the interbond proton-proton coupling κ can be evaluated by applying the linear dispersion law

$$\omega^2(\vec{k}) = \frac{\varepsilon_0}{m_p a^2} V''(\pm 1/2;\beta) + 4\frac{\kappa}{m_p}(\sin^2\frac{k_1 l}{2} + \sin^2\frac{k_2 l}{2}), \tag{7}$$

where the primes denote the differentiation, $\vec{k} = (k_1, k_2)$ is the wave vector and l the lattice spacing of an ice crystal, to the experimental data for the frequencies $\omega_s = \omega(\vec{k}=0) = \sqrt{K/m_p}$ and $\omega_a = \omega(\pm\pi/l, \pm\pi/l) = \sqrt{(K+8\kappa)/m_p}$ (K being the stiffness constant of the O–H bond) and for the activation energy of creation of defects. Using the experimental values $\omega_s = 3000$ cm^{-1} and $\omega_a = 3415$ cm^{-1} at $T = -150^o$C [12], we have found $K = 540$ N/m and $\kappa = 20$ N/m. The latter value is close to that ($\kappa = 41$ Kcal/mol Å^2 obtained by *ab initio* calculations [13]). The other parameter values are $l = 2.76$ Å, $a = 0.37$ Å, $\beta = 20.964$ and $\varepsilon_0 = 0.227$eV.

6. 2D soliton solutions: a numerical approach

The general problem of finding the 2D vector lattice field $\vec{u}_{mn}(t)$ satisfying the vector equation of motion [see Eqs. (1)-(3)]

$$\frac{d^2}{dt^2}\vec{u}_{mn} = \left(\frac{c_0}{l}\right)^2 [\nabla(\nabla\cdot\vec{u})]_{mn} - \omega_0^2 \frac{d}{d\vec{u}_{mn}} U(\vec{u}_{mn}) \ , \tag{8}$$

where $c_0 = (\kappa/m)^{1/2} l$ is the characteristic velocity, $\omega_0 = (\varepsilon_0/m)^{1/2}$ is the characteristic frequency, and $U(\vec{u}_{mn}) = V(\phi_{mn}) + V(\psi_{mn})$, in some domain G with given initial and boundary (on ∂G) conditions has been studied numerically in the case of static solutions which describe the *extended* positive (H_3O^+) and negative (OH^-) ionic defects under appropriate boundary conditions. Note that in the continuum limit Eq. (8) takes the form

$$\partial_t^2 \vec{u} - c_0^2 \nabla(\nabla\cdot\vec{u}) + \omega_0^2 \frac{d}{d\vec{u}} U(\vec{u}) = 0 \tag{9}$$

which corresponds to the Lagrangian

$$\mathcal{L} = \int dxdy \left[\frac{1}{2}(\partial_t \vec{u})^2 - \frac{1}{2}c_0^2(\nabla\cdot\vec{u})^2 - \omega_0^2 U(\vec{u})\right] \ . \tag{10}$$

The rectangular $1 \le m \le M$, $1 \le n \le N$ with even numbers M and N was chosen as domain G. To find the 2D soliton profile $\{\vec{u}_{mn}\}$ the potential energy part of the Hamiltonian (1) has been investigated in the interior $\{2 \le m \le M-1, 2 \le n \le N-1\}$ of the domain G by using the steepest-descent method. The point defects H_3O^+ and OH^- have been chosen as initial points for the descent. Under this minimization procedure the boundary conditions on ∂G were assumed to be fixed. As for initial points for the descent, we have chosen the following two simplest ice configurations: $\phi_{m,N/2} = \pm 1/2$ if $m = 1, 2, ..., M/2-1$; $\phi_{m,N/2} = \mp 1/2$ if $m = M/2, M/2+1, ..., M$ and $\phi_{mn} = 1$ if $n \ne N/2$ while $\psi_{mn} = 1$ for all m and n. Here the upper (lower) sign corresponds to the defect H_3O^+ (OH^-). Obviously, other (more complicated and disordered) configurations can be chosen as well. To visualize the 2D vector soliton profile $\{\vec{u}_{mn}\}$ it is convenient to use the lattice distribution P_{mn} of the total potential energy which is normalized to unity: $\sum_{m,n} P_{mn} = 1$. According to the differential form of Gauss' law [see Eq. (5)], the discrete 2D divergence can be chosen as another lattice distribution P_{mn}. Then other quantities such as $\bar{m} = \sum_{m,n} mP_{mn}$ and $\bar{n} = \sum_{m,n} nP_{mn}$ to be the coordinates of the soliton on the lattice can be introduced.

7. The Peierls-Nabarro relief and the density of defect pairs

Using the steepest-descent method described in the previous section we have found the soliton solutions of two types of symmetry: a solution with an *integral* center of symmetry when the soliton center is located at oxygen atom and a solution with a *half-integral* center of symmetry for which the soliton center is located at the middle of the bond. To select each of these solutions we need under the minimization process to fix the soliton center. For realistic parameter values the solitons in ice Ih become narrow and their energy depends on the center position $(\bar{m}, \bar{n})$ [*Peierls-Nabarro* (PN) *potential relief*]. To find the *periodic* profile of the PN relief, for example, in the x direction, we fix the position of the proton in any point of the $(M/2, N/2)$ th x bond and solve the minimization problem. Running the points in the interval $(-1/2, 1/2)$ of this bond, we find the profile of the PN potential for the soliton moving from the site $(M/2, N/2)$ to its neighbor $(M/2 + 1, N/2)$.

When the defect is centered at the midpoint of any (x or y) bond, its energy is higher than if it were located at an oxygen atom. The difference of these energies is the *height* of the PN barrier. For the paramer values discussed in Section 5 we have found that the energy of the defect with half-integral center is $E = 0.381eV$ while the energy of the defect with integral center is $E = 0.293eV$. Therefore, the height of the PN barrier is $\Delta E = E(\bar{m} + 1/2, \bar{n}) - E(\bar{m}, \bar{n}) = 0.088eV$. It is much less than ε_0. Therefore, the cooperativity of the hydrogen bonding, which can be described by the dimensionless parameter $g = \kappa l^2/\varepsilon_0$, is not enough for the *free* soliton dynamics but it essentially reduces the activation energy for the transfer. In fact, we have discovered that even in the limit $g \to \infty$ the PN barrier does not vanish while in the 1D case this barrier disappears for sufficiently strong interbond interactions. This is a result of the interaction of protons with their "perpendicular" neighbors resulting in *dichotomously branching* transfers of protons. Mathematically, the 2D soliton solution has always a singularity at its center, even in the limit $g \to \infty$.

One of the next important quantities of ice is the density of pairs of ionic defects. This quantity can be defined by

$$N_d = \frac{1}{MN} \sum_{m=1}^{M} \sum_{n=1}^{N} |\frac{1}{2} [\theta(\phi_{mn}) + \theta(\psi_{mn}) + \theta(-\phi_{m+1,n}) + \theta(-\psi_{m,n+1})] - 1| \qquad (11)$$

where $\theta(x) = 1$ if $x > 0$ and $\theta(x) = 0$ if $x \leq 0$. We have studied the dependence of this density on the cooperativity parameter g. The numerical simulations of Eqs. (2) and (3) have been done with the periodic boundary conditions, $M = N = 30$, $\beta = k_B T/\varepsilon_0 = 1/4$ and the (dimensionless) damping $\gamma = a\sqrt{m_p/\varepsilon_0}/t_r = 1$. The results are given in Table 1 from which it can be seen that the density of the defects exponentially decreases with the growth of the parameter g.

8. Summary and outlook

Thus, the 2D nonlinear dynamical model suggested and studied in this presentation seems to be an interesting new object from different points of view. First, its local topological equivalence to the 3D hexagonal structure allows us to study those nonlinear collective excitations in ice which do not propagate or migrate in the bulk of an ice crystal. In particular, the dynamical process of creation of a pair of ionic defects and the dependence of defect density on temperature in ice can be studied in the frame of this model. These studies should be a much better stimulant to the understanding of hydrogen-bonded 3D networks compared with a crude 1D soliton model [14]. Second, there is a whole class of 2D hydrogen-bonded systems (hydrated protein surface, lysozyme, etc.) where some experimental work on surface protonic conduction has been done [15]. Therefore, the thermal studies of diffusion motion and mobility of defects and some other aspects of the nonlinear proton dynamics on surface, including different disorder effects (deuteriums and other impurities, vacancies, etc.) are of intrinsic importance and these studies are currently in progress. Third, this model admits 2D topological soliton solutions with a *finite* height of the Peierls-Nabarro relief in the continuum limit. This phenomenon cannot exist in the corresponding 1D kink-bearing models. Its origin is due to the singularity of the corresponding 2D soliton solutions at their center.

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Table 1. Dependence of the mean density of ionic defects in square ice on the cooperativity g.

g	0.0	1.0	2.0	3.0	4.0	5.0	6.0
$\bar{N}_d$	0.375	0.125	0.051	0.021	0.013	0.005	0.001