SPECIAL FEATURES OF THE NONLINEAR DYNAMICS OF QUASIPARTICLES IN MOLECULAR STRUCTURES WITH HYDROGEN BONDS WITH ALLOWANCE FOR THE INTERACTION OF NOT ONLY THE NEAREST NEIGHBORS

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The dynamics of propagation of protons along a molecular chain of hydrogen bonds is analyzed with allowance for the interaction of the first and second neighbors in the proton sublattice. It is demonstrated that two new charge density excitation types (quasiparticles) arise in this system for which exact analytical dependences are found. The propagation velocity of one of these excitations is high enough, which explains the high mobility of protons along the chain of hydrogen bonds.

In the last few years, attempts of theoretical explanation of various physical and chemical processes from the viewpoint of nonlinear dynamics have been intensified. Of special interest is the use of the nonlinear differential equations with spatial gradients of higher than the second orders [1–4]. These equations naturally appear in a description of long-wavelength fluctuations of discrete crystal lattices with allowance for the interaction of not only nearest neighbors [5, 6].

The present work is aimed at elucidation of the special features of nonlinear excitations propagating along a molecular chain of hydrogen bonds with allowance for the interaction of the nearest and second neighbors.

It is well known that the proton conductivity along one-dimensional chains of hydrogen bonds for some compounds in the crystal phase (for example, solid alcohol and carbohydrate) is higher by several orders of magnitude than in the perpendicular direction [7]. It has been established that the proton mobility in ice crystals is only by an order of magnitude less than the electron mobility in metals [8]; moreover, the proton mobility in ice is caused by proton transfer along the hydrogen bonds [9–11]. When studying the proton transfer in the ice lattice, one-dimensional chains of water molecules with hydrogen bonds called Bernal–Fowler filaments were detected. The basic assumption of the theory of ice proton conductivity is that the proton can be transferred along the chain as ionic defects of H_3O^+ – hydroxonium ion – and OH^- – hydroxyl ion – formed in the process of dissociation of water molecules due to transfer of one of its protons to the neighboring molecule in the course of reaction $2H_2O \leftrightarrows OH^- + H_3O^+$.

Following [12], we consider an infinite chain of water molecules in which one proton from each water molecule forms the hydrogen bond, whereas the second proton forms the covalent bond with the oxygen atom rather than the hydrogen bond. This proton forms the hydroxyl ion with oxygen atom. As a result, the chain of water molecules is subdivided into two subsystems: the parent sublattice formed by hydroxyl groups and the proton sublattice. An important property of the hydrogen bond of water and alcohol molecules is that the curve of potential energy of the bonded proton has two minima corresponding to two possible equilibrium positions of the proton (Fig. 1). In the undeformed chain, each proton participating in the formation of hydrogen bond is connected on one side to the oxygen atom by the covalent bond and on another side by the hydrogen bond. After the proton has passed through the potential barrier, the covalent and hydrogen bonds change places. Therefore, the potential energy of the proton participating in the hydrogen bond formation is written in the form [7, 11, 12]
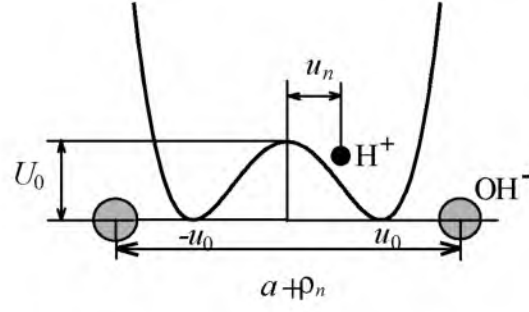

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Fig. 1. Potential well for the proton forming the hydrogen bond [7].

$$U(u_n) = U_0 \left(1 - \frac{u_n^2}{u_0^2}\right)^2, \qquad (1)$$

where U_0 is the potential barrier height, u_n is the proton displacement from the barrier top, and u_0 specifies the position of potential energy minima (Fig. 1).

In the undeformed state when all protons are either in the left or in the right potential wells, the positive charge is uniformly distributed over the entire chain of hydrogen bonds. For a local displacement of the proton, the uniform distribution is disturbed, and an excess positive charge is formed in regions of compression of the proton sublattice, while an excess negative charge is formed in regions of stretching of the proton sublattice. Motion of hydroxonium and hydroxyl ion defects is caused by proton hopping from potential well (1) to another.

The Hamiltonian of the examined system can be written in the form

$$H = H_p + H_g + H_{int}. \qquad (2)$$

Here H_p is the Hamiltonian of the proton sublattice considering Eq. (1) and the interaction of the first and second proton neighbors with the lattice interaction constants ω_1^2 and ω_2^2, respectively:

$$H_p = \sum_n \left\{ \frac{m}{2}\left[\left(\frac{du_n}{dt}\right)^2 + \omega_1^2(u_{n+1} - u_n)^2 + \omega_2^2(u_{n+2} - u_n)^2\right] + U(u_n) \right\}, \qquad (3)$$

where m is the proton mass. The second term in Eq. (2) is the Hamiltonian of the parent sublattice of hydroxyl ions in which we consider the interaction of only the nearest neighbors with the lattice constant Ω_1^2 [7,12]:

$$H_g = \sum_n \frac{M}{2} \left\{ \left(\frac{d\rho_n}{dt}\right)^2 + \Omega_1^2(\rho_{n+1} - \rho_n)^2 + \Omega_0^2 \rho_n^2 \right\}, \qquad (4)$$

where ρ_n is the relative displacement of hydroxyl ions, M is the hydroxyl mass, and Ω_0^2 is the characteristic constant of the parent sublattice. The third term in Eq. (2) is the Hamiltonian of interactions of displacements of hydroxyl ion and protons:

$$H_{int} = \lambda \sum_n \rho_n (u_n^2 - u_0^2), \qquad (5)$$

where λ is the sublattice interaction parameter.

Below we consider the long-wavelength approximation (to proceed to it, we must set $na \to x$, $u_n \to u(x)$, and $\rho_n \to \rho(x)$, $\sum_n \to \frac{1}{a} \int dx$ in Eqs. (3)–(5), where a is the equilibrium distance between the two neighboring hydroxyl ions). In [5] it was demonstrated that in the long-wavelength approximation, taking into account the interaction with the second neighbors in one-dimensional chains results in the occurrence of the fourth-order spatial derivatives in the equations of motion as well as in the re-determination of the velocity (and frequency) of natural sound waves. From Eqs. (3)–(5) in the long-wavelength approximation, we obtain the general continuous Hamiltonian of the examined system:

$$H = \frac{1}{a} \int \left\{ \frac{m}{2}(u_t^2 + s_0^2 u_x^2 + b u_{xx}^2) + U_0 \left(1 - \frac{u^2}{u_0^2}\right)^2 + \frac{M}{2}(\rho_t^2 + V_0^2 \rho_x^2 + \Omega_0^2 \rho^2) + \lambda \rho(u^2 - u_0^2) \right\} dx \,, \tag{6}$$

where u_t, u_x, u_{xx}, ρ_t, and ρ_x are derivatives with respect to t and x and the second derivative with respect to x of functions $u(x)$ and $\rho(x)$, respectively. The parameters of the given system [5] are the velocity of linear waves in the proton sublattice (proton sound) $s_0^2 = a^2(\omega_1^2 - 4\omega_2^2) > 0$, the dispersion parameter in the proton sublattice $b = a^4(16\omega_2^2 - \omega_1^2)/12$, and the velocity of linear waves in the parent sublattice $V_0 = a \, \Omega_1$. Conditions of applicability of the expansion with such accuracy were discussed in [5]. The system of equations of motion

$$\begin{cases} u_{tt} - s_0^2 u_{xx} + b u_{xxxx} - \omega_0^2 u \left(1 - \frac{u^2}{u_0^2}\right) + 2\frac{\lambda}{m} u \rho = 0, \\ \rho_{tt} - V_0^2 \rho_{xx} + \Omega_0^2 \rho + \frac{\lambda}{M}(u^2 - u_0^2) = 0, \end{cases} \tag{7}$$

corresponds to Hamiltonian (6), where $\omega_0^2 = 4U_0 / m u_0^2 > 0$.

We now seek for self-similar solutions of system (7) in the form $u(\xi)$ and $\rho(\xi)$, where the dimensionless coordinate $\xi = (x - x_0 - Vt)/a$ and V is the velocity of excitation propagation to be determined. With allowance for this, system (7) for $\lambda \neq 0$ can be reduced to the dimensionless form:

$$\begin{cases} \beta w_1^{IV} + (s^2 - 1)w_1'' - \alpha w_1(1 - w_1^2) + \gamma w_1 w_2 = 0, \\ \sigma w_2'' + w_2 = 1 - w_1^2, \end{cases} \tag{8}$$

where new dimensionless displacements of protons $w_1 = u/u_0$ and hydroxyl ions $w_2 = \rho/\rho_0$ have been introduced, $\rho_0 = \lambda u_0^2 / M\Omega_0^2$, the dimensionless excitation velocity is $s = V/s_0$, the nonlinearity parameter is $\alpha = a^2 \omega_0^2 / s_0^2 > 0$, the dispersion parameter is $\beta = b / a^2 s_0^2$, the parameter of interaction of sublattices is $\gamma = 2\lambda \rho_0 a^2 / m s_0^2$, and $\sigma = (V^2 - V_0^2)/a^2 \Omega_0^2$.

With initial conditions $w_2(0) = w_2'(0) = 0$, a formal solution of the second equation of system (8) can be written as follows:

$$w_2(\xi) = \int_0^{\xi} [1 - w_1^2(\zeta)] K(\xi - \zeta) d\zeta \,, \tag{9}$$

where the kernel is

$$K(\xi) = \begin{cases} \dfrac{1}{\sqrt{|\sigma|}}\sin\dfrac{\xi}{\sqrt{|\sigma|}}, & \sigma > 0, \\[2mm] \delta(\xi), & \sigma = 0, \\[2mm] \dfrac{1}{\sqrt{|\sigma|}}\sinh\dfrac{\xi}{\sqrt{|\sigma|}}, & \sigma < 0. \end{cases} \tag{10}$$

Here $\delta(\xi)$ is the Dirac delta-function. After substitution of Eq. (9) into the first equation of system (8), we obtain the nonlinear integro-differential equation:

$$\beta w_1^{IV} + (s^2 - 1)w_1'' - \alpha w_1(1 - w_1^2) + \gamma w_1 \int_0^\xi [1 - w_1^2(\zeta)]K(\xi - \zeta)d\zeta = 0 \tag{11}$$

equivalent to Eq. (8).

Let us consider first a molecular chain without interaction of proton and ion sublattices ($\lambda = 0$). In this case, Eqs. (7) are separated, and the second equation of this system is transformed into the conventional wave equation $\rho_{tt} - V_0^2 \rho_{xx} + \Omega_0^2 \rho = 0$ describing the longitudinal "sound" waves $\rho(x, t) \sim \exp(ikx - i\Omega t)$ with the frequency $\Omega^2 = \Omega_0^2 + V_0^2 k^2$. The first equation of system (7) in dimensionless variables at $\lambda = 0$ assumes the form (it also follows from Eq. (11) at $\gamma = 0$)

$$\beta w_1^{IV} + (s^2 - 1)w_1'' - \alpha w_1(1 - w_1^2) = 0 . \tag{12}$$

By definition, the nonlinearity parameter $\alpha > 0$, and the dispersion parameter β can change its sign [5]. Depending on signs of these parameters, Eq. (12) admits solutions of two types. For $\alpha > 0$ and $\beta > 0$, Eq. (12) has the solution

$$w_1(\xi) = A\frac{\sinh k\xi}{\cosh^2 k\xi} , \tag{13}$$

odd with respect to the point $\xi = 0$; we call it the antisymmetric state. Solution (13) describes the ion defect moving with the velocity $s^2 = 1 + 110\sqrt{11\alpha\beta}/121$; its amplitude is $A = \pm 2\sqrt{30/11}$, and its wave number is $k^2 = \sqrt{\alpha/11\beta}$. This ion defect corresponds to compression of the proton sublattice with the plus sign of the amplitude and stretching of the proton sublattice with the minus sign of the amplitude; therefore, it can be considered as a quasiparticle.

For $\alpha > 0$ and $\beta < 0$, Eq. (12) has the solution

$$w_1(\xi) = \frac{A}{\cosh^2 k\xi} , \tag{14}$$

even with respect to the point $\xi = 0$ with the amplitude $A = \pm\sqrt{15/8}$ and wave number $k^2 = \sqrt{\alpha/|\beta|}/8$; we call it the symmetric state. This solution also describes the quasiparticle for the proton sublattice deformation different from that described by Eq. (13) and moving with the velocity $s^2 = 1 - 5\sqrt{\alpha|\beta|}/2$.

Solutions (12) and (13) differ significantly from the solution of Eq. (12) obtained in [7] fat $\beta = 0$: $w_1(\xi) = \pm\tanh\xi\sqrt{\alpha/2(1 - s^2)}$, $s^2 < 1$. Based on the foregoing, we conclude that the strong enough interaction with the second neighbors in the proton sublattice changes significantly the dynamics of propagation of proton density excitations. In particular, quasiparticles of two types arise in this molecular chain, and antisymmetric quasiparticles (13) are propagated with the velocity $V > s_0$ exceeding that of the proton sound.

Let us consider now solutions of Eq. (11) with allowance for interaction of sublattices for $\gamma \neq 0$ but $\sigma = 0$, that is, for the proton motion with a fixed velocity $V = V_0$. For $\alpha > \gamma$ and $\beta > 0$, Eq. (11) has the solution describing antisymmetric state (13) with the parameters $s^2 = 1 + 110\sqrt{11(\alpha - \gamma)\beta}/121$, $A = \pm 2\sqrt{30/11}$, and $k^2 = \sqrt{(\alpha - \gamma)/11\beta}$. For $\alpha < \gamma$ and $\beta > 0$, Eq. (11) has the solution describing symmetric state (14) with the parameters $s^2 = 1 - 5\sqrt{\beta(\gamma - \alpha)}/2$, $A = \pm\sqrt{15/8}$, and $k^2 = \sqrt{(\gamma - \alpha)/\beta}/8$. From Eqs. (9) and (10) it follows that $w_2 = 1 - w_1^2$ for both states in the examined case. For $\beta < 0$, these conditions change places. As can be seen, coupling of the proton and parent sublattices results in a decrease in the potential barrier height and increase in the distance $\Delta\xi \sim 1/k$ passed by the proton from one potential well to another. This is in qualitative agreement with [7]. However, these solutions can exist only when the initial parameters of the system are related by the expression $V_0^2 = s_0^2(1 + 110\sqrt{11(\alpha - \gamma)\beta}/121)$ for the antisymmetric states and $V_0^2 = s_0^2(1 - 5\sqrt{(\alpha - \gamma)\beta}/2)$ for the symmetric states.

We also obtained two exact solutions of the system of equations (8) in general for $\gamma \neq 0$ and $\sigma \neq 0$. For $\alpha < \gamma$ and $\beta > 0$, system (8) has the simple symmetric solution:

$$w_1(\xi) = \frac{A_1}{\cosh^2 k\xi} + B, \quad w_2(\xi) = \frac{A_2}{\cosh^2 k\xi} \tag{15}$$

with the parameters

$$A_1 = \pm 2k^2\sqrt{\frac{30\beta}{\gamma - \alpha}}, B = \mp 1, \quad A_2 = \frac{4k^2}{\gamma - \alpha}\left\{20\beta k^2 \pm \sqrt{30(\gamma - \alpha)}\right\}, \tag{16}$$

$$k^2 = \frac{3(\gamma - \alpha)(c_1^2 - c_2^2) - 2c_1^2\sqrt{30\beta(\gamma - \alpha)}(5\gamma - 3\alpha) - R}{40c_1^2\beta(5\gamma - 3\alpha)}, c_1 = \frac{s_0}{a\Omega_0}, c_2 = \frac{V_0}{a\Omega_0}, \tag{17}$$

$$R = \sqrt{3(\gamma - \alpha)[3(\gamma - \alpha)(c_1^2 - c_2^2)^2 + 20c_1^2\beta(5\gamma - 3\alpha)]}. $$

The velocity of quasiparticle described by Eq. (15) is

$$s^2 = \frac{3c_1^2(\gamma - \alpha) + 3\gamma c_2^2 R}{6c_1^2(\gamma - \alpha)}. \tag{18}$$

Solution (15) exists only for molecular chains in which the initial parameters are related by a complex enough expression:

$$20\beta\gamma k^2 + \sqrt{30\beta(\gamma - \alpha)}[\alpha - 2\gamma + 8\beta k^4 + 2k^2(s^2 - 1)] = 0, \tag{19}$$

in which Eqs. (17) and (18) must be substituted.

For $\alpha > \gamma$ and $\beta > 0$, system (8) has a simple antisymmetric solution:

$$w_1(\xi) = A_1\frac{\sinh k\xi}{\cosh^2 k\xi}, \quad w_2(\xi) = \frac{A_2}{\cosh^2 k\xi} + B \tag{20}$$

with the parameters

$$A_1 = \pm 2k^2 \sqrt{\frac{30\beta}{\alpha - \gamma}}, \quad B = 1, \quad A_2 = \frac{6}{\gamma}\{10(2\gamma - \alpha) + 11k^2(s^2 - 1)\}, \tag{21}$$

$$k^2 = \frac{1 - s^2 \pm \sqrt{(1 - s^2) + 4\beta(\alpha - 2\gamma)}}{2\beta}. \tag{22}$$

The velocity of quasiparticle described by Eq. (20) is

$$s^2 = \frac{159\gamma^2 - 258\alpha\gamma + 99\alpha^2 \pm 10(3\alpha - 5\gamma)\sqrt{3\beta(\alpha - \gamma)(\alpha - 2\gamma)(33\alpha - 53\gamma)}}{3(\alpha - \gamma)(33\alpha - 53\gamma)}. \tag{23}$$

Solution (20) also exists only for molecular chains in which the initial parameters are related by a complex enough expression:

$$A_1^2 = 6A_2 k^2(c_2^2 - c_1^2 s^2), \tag{24}$$

in which Eqs. (21), (22), and (18) must be substituted.

It should be emphasized that exact solutions (15) and (20) exist only when very rigid restrictions are imposed on the parameters of the molecular chain. However, since there are a large number of the initial parameters in the molecular chain, and values of some of them undergo strong variations and even change their signs into opposite ones (for example, the dispersion parameter β and the sublattice coupling parameter λ can change signs), it is possible to meet Eqs. (19) and (24) providing the existence of quasiparticles of the considered types.

In conclusion, we note that taking into account the interaction of not only the nearest neighbors changes significantly the molecular chain dynamics. Charge density excitations of two types arise that differ strongly from the excitation in the chain with interaction of the nearest neighbors only. One of these excitations transfers the proton charge with high enough velocity exceeding the velocity of wave propagation in a linear chain, which explains the high mobility of protons along molecular chains of hydrogen bonds in ice crystals and solid alcohol.

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