Dichotomous collective proton dynamics in ice

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(Received 13 March 1997)

The collective proton dynamics in ice is studied on the basis of the two-dimensional (2D) nonlinear lattice model which takes the dichotomous branching of proton transfers in hydrogen-bonded networks into account. The essential point of this model is that the network topology of the square proton lattice satisfies the Bernal-Fowler ice rules of the 3D ice crystal structure. The model is considered as a straightforward extension of the standard 1D coupled double-well oscillator model described by the discrete nonlinear Klein-Gordon equation to two dimensions while imposing the ice rules. This generalization under the ice constraints has been shown to be unique. A relation between the boundary conditions and topological charge (like Gauss’ law) is established. For any domain of the square ice lattice with nonzero topological charge and an ideal ice configuration chosen randomly on its boundary, the extended positive (H3 O+) and negative (OH−) ionic defects are described in terms of 2D vector topological solitons. The definition of the 2D kinks and antikinks is given by using Gauss’ law. An anisotropic generalization of the 2D ice model and an appropriate numerical scheme allows us to study the dynamical properties of the 2D solitons in comparison with the corresponding 1D solutions. Particularly, contrary to the 1D case, the existence of a nonzero Peierls-Nabarro relief has been proved to exist in all cases, even if intersite proton-proton interactions are infinitely strong, so that the free 2D soliton dynamics is impossible in the ice crystal. On the other hand, our studies of the thermalization of the 2D ice lattice clearly demonstrate the crucial role of the cooperativity of hydrogen bonding in the nucleation and dynamics of the defect pairs H3 O+ and OH−, explaining their very low density known from experimental data in ice physics. [S0163-1829(98)08701-3]

I. INTRODUCTION

Much work has been devoted to the dynamics of the one-dimensional (1D) chain of coupled double-well oscillators (the so-called “φ4” model) and its applications in condensed matter physics since the early papers of Krumhansl and Schrieffer1 and Aubry.2 Since so much is known analytically3–7 about the soliton solutions, this model as well as the Frenkel-Kontorova chain8,9 became very convenient and popular tools for theoretical studies of dynamical and statistical properties for a number of materials with strong quasi-1D anisotropy.10 One of the interesting systems of this class is a chain of hydrogen bonds11 where the proton transfers in adjacent hydrogen bonds are correlated because of the cooperative nature of hydrogen bonding. Using this circumstance, extensive studies (see the recent review by Scott12 and references therein) on the solitonic mechanism of the proton transport in 1D hydrogen-bonded chains were carried out where the local potential for each hydrogen-bonded proton was assumed to have a symmetric double-well form and the protons in adjacent bonds were supposed to be coupled harmonically. Therefore it would be interesting and promising to follow in the same way, in order to describe the proton dynamics in an ice crystal of higher dimensions. In other words, we would still have the discrete nonlinear Klein-Gordon (DNKG) equation but in two or three dimensions.

It is well known13 that any of the ice structures (Ih, Ic, etc.) forms a 3D network in which each oxygen atom is surrounded tetrahedrally by its four nearest-neighbor hydrogen atoms as shown in Fig. 1. According to the so-called Bernal-Fowler (BF) ice rules,13 in this network each hydrogen atom (or proton) is situated on the line joining each pair of oxygens but is approximately 1 Å from one oxygen and 1.76 Å from the other. The arrangement of hydrogen atoms in the complete lattice is such that each oxygen atom has two hydrogen atoms attached to it at distances of about 1 Å, thereby forming a water molecule H2O (Fig. 1). An ice structure which obeys these rules is referred to as an ideal crystal. There is a large number of configurations corresponding to the ideal structure.
FIG. 1. Tetragonal coordinate system for the proton displacements in hydrogen bonds. The oxygen atoms are shown by large circles and the protons subjected to a double-well potential are represented by small black balls.

Besides the ideal structure, there are also configurations with ionic and orientational (Bjerrum) defects. The structure of ice can change 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 paper, we consider only the ionic defects: positive H$_3$O$^+$ and negative OH$^-$. Their creation and dynamics are associated only with translational motions of protons along hydrogen bonds. Therefore, in order to study properly proton transfers in ice or in other networks of hydrogen bonds such as hydrated protein or lysozyme, the dichotomous branching of proton translations along hydrogen bonds, which is due to the BF rules, should be involved as the main feature of proton dynamics. Note that in the 1D soliton theory of proton transport, any translational displacement of a proton creates a charge redistribution of the electronic shells of the two surrounding oxygen atoms, resulting in the appearance of effective forces which displace the nearest-neighbor protons in the two adjacent bonds, according to the standard chain model of coupled double-well oscillators. In the 3D realistic ice-like network, the proton motion in each hydrogen bond is dynamically correlated (through oxygen atoms) with the proton displacements in the six adjacent hydrogen bonds, so that the interbond interaction between the nearest-neighbor protons involves now four protons (as can be seen from Fig. 1), instead of two, in the case of a hydrogen-bonded chain.

It was an attractive idea to extend the class of the kink-bearing families to two dimensions on the basis of the ice-like structure, introducing the local proton potential in each hydrogen bond of the 2D ice-like network. In other words, it was assumed that apart from the interbond interaction of the protons, there is an interaction of each proton with the two adjacent oxygen ions depending 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 barrier top situated at the midpoint of the hydrogen bond as shown in Fig. 1. An explicit form of the on-site proton potential can be calculated from the pair ion-proton interactions of the standard (Morse, Lennard-Jones, etc.) type.

To describe all possible arrangements of protons on the four bonds around each oxygen, a tetragonal system (see Fig. 1) with the four-vector $\mathbf{z}=(z_1,z_2,z_3,z_4)$ describing the proton displacements from the bond midpoints can be introduced. As shown in Fig. 1, the positive directions of these displacements have been chosen as those which are directed away from the oxygen atom. Clearly, another choice of the positive directions could be chosen, for example, any two directions directed from the oxygen atom and the two remainders directed to the oxygen atom. At the stable (zero-energy) equilibrium positions, the proton displacements take the values $\pm 1$. Therefore, all six possible proton arrangements corresponding to any configuration of ice can be written in the following vector form:

$$
e_1=(1,1,-1,1), \quad e_2=-e_1, \quad e_3=(1,-1,1,1),$$

$$
e_4=-e_3, \quad e_5=(1,-1,1,1), \quad e_6=-e_5. \quad (1)$$

There are four possible configurations for the positive ionic defect H$_3$O$^+$. $p_1=(1,1,-1,1), \quad p_2=-(1,1,-1,1),$ $p_3=-(1,-1,1,1), \quad$ and $p_4=-(1,-1,1,1),$ and four configurations for the negative ionic defect OH$^-$. $n_i=-p_i,$ $i=1,2,3,4.$ These are point defects and they correspond to the case without any interbond interaction. They become extended if any cooperativity of hydrogen bonding is taken into account.

In order to describe properly the collective proton dynamics in the 2D or 3D ice lattices, a four-proton interbond interaction has been suggested. Starting from the most general expression of a tetragonally symmetric quadratic form $A(\mathbf{z},\mathbf{z})$ and substituting into this form the equilibrium conditions (1), the form $A$ can be shown to have the unique representation

$$A=A(\mathbf{z},\mathbf{z})=(z_1+z_2+z_3+z_4)^2, \quad (2)$$

which reflects the tetragonal symmetry and describes the four-proton interbond coupling in an ice crystal.

The paper is organized as follows. In the next section, we define the 2D dynamical model in which, on the one hand, each hydrogen-bonded proton is subjected to an on-site double-well potential and, on the other hand, the interbond proton interaction is introduced according to the BF ice rules, using the representation (2). The ground states and boundary conditions for this model are discussed in Sec. III. Some indications how to evaluate the parameter values of the ice model are given in the next section. In Sec. V, we develop a numerical method for seeking 2D vector soliton solutions. For a better understanding of results obtained and their comparison with those of the corresponding 1D model, an anisotropic generalization of the 2D model is introduced there. The thermal proton dynamics is studied in Sec. VI. Finally, the summary and outlook are given in Sec. VII.

II. DYNAMICAL SQUARE ICE MODEL

The fundamental BF ice rules will not be obviously violated if the tetragonal structure given by Fig. 1 is projected (shrinked) onto a plane, forming the square lattice as shown
The total Hamiltonian in the form of the minima in the proton on-site potential. Then we can write

\[ m \times m_n \]

respectively. At any site \((m, n)\) between the \((m-1, n)\)th and \((m, n)\)th lattice sites and by \(y_{mn}\) the proton displacement from the midpoint in the vertical bond between the \((m, n-1)\)th and \((m, n)\)th sites. We call these bonds the \((m, n)\)th \(x\) bond and the \((m, n)\)th \(y\) one, respectively. At any site \((m, n)\) all of four displacements \(x_{mn}, x_{m+1,n}, y_{mn}, \) and \(y_{m,n+1}\) are involved in the interbond interaction through the \((m, n)\)th oxygen atom. Using the representation of the interbond interaction (2) and taking into account the square structure of the network of hydrogen bonds, where two directions are incoming and two outgoing, we define the proton displacements at the \((m, n)\)th oxygen as follows:

\[
\begin{align*}
z_1 &= x_{m+1,n}/a, \\
z_2 &= -x_{mn}/a, \\
z_3 &= y_{m,n+1}/a, \\
z_4 &= -y_{mn}/a,
\end{align*}
\]

where \(a\) is the distance between the barrier top and one of the minima in the proton on-site potential. Then we can write the total Hamiltonian in the form

\[
H = \sum_{m,n} \left[ \frac{1}{2} m \left( \frac{x_{mn}^2 + y_{mn}^2}{a^2} \right) + \frac{1}{2} \kappa (x_{m+1,n} - x_{mn} + y_{m,n+1} - y_{mn})^2 + \varepsilon_0 V(x_{mn}/a) + \varepsilon_0 V(y_{mn}/a) \right],
\]

where \(m = m_p\) is the proton mass, the overdot denotes the differentiation over time \(t\), and \(\kappa\) is the proton-proton interbond interaction constant. A dimensionless double-well potential \(V(\phi)\) has two zero-energy equilibrium positions at \(\phi = \pm 1\) as shown in Figs. 1 and 2 and it is normalized in such a way that \(V(0) = 1\), so that \(\varepsilon_0\) is simply the height of the on-site potential barrier. The Hamiltonian (4) assumes that all the protons in the lattice are allowed to move only along hydrogen bonds.

The on-site double-well potential can be constructed explicitly as the sum of two symmetrically displaced pair ion-proton potentials of the standard type, for instance, the Morse potentials. As a result, we obtain an on-site potential with two degenerate wells. Thus, the explicit form of the double-Morse potential is

\[
V(\phi) = \left[ \alpha - \cosh(b \phi) \right]^2, \quad \alpha = \cosh b, \quad (5)
\]

where the parameter \(b\) can be fitted according to \textit{ab initio} calculations. This parameter can also be estimated on the basis of experimental data and the procedure of how to find its appropriate values will be described below. In the limiting case \(b \to 0\), the double-well potential (5) takes the form of the well-known \(\phi^4\) potential:

\[
\lim_{b \to 0} V(\phi) = (1 - \phi^2)^2. \quad (6)
\]

The corresponding equations of motion take the difference-differential form

\[
\begin{align*}
\phi_{mn} &= (c_0/l)^2 (\phi_{m+1,n} - 2 \phi_{mn} + \phi_{m-1,n} - \psi_{m,n+1} - \psi_{m,n-1}) \\
&\quad - \psi_{m-1,n+1} + \psi_{m-1,n} - \omega_0^2 V' (\phi_{mn}), \\
\psi_{mn} &= (c_0/l)^2 (\phi_{m+1,n} - \phi_{mn} - \phi_{m+1,n-1} + \phi_{m,n-1} + \psi_{m,n+1} - 2 \psi_{m,n} + \psi_{m,n-1}) - \omega_0^2 V' (\psi_{mn}),
\end{align*}
\]

where \(l\) is the lattice spacing, \(c_0 = (\kappa/m)^{1/2}\) is the characteristic velocity, and \(\omega_0 = (c_0/lm)^{1/2}a\) is the characteristic frequency.

The Hamiltonian (4) and the equations of motion (7) can be rewritten in a vector form. To this end, we introduce the dimensionless two-component vector field on the 2D lattice by \(\textbf{u}_{mn} = (\phi_{mn}, \psi_{mn})\) where \(\phi_{mn} = x_{mn}/a\) and \(\psi_{mn} = y_{mn}/a\). Next, we define the 2D discrete divergence as the sum of the relative proton displacements in the horizontal and vertical hydrogen bonds,

\[
\nabla \cdot \textbf{u}_{mn} = \phi_{m+1,n} - \phi_{mn} + \psi_{m,n+1} - \psi_{mn},
\]

and the difference gradient operator according to

\[
\nabla f_{mn} = (f_{m+1,n} - f_{mn} - f_{m,n-1}) - f_{mn},
\]

applied to a scalar lattice field \(f_{mn}\). We also introduce the 2D on-site proton potential as the sum

\[
U(\textbf{u}_{mn}) = V(\phi_{mn}) + V(\psi_{mn}).
\]

Then the vector form of the Hamiltonian (4) and corresponding equations of motion (7) is

\[
H = \sum_{m,n} \left[ \frac{1}{2} \textbf{u}_{mn}^2 + \frac{1}{2} \left( \frac{c_0}{l} \right)^2 (\nabla \cdot \textbf{u}_{mn})^2 + \omega_0^2 U(\textbf{u}_{mn}) \right],
\]

\[
\ddot{\textbf{u}}_{mn} = \left( \frac{c_0}{l} \right)^2 \nabla (\nabla \cdot \textbf{u}_{mn}) - \omega_0^2 \frac{\partial}{\partial \textbf{u}_{mn}} U(\textbf{u}_{mn}),
\]
where \(\partial / \partial u_{mn} = (\partial / \partial \phi_{mn}, \partial / \partial \psi_{mn})\).

The Hamiltonian (11) (or its corresponding Lagrangian) and the equations of motion (12) can be written in the continuum limit by the substitutions \(ml \rightarrow x\) and \(nl \rightarrow y\). Explicitly, we obtain

\[
\overline{\partial}_t^2 \mathbf{u} - c_0^2 \nabla \cdot \nabla (\mathbf{u}) + \omega_0^2 \partial / \partial u \mathbf{U}(\mathbf{u}) = 0,
\]

where \(\mathbf{u} = (\phi, \psi)\) is the two-component vector field with the components \(\phi(x,y,t)\) and \(\psi(x,y,t)\), and \(\nabla = (\partial_x, \partial_y)\) is the 2D gradient operator. In the 1D case where \(\mathbf{u} = (\phi, 0)\), \(\phi = \phi(x,t)\), the vector equation of motion (13) is reduced to the standard nonlinear Klein-Gordon equation

\[
\overline{\partial}_t^2 \phi - c_0^2 \partial_x^2 \phi + \omega_0^2 V'(\phi) = 0,
\]

describing the class of kink-bearing models.\(^{5,6,10,20}\) Therefore, the 2D network of hydrogen bonds is an interesting physical object described by the 2D vector DNKG equation. Imposing the BF rules as constraints allows us to extend the 1D DNKG equation to the 2D lattice in a unique way.

### FIG. 3. The simply connected domain \(G\) contains two positive and one negative defects. Its boundary \(\partial G\) has \(N_{in} = 15\) and \(N_{out} = 13\) protons, so that \(Q = 1\).

### III. GROUND STATES AND BOUNDARY CONDITIONS

Since the 2D vector model defined by the Hamiltonian (11) [or the corresponding vector equations of motion (12)] belongs to the kink-bearing family, we need to treat properly the boundary conditions and topological charge; i.e., the relation between these quantities should be given along the lines of the 1D theory.\(^{20}\) On the other hand, the calculation of the number of energetically equivalent ground (vacuum) states was an interesting and difficult problem for a long period, originated by Pauling.\(^{21}\) In the 1D case, the solution to this problem is trivial because there are only two ground states: (i) All hydrogen-bonded protons are situated in the left or (ii) in the right well of the on-site double-well potential. Realistic ice is observed to have at low temperatures a residual entropy, caused by an indeterminacy in the proton distribution. The physical object described by the 2D vector DNKG equation.

\begin{align*}
\frac{1}{2} (N_{in} - N_{out}) &= \frac{1}{2} \sum_{(m,n) \in \partial G} (\mathbf{u}_{mn} \cdot \mathbf{n}_{mn}) = Q, \quad (15) \\
\frac{1}{2} \int_{\partial G} (\mathbf{u} \cdot d\mathbf{n}) &= Q, \quad (16)
\end{align*}

some elements of the randomness of initial conditions should also be involved in studies of the collective proton dynamics.

Now we specify the boundary conditions for Eqs. (7) or the vector equation (12). Let \(G\) be an arbitrary (simply connected) lattice domain surrounded by a closed path \(C_0\) which intersects each of the \(x\) and \(y\) bonds at its middle point (see Fig. 3). If we define at the \((m,n)\)th site the vector \(l_{mn}\) of the length \(l\) directed along this path, then \((\mathbf{u}_{mn} \cdot l_{mn}) = 0\), so that the total circulation of the lattice field \(\mathbf{u}_{mn} \) along any closed path is also zero. If all of the protons located in the bonds, which are intersected by this path, are found in one of the ground states, then the following two cases may occur: Each "boundary" proton lies either inside or outside the domain \(G\). The path \(C_0\) is defined to be positively oriented if the boundary protons located to the right of it turn out to belong to the interior of \(G\). The domain \(G\) can be generalized to have a boundary consisting of a finite number of simply closed paths \(C_i\) for \(i = 0, 1, \ldots, j\), where \(C_0\) contains the paths \(C_1, \ldots, C_j\) in its interior. If the latter paths are oriented in the same way as the path \(C_0\), then we can define the boundary \(\partial G\) as the algebraic sum of \(C_0, C_1, \ldots, C_j\). 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 are able to calculate the total topological charge \(Q\) of the domain \(G\). Indeed, by induction this charge can be proved to be the difference \((N_{in} - N_{out})/2\) where \(N_{in}\) (\(N_{out}\) is the total number of boundary protons inside (outside) \(G\)). This law can be written like Gauss’ theorem in the following discrete form:

\begin{align*}
\frac{1}{2} (N_{in} - N_{out}) &= \frac{1}{2} \sum_{(m,n) \in \partial G} (\mathbf{u}_{mn} \cdot \mathbf{n}_{mn}) = Q, \quad (15) \\
\frac{1}{2} \int_{\partial G} (\mathbf{u} \cdot d\mathbf{n}) &= Q, \quad (16)
\end{align*}
where the element $d\mathbf{n}$ is normally oriented to $\partial G$ and measured in units of the lattice spacing $l$. If $Q$ is positive (negative), it gives the number of extra “2D kinks,” i.e., negative defects ("2D antikinks," i.e., positive defects) inside $G$. This 2D kink (antikink) definition is in correspondence with the 1D case, when a solitary wave is referred to as a kink (antikink) solution if its profile is a monotonically increasing (decreasing) function. In other words, the 1D or 2D kink describes a vacancy, i.e., a dilatation in the lattice, while the antikink corresponds to an excess particle in the lattice, i.e., its compression.

Next, it is natural to define the sum of local proton displacements in the horizontal and vertical hydrogen bonds (the 2D divergence) as the density of topological charge $\rho_{mn}$, so that

$$\sum_{(m,n) \in G} \rho_{mn} = Q. \quad (17)$$

Then we can write a differential form of Gauss’ law (15) as

$$\frac{1}{2} (\nabla \cdot \mathbf{u})_{mn} = \rho_{mn} \quad (18)$$

or its continuum version

$$\frac{1}{2} (\nabla \cdot \mathbf{u}) = \rho. \quad (19)$$

Summing Eq. (18) over all the sites in the domain $G$ and using Eq. (17), we immediately obtain the integral form of Gauss’ law (15) for the flux of the lattice field $\mathbf{u}_{mn}/2$.

It should be noticed that the maximal topological charge of a domain $G$ depends linearly on the length of the closed path $\partial G$ surrounding this domain. By induction one can derive that it equals $L/2$ where $L$ is given in units of the lattice spacing $l$.

### IV. SMALL-AMPLITUDE EXCITATIONS AND PARAMETER VALUES

In this section, we will describe how to evaluate the parameters for the interbond and intrabond interactions from comparison of experimental data and numerical calculations of defect interactions. To this end, we study first the linear limit of the equations of motion (7) for one of the ideal configurations when all the protons oscillate around one of the two minima. Inserting the plane wave expression

$$\mathbf{u}_{mn}(t) = \mathbf{u}_0 + \mathbf{A} \cos(k_1 ml + k_2 nl - \omega t) + \mathbf{B} \sin(k_1 ml + k_2 nl - \omega t), \quad (20)$$

where $\mathbf{u}_0$ is any of the four vectors $(\pm 1, 0), (0, \pm 1)$, and $\mathbf{A} = (A_1, A_2)$ and $\mathbf{B} = (B_1, B_2)$ are arbitrary constant vectors, into the linearized version of Eqs. (7), we find the following linear dispersion law:

$$\omega^2(k) = \omega^2(k_1, k_2) = \omega^2_0 + 4 \frac{e_0^2}{l^2} \left( \sin^2 \frac{k_1 l}{2} + \sin^2 \frac{k_2 l}{2} \right), \quad (21)$$

where $k = (k_1, k_2)$ is the wave vector and $\omega_0$ is the frequency of small-amplitude proton oscillations at one of the minima of the double-well potential $V(\phi)$. Then, according to Eqs. (21) and (22), we define

$$\omega_s = \omega(0, 0) = \omega_0$$

and $\omega_a = \omega(\pm \pi/l, \pm \pi/l) = (\omega_0^2 + 8 \kappa/m)^{1/2}$, \quad (23)

where the symmetric ($\omega_s$) and antisymmetric ($\omega_a$) frequencies can be determined from spectroscopic measurements. For ice these values are available and for this case we have $\omega_s = 3000 \text{ cm}^{-1}$ and $\omega_a = 3415 \text{ cm}^{-1}$ (at temperature $T = -150 {}^\circ C$). Therefore, having these data, one can easily calculate the stiffness constant of the interbond interaction according to the relation

$$\kappa = m(\omega_s^2 - \omega_a^2)/8, \quad (24)$$

which immediately follows from Eqs. (23). By calculations we find that $\kappa = 20 \text{ N/m}$. The latter value is in good agreement with ab initio calculations obtained by Godzik.\(^{25}\)

An important parameter is introduced by Peyrard and Kruskal\(^9\) and called the discreteness parameter. This parameter determines the ratio $g = \kappa a^2 / \varepsilon_0$ of the elastic (four-proton intersite) coupling energy to the on-site potential energy. In the limit of small $d$, for the usual 1D kink-bearing theory, discreteness effects are absent, so that the continuum approximation can be applied in this case. As will be shown below, in the present 2D model, due to the specific form of the four-proton intersite (dichotomous) coupling energy [see the Hamiltonian (4)], the displacements $x_{mn}$’s and $y_{mn}$’s do not smoothly change from site to site (in the central region of a topological defect), even in the limit $d \rightarrow 0$. Therefore, strictly speaking, the topological defects are always discrete objects, including the limiting case $d \rightarrow 0$. Consequently, instead of the parameter $d$, we consider the dimensionless parameter $g$ which is referred throughout this paper as to the cooperativity of the hydrogen bond or simply the (four-proton interbond or intersite) coupling parameter. Because of Eq. (24), it can be expressed in terms of the frequencies $\omega_s, \omega_a$ as follows:

$$g = (a/d)^2 = ma^2 (\omega_s^2 - \omega_a^2)/2\varepsilon_0. \quad (26)$$

The values for the energy height $\varepsilon_0$ can be evaluated from ab initio calculations.\(^{18}\) On the other hand, below we will describe how this energy can be fitted, using experimental data and some calculations used in the kink-bearing theory. Therefore in what follows we consider the coupling parameter $g$ as an adjustable parameter, investigating its significant role on the 2D proton dynamics.

For numerical calculations we choose the geometrical parameters which correspond to the ice $I_h$, namely, $l = 2.76 \text{ Å}$ and $a = 0.38 \text{ Å}$. The parameter $b$ in the intrabond potential (5) can be estimated by using Eq. (22) and experimental values [see the first equation of (23)] if the height $\varepsilon_0$ is
given. Using Eq. (26) and taking into account that 
\( \alpha_0 = \sqrt{\varepsilon_0/m/a} \), for the double-Morse potential (5) we find the equation

\[
\cosh b + 1 \frac{b^2}{\cosh b - 1} = \frac{\omega_s^2}{\omega_d^2} g.
\]

which can be solved numerically with respect to the parameter \( b \), resulting in a certain dependence \( b = b(g) \) [or \( b = b(d) \)].

Let us discuss how the cooperativity \( g \) (or the discreteness parameter \( d \)) can be found from calculations of the kink-antikink interaction energy and comparison of these results with available experimental results on the activation energy of the creation of defect pairs. The energy of a kink-antikink interaction which depends on the distance between them can be calculated in the standard way, using minimization techniques.\(^{26}\) The dependence of this energy on the distance between a kink and an antikink is shown schematically in Fig. 4 for small (solid curve) and large (dashed curve) values of \( g \). The wavelike dependence (with the wavelength equal to the lattice spacing) corresponds to the highly discrete case, representing a Peierls-Nabarro (PN) effect.\(^{17}\) Its maximal values give the energy \( E_1 + E_2 \) where \( E_1 \) is the energy of the kink (or antikink) if its center is situated at an oxygen atom (oxygen-centered defect) and \( E_2 \) is the energy of the kink centered at the midpoint of a hydrogen bond (bond-centered defect). The former kink state with energy \( E_1 \) is stable while the latter state (when the central proton is at the top of the on-site potential barrier) is unstable, so that \( E_1 < E_2 \). In the limiting case \( g \to 0 \), the energy \( E_1 \) is obviously zero, so that the energy \( E_1 \) of the kink found in the unstable state exactly equals the PN relief height \( \Delta E = E_2 - E_1 \). In the opposite limiting case when \( g \to \infty \) \( (d \to 0) \), the dependence of the kink-antikink interaction energy on the distance between them is a smooth (in the 1D case) function, as shown in Fig. 4 by the dashed curve. When the kink and antikink describing the pair of extended defects are sufficiently separated, their “dissociation” energy becomes \( 2E_1 \) because \( E_2 = E_1 \). Therefore, calculating the energies of a defect (kink or antikink) when it is centered at an oxygen atom (\( E_1 \)) and at the midpoint of a hydrogen bond (\( E_2 \)), we can identify the sum \( E_1 + E_2 \) as the activation energy of the defect pair creation given by experimental data.\(^{13,24}\) Clearly, the calculated energy \( E_1 + E_2 \) depends on the values of \( g \) and therefore the latter parameter can be fitted, equating an experimental value of the activation energy of the defect pair creation to the calculated sum \( E_1 + E_2 \).

V. ANISOTROPIC GENERALIZATION AND A NUMERICAL METHOD

In this section, using minimization techniques, we will study numerically 2D profiles of standing soliton solutions to the equations of motion (7) and a corresponding PN relief. In order to check whether or not the 2D solitons can move, we will also simulate these equations under the soliton initial conditions. To find moving 2D soliton profiles, we develop a numerical procedure. In our numerical studies, we generalize the 2D model described in Sec. II, assuming that the stiffness constant \( \kappa \) has an anisotropy in the \((x,y)\) plane. To this end, we define the 2D discrete anisotropic divergence and gradient operators of the vector lattice field \( u_{mn} \) as follows [compare with Eqs. (8) and (9)]:

\[
\nabla \eta \cdot u_{mn} = \phi_{m+1,n} - \phi_{mn} + \eta(\psi_{m,n+1} - \psi_{mn}),
\]

\[
\nabla_{\eta G}u_{mn} = \{f_{mn} - f_{m-1,n}, \eta(f_{mn} - f_{m,n-1})\},
\]

where \( 0 \leq \eta \leq 1 \) is the anisotropy constant. The limit \( \eta \to 0 \) gives the quasi-1D case when wave motion can occur only in the \( x \) direction. In the other (isotropic and realistic) limit when \( \eta \to 1 \), we simply keep the previous notations, putting \( \nabla \eta = \nabla \).

Since we will study the proton dynamics at \( g = 0 \) as a particular case, it is convenient to introduce dimensionless time in the form where the parameter \( g \) is absent:

\[
\tau = (\varepsilon_0/m)^{1/2}/a.
\]

Then the (dimensionless) anisotropic version of the Hamiltonian (11), given in the energy units \( \varepsilon_0 + \sqrt{\varepsilon_0/m/a} \), and the corresponding vector equations of motion (12) become

\[
H_{\eta} = \sum_{m,n} \left[ \frac{1}{2} \left( \frac{d u_{mn}}{d\tau} \right)^2 + \frac{1}{2} g(\nabla \eta \cdot u_{mn})^2 + U(u_{mn}) \right],
\]

\[
\frac{d^2}{d\tau^2} u_{mn} = g(\nabla \eta \cdot u_{mn}) - \frac{\partial}{\partial u_{mn}} U(u_{mn}).
\]

Note that here we have kept the same notation for the lattice fields, writing \( u_{mn}(\tau) = u_{mn}(\tau) \).

The general problem of finding the lattice vector field \( u_{mn}(\tau) \) in any domain \( G \) with given initial and boundary conditions (on \( \partial G \)) can be solved numerically, using a minimization procedure. As a first step, we study static soliton solutions. To this end, we choose the rectangular domain \( \{1 \leq m \leq M, 1 \leq n \leq N\} \) with even numbers \( M \) and \( N \) and investigate the following minimization problem for the total potential energy:

\[
E_\eta = E_\eta(u_{mn}) = \frac{1}{2} g \sum_{m=1}^{M-1} \sum_{n=1}^{N-1} (\nabla \eta \cdot u_{mn})^2 + \sum_{m=1}^{M} \sum_{n=1}^{N} U(u_{mn})
\]

\[
\rightarrow \min \{u_{mn}\}_{m=2,n=2}^{M-1,N-1}.
\]
This problem was solved by using the method of conjugate gradients where the point defect $\text{H}_3\text{O}^+$ (or $\text{OH}^-$) was chosen as an initial point for the descent.

To describe the vector soliton profile $u_{mn}$, we can use the lattice distribution $P_{mn}$ of either the total potential energy $E_h$ or the topological charge $Q$ normalized to unity:

$$
\sum_{m,n} P_{mn} = 1. \tag{33}
$$

In the former case, the potential energy distribution should be symmetrized, so that the 2D scalar lattice function $P_{mn}$ is taken in the form

$$
P_{mn} = P^e_{mn} = (g |\nabla_{\eta} \cdot u_{mn}|^2 + V(\phi_{mn}) + V(\phi_{m+1,n}) + V(\psi_{mn}) + V(\psi_{m+1,n+1})]/2E_{\eta}. \tag{34}
$$

In the latter case, the normalized charge distribution follows from the differential form of Gauss’ law (18) and therefore it can be written in the form

$$
P_{mn} = P^c_{mn} = |(\nabla_{\eta} \cdot u_{mn})/2Q| = |\phi_{m+1,n} - \phi_{mn} + \eta(\psi_{m,n+1} - \psi_{mn})|/2Q. \tag{35}
$$

The two limiting cases of the soliton solutions $\eta=0$ and $\eta=1$ are illustrated by Figs. 5 and 6, respectively. Note that in the isotropic case ($\eta=1$), the grounds states surrounding a defect ($\text{H}_2\text{O}^+$ or $\text{OH}^-$) were chosen stochastically. The coupling parameter $g$ was taken sufficiently large, namely, $g=900$, in order to provide the well-defined displacive limit in the corresponding 1D theory.\textsuperscript{1,2} The number of lattice sites was $M=N=200$. The comparison of the 1D and 2D soliton profiles plotted in these figures clearly demonstrates the difference between these solutions. Thus, the 1D profile is a smooth and sufficiently broad function while the corresponding 2D profile becomes narrower and a singularity appears at its center. This result concludes that the 2D soliton solution cannot be a well-defined object in the continuum limit, so that no contradictions with the Derrick theorem\textsuperscript{20,27} are expected.

In order to understand more clearly the origin of the singularity at the center of the 2D profile, it is useful to calculate the 2D PN relief. For this purpose we need some additional definitions, namely, the coordinates of the soliton center on the lattice as well as the soliton width (e.g., diameter or radius). The soliton coordinates can be given by

$$
m_c = \sum_{m,n} mP_{mn} \quad \text{and} \quad n_c = \sum_{m,n} nP_{mn}, \tag{36}
$$

while the soliton radius can be defined as a function of the polar angle $\vartheta$:

$$
R = R(\vartheta) = \frac{1}{2} + \sum_{m,n} |(m-m_c)\cos\vartheta + (n-n_c)\sin\vartheta|P_{mn}. \tag{37}
$$

Due to the (elliptic) symmetry of the soliton profile, it is sufficient to consider the angle $\vartheta$ in the quadrant $0 \leq \vartheta \leq \pi/2$. Particularly, $R_1 = 1/2 + \sum |m-m_c|P_{mn}$ is the large half-axis of the ellipse (soliton radius in the $x$ direction)
TABLE I. The energy of the oxygen-centered energy \( E_1 \), the pinning energy \( \Delta E = E_2 - E_1 \), the initial (at \( \tau = 0 \)) kinetic energy \( E_k \), and the diameters \( D_1^c, D_2^c, D_1^r, \) and \( D_2^r \) calculated for several values of the anisotropy parameter \( \eta \) in the lattice with the coupling \( g = 900 \).

<table>
<thead>
<tr>
<th>( \eta )</th>
<th>( E_1 )</th>
<th>( \Delta E )</th>
<th>( E_k )</th>
<th>( D_1^c )</th>
<th>( D_2^c )</th>
<th>( D_1^r )</th>
<th>( D_2^r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>28.3</td>
<td>&lt;10^{-14}</td>
<td>3.6</td>
<td>10.4</td>
<td>1.0</td>
<td>15.7</td>
<td>1.0</td>
</tr>
<tr>
<td>0.001</td>
<td>28.3</td>
<td>2.8\times10^{-5}</td>
<td>3.6</td>
<td>10.4</td>
<td>1.0</td>
<td>15.7</td>
<td>1.1</td>
</tr>
<tr>
<td>0.010</td>
<td>28.2</td>
<td>2.9\times10^{-3}</td>
<td>3.7</td>
<td>10.4</td>
<td>1.0</td>
<td>15.7</td>
<td>2.1</td>
</tr>
<tr>
<td>0.100</td>
<td>23.2</td>
<td>1.6\times10^{-1}</td>
<td>9.8</td>
<td>8.6</td>
<td>1.2</td>
<td>14.4</td>
<td>5.0</td>
</tr>
<tr>
<td>1.000</td>
<td>7.0</td>
<td>3.6\times10^{-1}</td>
<td>32.1</td>
<td>4.1</td>
<td>3.5</td>
<td>11.8</td>
<td>11.6</td>
</tr>
</tbody>
</table>

and \( R_2 = 1/2 + \sum |n - n_c| P_{mn} \) is the small half-axis of the ellipse (soliton radius in the \( y \) direction). Clearly, all these quantities depend on the anisotropy constant \( \eta \) and in the limit \( \eta \rightarrow 1 \) an elliptic soliton profile is transformed into a circle. These definitions are useful because in the limit of point defects (when \( g = 0 \)), we have the natural values of the defect radius. Thus, if the oxygen-centered defect is situated at the \( (m_0, n_0) \)th lattice site, then \( P_{mn} = \delta_{m_0} \delta_{n_0} \), and, according to Eqs. (36) and (37), we obtain \( m_c = m_0 \), \( n_c = n_0 \), and \( R_1 = R_2 = 1/2 \).

In the other case, when the bond-centered defect is centered between the \((m_0, n_0)\)th and \((m_0+1, n_0)\)th sites, i.e., \( P_{m_0n_0} = P_{m_0+1n_0} = 1/2 \) and \( P_{mn} = 0 \) at the rest of lattice sites, then \( m_c = m_0 + 1/2, \ n_c = n_0 \), and \( R_1 = 1, \ R_2 = 1/2 \).

Solving the minimization problem (32), one can calculate the pinning energy of the soliton and its diameter \( D = 2R \). In these calculations, we restricted ourselves only to the “regular” configurations of the ideal ice structure, for which all the protons are situated either in the left or in the right (upper or lower) well in the \( x \) (\( y \)) direction. One of these four configurations is presented in Fig. 2. The simplest way to create a point (positive or negative) defect in such a regular planar lattice is to change the proton positions in any of four half-axes from one well to the other. Then it is possible to observe that the defect is able to migrate only on the half-plane but not on the whole planar lattice.

In general, the energy of a standing defect depends on the position of its center within a unit cell of the square ice lattice. The calculation of the minimal \( (E_1) \) and maximal \( (E_2) \) defect energies was performed as follows. Take, for instance, a negative point defect as an initial point for the minimization process (32). Let \( \phi_{mn} = 1 \) for \( m = M/2 + 1,..., M \) and \( n = N/2 \); for the rest of lattice sites we put \( \phi_{mn} = -1 \). The second component is given by \( \psi_{mn} = -1 \) for all the sites. Such an initially given point defect is oxygen centered with the components \( m_c = M/2 \) and \( n_c = N/2 \). The resulting extended defect profile obtained by solving the minimization problem (32) has the same center at the \((m_c, n_c)\)th oxygen with a certain minimal energy \( E_1 \). To get the bond-centered defect situated at the bond midpoint \( m_c = M/2 + 1/2 \) which has a maximal energy \( E_2 \), it is necessary to put \( \phi_{M/2,N/2} = 0 \) and keep this value fixed under the minimization procedure.

First, we studied soliton solutions when the four-proton coupling was very strong: \( g = 900 \). At this value the soliton profile smoothly depends on \( m \) and \( n \), except for the soliton center. The energy difference \( \Delta E = E_2 - E_1 \) gives the height of the PN relief, i.e., that part of the defect energy which is pinned to the lattice. It corresponds to the activation energy of the defect motion. The values of the defect energy \( E_1 \) (in stable oxygen-centered states), the pinning energy \( \Delta E = E_2 - E_1 \), and the diameters \( D_1^c, D_2^c, D_1^r, \) and \( D_2^r \), where \( e \) stands for the energy distribution (34) and \( c \) for the charge distribution (35), are presented in Table I for five values of the parameter \( \eta \). When \( \eta = 0 \) \( (D_2^c = D_2^r = 1) \), the proton displacements occur only in one chain \( \{m,n = N/2\}^M_{m=1} \) with the energy and charge distributions \( P_{mn}^{e,c} \) illustrated by Fig. 5. In this case, the pinning of the defect is absent \( (\Delta E = 0) \). Practically, the soliton remains a 1D object also at \( \eta = 0.001 \) and 0.01. Here the pinning is negligible and it does not have essential influence on the soliton dynamics. However, for \( \eta = 0.1 \) the effect of the two dimensionality of the lattice becomes visible, and we have \( \Delta E/E_1 = 0.007 \). The soliton becomes a completely 2D isotropic object at \( \eta = 1 \) \( (D_2^c = D_2^r = D_1^c = D_1^r) \). For this case the energy and charge distributions of the 2D soliton are presented in Fig. 6. The large pinning energy \( \Delta E/E_1 = 0.05 \) should result in the impossibility of uniform motion. Below, this result will be confirmed by numerical simulations.

The oxygen-centered defect energy \( E_1 \) calculated as a function of \( \sqrt{g} = a/d \) is given by Fig. 7(a) at \( \eta = 0, 0.001, 0.01, 0.1, \) and 1. As can be seen from this figure, the defect energy monotonically increases with the growth of the coupling parameter \( g \). In the quasi-1D limit, when \( \eta = 0 \), the energy increases as \( \sqrt{g} \). The increase of the parameter \( \eta \) leads to the monotonic decrease of the energy \( E_1 \) at each fixed \( g \). The dependence of the defect diameters \( D^c \) and \( D^r \) on \( \sqrt{g} \) at \( \eta = 0 \) and \( \eta = 1 \) is plotted in Fig. 7(b). It is shown that the soliton diameters increase proportionally to \( \sqrt{g} \) in both the 1D and 2D cases. Figure 7(c) plots the pinning energy \( \Delta E \) against \( \sqrt{g} \) for the values \( \eta = 0, 0.001, 0.01, 0.1, \) and 1. In the 1D limit \( (\eta = 0) \), the PN relief height \( \Delta E \) exponentially decreases with the growth of \( g \). However, for all \( \eta > 0 \) the dependence of \( \Delta E \) on \( g \) crucially changes. More precisely, for each \( \eta > 0 \) there exists a finite limiting value of the pinning energy \( \Delta E \) in the limit \( g \rightarrow \infty \). Thus, for \( \eta = 1 \) this limiting value is \( \Delta E = 0.36 \). Therefore, the pinning energy which corresponds to the Hamiltonian (4) is always nonzero, even in the limiting case of infinitely large values of the proton-proton coupling parameter \( g \). Thus, in ice with dichotomous dynamics, in contrast to the 1D hydrogen-bonded chain, the free soliton dynamics is impossible.

From the physical point of view, the existence of a finite PN relief in the limit \( g \rightarrow \infty \) can be understood and explained...
be satisfied if the differences
an antikink
2D model, the difference
fant, this difference has the same sign from site to site. In our
when the protons are found at the barrier top.
site part of the potential energy is lower compared with that
four-proton arrangement is more preferential because the on-
also tend to zero if
57
242
A. V. ZOLOTARYUK, A. V. SAVIN, AND E. N. ECONOMOU
as follows. In the usual 1D kink-bearing model, all the
particles (protons) which belong to the central part of a kink (or
an antikink) are found in the vicinity of the barrier top; they
are distributed in the continuous way. There exists either
dilatation (kink) or compression (antikink) of all these
particles. In the limit $g \to \infty$, all the particles at the kink (or
antikink) center tend to be placed at the barrier top in an
on-site potential $V(\phi)$. In other words, each difference
$\phi_{n+1} - \phi_n$ tends to zero if $g \to \infty$ but, what is more
important, this difference has the same sign from site to site. In our
2D model, the difference $\phi_{m+1,n} - \phi_{mn} + \psi_{m,n+1} - \psi_{mn}$ must
tend to zero if $g \to \infty$. However, the latter condition can be satisfied if
the differences $\phi_{m+1,n} - \phi_{mn}$ and $\psi_{m,n+1} - \psi_{mn}$ are finite but have opposite signs. This means
that it is not necessary for neighboring protons to climb on
the top as in the 1D case. In other words, the four adjacent
protons at each oxygen can be arranged in such a way that a
pair of them is compressed while the other pair is dilated, so
that the total difference $\phi_{m+1,n} - \phi_{mn} + \psi_{m,n+1} - \psi_{mn}$ equals
zero. Though the coupling $g$ is strong, all these four protons
are found on the slope of the on-site potential barrier. Such
a four-proton arrangement is more preferential because the on-
site part of the potential energy is lower compared with that
when the protons are found at the barrier top.

To find moving soliton solutions with any velocity
$v=(v_1,v_2)$, we can generalize the minimization procedure
developed before\textsuperscript{28} for seeking 1D soliton profiles. First, we
note that in the continuum limit we can consider the subspace
of functions describing traveling waves in the direction
$v$, writing $u_{mn}(\tau)=u(\xi_1,\xi_2)$, $\xi_1=m-s_1\tau$, and $\xi_2=n-s_2\tau$, where $s=(s_1,s_2)=v/c_0$ is the
numbers velocity of a traveling wave. For solutions of this type we have the relation

$$
\frac{d}{d\tau} u_{mn} = -(s \cdot \nabla) u(\xi_1,\xi_2), \quad \nabla = (\partial_{\xi_1}, \partial_{\xi_2}). \tag{38}
$$

On the other hand, the following representation can be
written for the spatial differences:

$$
u_{m+1,n} - u_{mn} = \partial_{\xi_1} u(\xi_1,\xi_2), \quad u_{m,n+1} - u_{mn} = \partial_{\xi_2} u(\xi_1,\xi_2). \tag{39}
$$

Using Eqs. (38) and (39), for sufficiently smooth traveling
wave solutions we can approximately represent the time
derivatives through the spatial differences according to

$$
\frac{d}{d\tau} u_{mn} \approx -s_1(u_{m+1,n} - u_{mn}) - s_2(u_{m,n+1} - u_{mn}). \tag{40}
$$

Substituting the time derivative in the Lagrangian which
responds to the equations of motion (31) by the right-hand-
side (RHS) of Eq. (40), we obtain the multidimensional
function

$$
\mathcal{L}_\eta(u_{mn} ; s) = \mathcal{E}_\eta(u_{mn}) - \frac{1}{2} \sum_{m=1}^{M-1} \sum_{n=1}^{N-1} \left[ s_1 (u_{m+1,n} - u_{mn}) + s_2 (u_{m,n+1} - u_{mn}) \right]^2, \tag{41}
$$

where the function $\mathcal{E}_\eta$ is defined by Eq. (32). On the other
hand, a similar approximation scheme can be directly applied
to the set of Eqs. (31) if we substitute the second time
derivative by the following spatially discretized version:

$$
\frac{d^2}{d\tau^2} u_{mn} \approx s_1^2 (u_{m+1,n} - 2u_{mn} + u_{m-1,n}) + s_2^2 (u_{m,n+1} - 2u_{mn}
+ u_{m,n-1}). \tag{42}
$$

Then the equations of motion (31) take the form of the
system of discrete equations $\partial \mathcal{L}_\eta(u_{mn} ; s) / \partial u_{mn} = 0$ with $\mathcal{L}_\eta$ defined
by Eq. (41). Thus, the problem of looking for solutions of
a permanent profile and moving with a constant velocity $s$ is
reduced to seeking extremum points of the Lagrangian
function (41). However, since the quadratic form

$$
F = F(u_{mn}) = \frac{1}{2} \sum_{m,n} \left( \nabla \cdot u_{mn} \right)^2 - \left[ s_1 (u_{m+1,n} - u_{mn})
+ s_2 (u_{m,n+1} - u_{mn}) \right]^2 \right] \tag{43}
$$

is not a positively definite function, the extremum points (if
they exist) might be of the saddle type. Obviously, such
saddle points cannot be found by minimization of the
function (41), similarly to the scheme (32). However, we can
implement a “reflection” of the Lagrangian surface in such
a way that saddle points are transformed into minima at this
“deformed” surface. A straightforward way to redefine the
minimization process applied to the present model can be
given by
DICHOTOMOUS COLLECTIVE PROTON DYNAMICS IN ICE

\[ \mathcal{F}_\eta = \frac{1}{2} \sum_{m=1}^{M-1} \sum_{n=1}^{N-1} \left( \frac{\partial \mathcal{L}_\eta}{\partial \dot{\phi}_{mn}} \right)^2 + \left( \frac{\partial \mathcal{L}_\eta}{\partial \phi_{mn}} \right)^2 \]

\[ \rightarrow \min \{ u_{mn} \}_{m=1}^{M-1},n=1 \ldots N-1. \] (44)

This numerical procedure allows one to give an exact answer to the question of the existence of smooth soliton solutions to the system of the equations of motion (31). Such solutions (if they exist) exactly correspond to minima of the discrete functional \( F_\eta \) with its value \( F_\eta = 0 \). Only those minima which correspond to smooth solitonlike profiles are chosen as appropriate solutions to our problem. Other minima describing profiles accompanied by any ripples, etc., are excluded from further consideration. As a result, we have discovered that for all \( \eta > 0 \) and \( s = (s_1, s_2) \neq 0 \) there are no minima corresponding to smooth soliton profiles. Such smooth solutions exist only (i) in the 1D limit (\( \eta = 0 \), \( s_1 = s \), and \( s_2 = 0 \)) when the quadratic form (43) is positively definite for all \( 0 \leq s < 1 \) and (ii) on the 2D lattice if they are static (\( s = 0 \)).

In order to confirm the absence of a free (without any bias field applied) 2D soliton motion, we simulated the equations of motion (31) in the rectangular region \( \{1 \leq m \leq M, 1 \leq n \leq N\} \) with \( M = 400 \) and \( N = 100 \). The initial conditions \( u_{mn}(0) = u_{mn}^0 \) and \( u_{mn}'(0) = -s^0(u_{m+1,n}^0 - u_{mn}^0) \) were chosen in correspondence with the static profile determined by solving the minimization problem (32). The initial velocity was chosen as \( s^0 = 0.5 \). These initial conditions provide free soliton motion only in the 1D limit, along the chain \( \{m, n = N/2\}_{m=1}^{M} \). However, for \( \eta > 0 \) the 2D soliton was shown to be pinned to the lattice, even in the case when the initially given kinetic energy of the defect \( E_k \) significantly exceeded the pinning energy \( \Delta E \) (see Table I). Therefore, despite this energy being sufficient for activated motion of the defect with any anisotropy \( 0 \leq \eta \leq 1 \), free 2D soliton motion cannot exist. The results of simulations are presented in Fig. 8 where the time evolution of the soliton center position \( m_c = m_c(\tau) \) has been plotted. The soliton position was determined as the intersection of the line obtained by a subsequent linking of the points \( \{(m, \phi_{mn,N/2})\}_{m=1}^{M} \) with the line \( \phi = 0 \) on the plane \( (m, \phi) \). For the values \( \eta = 0 \) and \( \eta = 0.001 \) the soliton moves uniformly along the chain \( \{m, n = N/2\}_{m=1}^{M} \) with constant velocity \( s = 0.45 \). When \( \eta = 0.01 \), the velocity is \( s = 0.44 \). However, for larger values of \( \eta \) (0.1 and 1) the 2D soliton remains at rest. As shown in Fig. 8, for \( \eta = 0.1 \) the soliton initially oscillates, emitting small-amplitude waves. Therefore, for sufficiently large \( \eta \) the 2D soliton cannot propagate in the lattice with a permanent velocity. Its initial kinetic energy is spent only by emission of small-amplitude waves and excitation of internal oscillating eigenmodes.

Thus, the investigation carried out in the present paper allows one to conclude that in the 2D network of hydrogen bonds, the ionc defects \( \text{H}_2\text{O}^+ \) and \( \text{HO}^- \) cannot possess the free soliton dynamics. Their motion in the network can occur only as random thermally activated jumps from site to site.

VI. THERMAL DEFECT DYNAMICS

Since, as was shown in the previous section, the cooperativity of the hydrogen bond is not a sufficient factor which could result in the free 2D soliton dynamics, it is interesting to investigate the role of this cooperativity on the stochastic proton dynamics. The important quantity from the experimental point of view is the averaged density of ionic defect pairs in ice.\(^13\) In order to calculate this density, we use the Langevin approach. In the presence of a nonzero temperature \( T \), the corresponding random and damping forces are added to the RHS of the equations of motion (7) or (12). The dimensionless form of the resulting equations can be written as follows:

\[ \frac{d^2}{d\tau^2} u_{mn} = g \nabla \cdot u_{mn} - \frac{\partial}{\partial u_{mn}} U(u_{mn}) - \gamma d \frac{d}{d\tau} u_{mn} + X_{mn}, \] (45)

where \( \gamma = a \sqrt{m/e_0 T} \), is the dimensionless damping coefficient, \( \tau \) is the relaxation time, and \( X_{mn} = (\xi_{1mn}, \xi_{2mn}) \) is the vector random force describing the interaction of the \( (m,n) \)th proton with a thermal bath. The stochastic force components \( \xi_{1mn}(\tau) \) and \( \xi_{2mn}(\tau) \) are independent at differing lattice sites as well as between each other, so that they are given by the following covariance matrix (white noise):

\[ \langle \xi_{mn}(\tau) \xi_{m'n'}(\tau') \rangle = 2D \gamma \delta_{\tau' \tau} \delta_{mn} \delta_{m'n'} \delta(\tau - \tau'), \] (46)

where \( D = k_B T/e_0 \) is the noise intensity (dimensionless temperature) with \( k_B \) being Boltzman’s constant.

Simulations of Eq. (45) were carried out on the torus corresponding to the cyclic boundary conditions. The noise and damping parameters were chosen to be \( D = 1/4 \) and \( \gamma = 1 \), respectively. Note that the relation \( k_B T = e_0/4 \) is the most appropriate choice from the standpoint of computational time. As before, the coupling \( g = (a/d)^2 \) was considered as a
various parameter. The appearance of the thermal equilibrium of the proton lattice was controlled by using the function

\[ f(\tau) = \frac{1}{2DMN} \sum_{m=1}^{M} \sum_{n=1}^{N} u_{mn}^2(\tau). \]  

Note that the time-averaged value of this quantity is 1.

Initially, the lattice was chosen to be in the perfect state with \( u_{mn}(0)=(1,1) \) and \( u'_{mn}(0)=(0,0) \). The topological charge per the \((m,n)\)th site can be defined by

\[ Z_{mn}(\tau) = \theta(\phi_{mn}) + \theta(-\phi_{m+1,n}) + \theta(\psi_{mn}) + \theta(-\psi_{m,n+1}) - 2, \]

where \( \theta(x) = 1 \) if \( x > 0 \) and \( \theta(x) = 0 \) if \( x \leq 0 \). For the perfect configuration the total charge is \( \Sigma Z_{mn} = 0 \). Obviously, the number of defect pairs can be given by

\[ N_d(\tau) = \frac{1}{2} \sum_{m=1}^{M} \sum_{n=1}^{N} |Z_{mn}(\tau)|. \]

Then the averaged (both in time and per site) density of ionic defect pairs is defined by

\[ \bar{N}_d = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau N_d(\tau) d\tau / MN. \]

Clearly, the density \( \bar{N}_d \) should monotonically decrease with the growth of the coupling parameter \( g \). Numerical simulations of Eq. (45) were carried out for the lattice consisting of \( M=N=30 \) sites. The results are illustrated in Fig. 9, from which it can be seen that the defect density exponentially decreases with the growth of the cooperativity \( g \). In this figure, at each lattice site, a dash (horizontal or vertical) stands for the valent bond O-H, so that the presence of two dashes at one site corresponds to the water molecule H\( _2 \)O, three dashes to the positive defect H\( _2 \)O\(^+ \), and one dash to the negative defect OH\(^- \). The creation of positive (with four protons attached to an oxygen) and negative (without any proton at an oxygen) defects is also possible if \( g = 0 \). However, for \( g > 0 \) these defects become unstable: Each positive (negative) defect of this type dissociates into the two defects H\( _2 \)O\(^+ \) (OH\(^- \)).

VII. SUMMARY AND OUTLOOK

It is an attractive point of view to generalize the one-dimensional (1D) discrete nonlinear Klein-Gordon (DNKG) model to higher dimensions and to study multidimensional localized modes.\(^{29}\) Particularly, 2D or 3D topological defects in lattices are of great interest owing to the Derrick theorem\(^{29,27}\) applied to the continuum version of the KG model. Clearly, depending on a specific physical problem, a generalization should be carried out in its own way. In particular, one should mention the studies of the 2D generalizations of the 1D Frenkel-Kontorova model which describe 2D layers of atoms.\(^{30,31}\) Our extension of the 1D DNKG model with the on-site potential of double-well topology is characterized by the fundamental Bernal-Fowler (BF) ice rules which determine ice structure in three, even in two, dimensions; these rules are not relevant or applicable in the 1D space. The exceptional case is a quasi-1D hydrogen-bonded (HB) chain,\(^{11}\) the structure of which differs from that of ice.

Imposing the BF constraints, the collective proton dynamics involves the dichotomous branching of proton transfers which is completely random if the cooperativity of the hydrogen bond is ignored. Therefore, it was interesting to study the dichotomous branching effects on the basis of a dynamical model. The simplest model of this type is the square ice lattice illustrated in Fig. 2. This 2D network of hydrogen bonds becomes a much more complicated system compared to the standard 1D kink-bearing DNKG model. The main difference between the 1D and 2D models is that the number of ground state configurations of the 2D ideal ice structure becomes very large, increasing with a lattice domain, instead of only two ground states (for any chain length) in the 1D case.

The 2D nonlinear dynamical model studied in this paper is an interesting object from different points of view. First, its local topological equivalence to the 3D hexagonal structure allows us to study those nonlinear collective modes in
ice which do not propagate or migrate in the bulk of an ice crystal. In particular, the dynamical process of the creation of ionic defect pairs and the dependence of the density of these pairs on temperature in ice can be studied on the basis of this model. These studies should be a much better stimulant to the understanding of 3D HB networks compared with the crude 1D soliton model. Another kind of standing localized mode that is a time-periodic discrete breather (being currently of great interest) can also be considered in this model. The proof of the existence of such breather modes in the 1D DNKG model is based on Aubry’s concept of anti-integrability. The generalization of these investigations to higher dimensions is straightforward and the results will be essentially the same. Second, there is a whole class of 2D HB systems (hydrated protein surface, lysozyme, etc.) where some experimental work on the surface protonic conduction has been already carried out. Therefore, thermal studies of the diffusion motion and mobility of defects and some other aspects of the nonlinear proton dynamics on surfaces, including different disorder effects (deuteriums, vacancies, and other impurities), are of intrinsic importance and these studies are currently in progress. Third, the present model admits 2D topological soliton solutions with a finite height of the Peierls-Nabarro (PN) relief. A nonzero PN relief has been shown to exist for any strength of the intersite four-proton coupling $g$, even in the limiting case of infinitely large values of this coupling. This phenomenon is known not to exist in 1D kink-bearing models.

ACKNOWLEDGMENTS

This work has partially been supported by the EEC under INTAS Grant No. 94-3754. A.V.S. and A.V.Z. would like to express their gratitude to the Physics Department of University of Crete for hospitality where the main part of this work has been carried out. This work was also made possible in part by Grant No. UC-3200 from the Joint Fund of the Government of Ukraine and International Science Foundation. Stimulating and useful discussions with S. Aubry and G. Careri are gratefully acknowledged.

10 For a review, see, e.g., A. R. Bishop, J. A. Krumhansl, and S. E. Trullinger, Physica D 1, 1 (1980).