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NONLINEAR DYNAMICS OF HYDROGEN-CONTAINING SYSTEMS: FERROELECTRICS AND IONIC CHANNELS OF BIOMEMBRANES

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We analyze a multicomponent soliton model of systems with hydrogen bond (hydrogen-containing ferroelectrics and biomembrane ionic channels), taking into account the interaction of proton and ion subsystems or of proton and ordered subsystems. Based on the system simulation, experimental data on triglycine sulfate and ionic channels of biological membranes are analyzed.

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1. Introduction

The proton transportal through hydrogen bond chains plays a key role in dynamics of all known hydrogen-containing systems, causing a number of fine nonlinear and quantum effects especially important during phase (or conformational) transitions. The hydrogen bond in various systems is usually described by the proton potential energy with two minima (double potential well). The bond dynamics is controlled by proton transition between these minima under various conditions. In complex systems, one should take into account the explicit interaction of basic subsystems, which leads necessarily to consideration of the multicomponent models [1–4]. Existence of the ordered subsystem with a phase transition gives rise to the two-component model describing the phase transition displacement in that subsystem under the impact of the proton subsystem [5, 6].

In this paper we study analytically and numerically nonlinear multicomponent models of systems with hydrogen bond, based on the two-component model earlier developed for biomolecular chains and hydrogen-bound ferroelectrics [1–4, 6–11].

2. Interaction of proton and ion subsystems in the two-component model

If one considers motion of the second "carrying" subsystem of negative ions (hydroxyl groups in water) or heavy molecular groups, the equation (two-component model) [12] is introduced to describe these groups, taking into account the interaction between proton and ion subsystems. In this case, the equation of an ion component is analogous to that of the proton component motion, however, the former being as a rule easier (linear). This allows its exact solution and then substitution into the equation of the proton component. Therefore, the solution to the nonlinear equation of proton subsystem is modified and the arising effects are very important.

For example, the potential barrier height is varied in the double proton well, which changes the proton motion (tunneling) mode. That motion, frequency, and soliton velocity are modulated by ion sublattice vibrations. Furthermore, there exists also the reverse impact of the proton sublattice on the

ion one due to the interaction of the subsystems [1, 4, 12]. The proton subsystem Hamiltonian is written as

$$H_1 = \int dx \left\{ \frac{1}{2} m \left(\frac{\partial u}{\partial t} \right)^2 + \frac{1}{2} m c_0^2 \left(\frac{\partial u}{\partial x} \right)^2 + V\left[u(x,t) \right] \right\}, \tag{1}$$

where m is the proton mass, u is the proton displacement from the middle l_0 between two neighboring frozen negative ions in the two-well anharmonic potential

$$V(u) = \frac{1}{2} A u^2 + \frac{1}{4} B u^4 \quad (A < 0,\ B > 0), \tag{2}$$

ω_0 is the characteristic frequency of proton–proton vibrations and $c_0 = l_0 \omega_0 = l_0 / t_0$ is the proton (sound) velocity. In the continuous limit, one has $l_0 = c_0 / \omega_0 \to 0$.

The ion (oxygen) subsystem Hamiltonian is given by

$$H_0 = \int dx \left[\frac{1}{2} M \left(\frac{\partial \rho}{\partial t} \right)^2 + \frac{1}{2} M v_0 \left(\frac{\partial \rho}{\partial x} \right)^2 + \frac{1}{2} M \Omega_0^2 \rho^2 \right], \tag{3}$$

where M is the mass of heavy ion groups, Ω_0 is the frequency of an optical mode of ion sublattice vibrations, ρ is the relative displacement of neighboring groups, $v_0 = l_0 \Omega_1$ is the characteristic velocity in the ion sublattice, and Ω_1 is the characteristic frequency of ion harmonic vibrations.

The Hamiltonian of interaction between the proton and ion subsystems (see [11])

$$H^{0,1} = \chi \rho \left(u^2 - u_0^2 \right) \tag{4}$$

leads to the equations of motion in the accompanying coordinate $s = x - vt$,

$$m c_0^2 \left(1 - \frac{v_0^2}{c_0^2} \right) \frac{\partial^2 u}{\partial s^2} - \left[(A + 2\chi\rho) u + B u^3 \right] = 0, \tag{5}$$

$$M \left(v^2 - v_0^2 \right) \frac{\partial^2 \rho}{\partial s^2} - M \Omega_0^2 \rho + \chi \left(u^2 - u_0^2 \right) = 0. \tag{6}$$

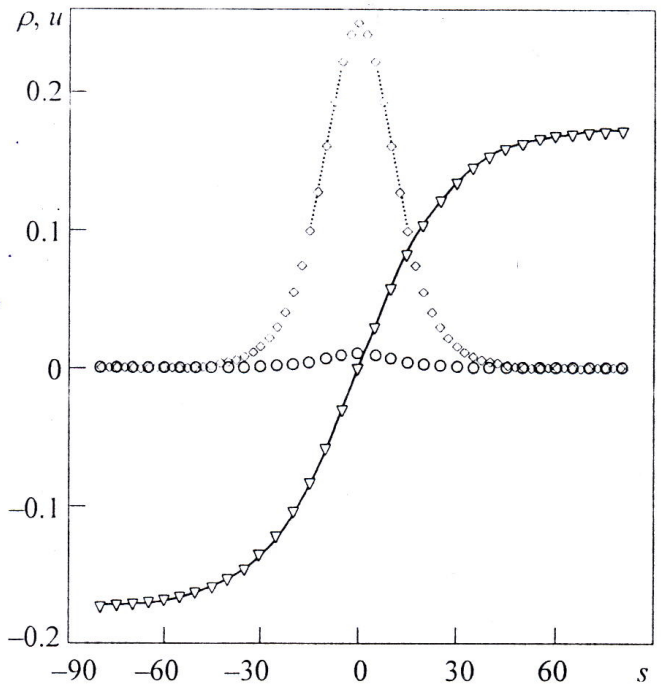

Figure 1. Dependence of the proton displacement u (kink) and the relative displacement ρ of oxygen ions (bell) on the coordinate s at $\rho_0 = 0.01$ (solid line and ○) and 0.25 (▽ and ◇).

Set (5), (6) is readily solved in a specific case when $v = v_0$ and one finds from (6) that

$$\rho = -\frac{\chi}{M\Omega_0^2} \left(u^2 - u_0^2 \right). \tag{7}$$

Solution in this case is written as

$$\rho = \rho_0 \operatorname{sech}^2 \left(a^* s \right) \quad \text{for the ion subsystem,} \tag{8}$$

$$u = u_0 \tanh \left(\frac{a^* s}{\sqrt{2}} \right) \quad \text{for the proton subsystem,} \tag{9}$$

where

$$\rho_0 = \frac{\chi u_0^2}{M \Omega_0^2}, \tag{10}$$

$$a^* = \frac{1}{c_0} \left(\frac{A^*}{m} \right)^{1/2}, \tag{11}$$

$$A^* = A + \frac{2\chi^2 u_0^2}{M\Omega_0^2} = A \left(1 + \frac{\chi^2}{2M\Omega_0} \frac{u_0^4}{v_0} \right). \tag{12}$$

These solutions at various parameters ρ_0 are plotted in Fig. 1.

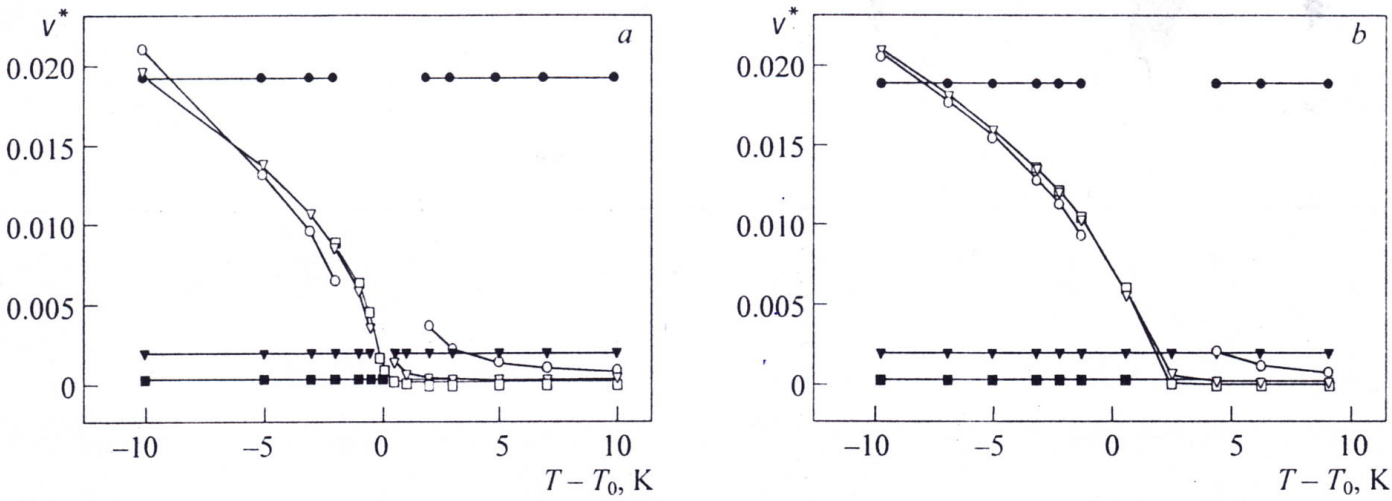

Figure 2. Temperature dependence of the velocity in the absence of (*a*) and with (*b*) the proton subsystem excitation at fields $E = 10^2$ (■, □), 10^3 (▼, ▽), and 10^4 V·m^{-1} (●, ○); closed and open symbols correspond to v_1^* and v_2^*.

3. Interaction between the proton and ordered subsystems in the two-component model

In this case, the proton subsystem Hamiltonian remains as before, while the Hamiltonian of another ordered subsystem with the order parameter ξ takes on the form

$$H_2 = Fv_c\left[F_0 + \frac{1}{2}\alpha\xi^2 + \frac{1}{4}\beta\xi^4 + \frac{1}{6}\gamma\xi^6 + \delta\left(\frac{\partial\xi}{\partial x}\right)^2\right], \quad (13)$$

where F is the free energy density and v_c is the second sublattice unit cell volume. Introducing the Hamiltonian of interaction between the proton and ordered subsystems,

$$H_{int} = D_0\left(u^2 - u_0^2\right)\xi^2 + Q_0 u\xi, \quad (14)$$

one finds the nonlinear equation for parameter ξ as

$$2\delta\frac{d^2\xi}{ds^2} + \lambda_2 v_2\frac{d\xi}{ds} - \left\{\left[\alpha + D\left(u^2 - u_0^2\right)\right]\xi + \beta\xi^3 + \gamma\xi^5 - E_2 + Qu\right\} = 0. \quad (15)$$

Here $\Gamma = 1/\lambda_2$ is the Landau–Khalatnikov coefficient of the second subsystem without critical behavior in temperature and $\alpha = \alpha_0' + \alpha_0(T - T_0) = \alpha_0(T - T_c)$, where α_0', α_0, $\gamma > 0$, $\beta < 0$ are coefficients of the Landau–Ginzburg–Devonshire thermodynamic expansion, T_0 and T_c are the phase transition and Curie–Weiss temperatures, $\delta > 0$ is a factor at the gradient term, E_2 is the external (electric in the case of polarization) field, and $D = D_0/v_c$ and $Q = Q_0/v_c$ are constants of the interaction between the subsystems.

The equation of motion for the proton subsystem in the field of external forces $F = qE_1$ (where q is the effective proton charge and qu is the proton subsystem polarization) takes on the analogous form

$$mc_0^2\left(1 - \frac{v_1^2}{c_0^2}\right)\frac{d^2u}{ds^2} + \lambda_1 v_1\frac{du}{ds} - \left[\left(A + D\xi^2\right)u + Bu^3 - \left(qE_1 - Q\xi\right)\right] = 0 \quad (16)$$

in the accompanying variable $s = x - v_1 t$ ($v_1 \neq v_2$ in general).

The analysis (see [1]) of set (15), (16) shows that its solutions have the form of kinks of a more complex form than (9), and the soliton motion of protons and the phase boundary of the ordered subsystem at velocities v_1 and v_2 are possible only in fields lower than certain critical values $E_1 \leq E_{c1}$,

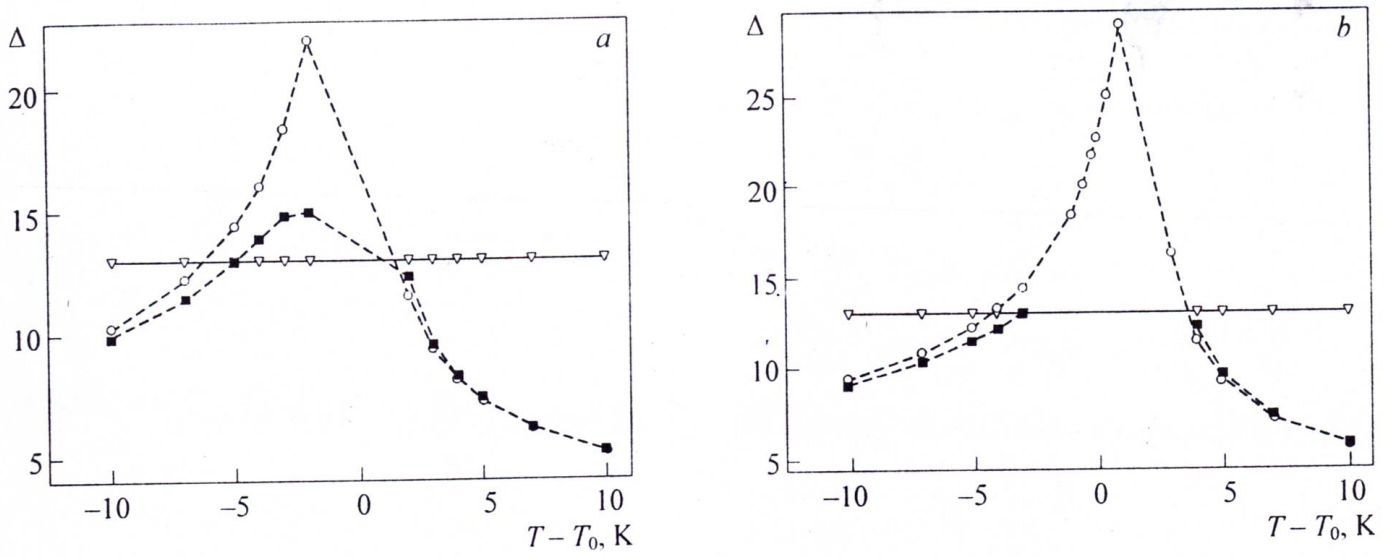

Figure 3. Temperature dependence of the kink halfwidth in the absence of (*a*) with (*b*) the proton subsystem excitation at electric fields $E = 10^3$ (solid line for Δ_1 and ○ for Δ_2) and 10^4 V·m^{-1} (▽ for Δ_1 and ■ for Δ_2).

$E_2 \le E_{c2}$. In a reduced form and for $\gamma = 0$, set (15), (16) transforms to

$$\begin{aligned} &\frac{d^2\zeta}{dz^2} + v_1^* \frac{d\zeta}{dz} + F_1(\zeta) = 0, \\ &\frac{d^2Y}{dz^2} + v_2^* \frac{dY}{dz} + F_2(Y) = 0, \end{aligned} \tag{17}$$

where the polynomials

$$\begin{aligned} F_1(\zeta) &= -(\zeta - \zeta_1)(\zeta - \zeta_2)(\zeta - \zeta_3), \\ F_1(Y) &= -(Y - Y_1)(Y - Y_2)(Y - Y_3), \end{aligned} \tag{18}$$

are expressed in terms of their roots

$$\begin{aligned} \zeta_1, y_1 &= \frac{2}{\sqrt{3}} \cos\left[\frac{1}{3}\cos^{-1}\left(-\frac{3\sqrt{3}}{2}E_{1,2}^*\right)\right], \\ \zeta_2, y_2 &= -\frac{2}{\sqrt{3}} \cos\left[\frac{\pi}{3} - \frac{1}{3}\cos^{-1}\left(-\frac{3\sqrt{3}}{2}E_{1,2}^*\right)\right], \\ \zeta_3, y_3 &= -\frac{2}{\sqrt{3}} \cos\left[\frac{\pi}{3} + \frac{1}{3}\cos^{-1}\left(-\frac{3\sqrt{3}}{2}E_{1,2}^*\right)\right]. \end{aligned} \tag{19}$$

The solutions have the form of kinks

$$\begin{aligned} \zeta(z) &= \zeta_2 + (\zeta_1 - \zeta_2)\left[1 + \exp\left(\pm\frac{z}{\Delta_1}\right)\right]^{-1}, \\ Y(z) &= Y_2 + (Y_1 - Y_2)\left[1 + \exp\left(\pm\frac{z}{\Delta_2}\right)\right]^{-1}, \end{aligned} \tag{20}$$

for velocities (see Fig. 2)

$$\begin{aligned} v_1^* &= \lambda_1 v_1 \left[\frac{m}{|A^*|\left(c_0^2 - v_1^2\right)}\right]^{1/2} = \lambda_1 v_1 \Delta_{01}\left(c_0^2 - v_1^2\right)^{-1/2}, \\ v_2^* &= \lambda_2 v_2 \left[\frac{1}{2\delta|\alpha^*|}\right]^{1/2} = \lambda_2 v_2 \left[\Delta_{02}|\alpha^*|\right]^{-1} \end{aligned} \tag{21}$$

and the halfwidth (see Fig. 3)

$$\begin{aligned} &\Delta_1 = \frac{\sqrt{2}}{\zeta_1 - \zeta_2}, \qquad \Delta_2 = \frac{\sqrt{2}}{Y_1 - Y_2}, \\ &\zeta = \frac{u}{u_0^*}, \quad u_0^* = \left(\frac{|A^*|}{B}\right)^{1/2}, \quad A^* = A + D\xi^2, \\ &Y = \frac{\xi}{\xi_0^*}, \quad \xi_0^* = \left(\frac{|\alpha^*|}{\beta}\right)^{1/2}, \quad \alpha^* = \alpha + Du^2. \end{aligned} \tag{22}$$

4. Data discussion and conclusion

Solutions for a number of the model parameters are numerically calculated on a basis of the formulas found earlier in [1–3] and with the same parameter values as in [1]. An analysis of variations in the kink velocity and halfwidth in the phase transition vicinity at microwave excitation of the proton subsystem and in the absence of such excitation (see Fig. 2, where the temperature T is measured from the transition point) shows the phase transition temperature shift by 2–3°, which conforms to the experimental data of [3] on triglycine sulfate.

Thus, the basic results of this work are the following:

(i) Differential equations are derived to describe nonlinear dynamics of soliton (kink) excitations in the model of proton and ordered subsystems interacting in hydrogen-containing systems (biomembrane ionic channels and hydrogen-containing ferroelectrics).

(ii) Possible solutions to the set of differential equations for nonlinear waves are studied in continual approximation and soliton solutions are found in special cases.

(iii) A code is developed for numerical study of the solutions found; calculations are performed for various model parameters.

(iv) A number of numerical results are analyzed and compared to the experimental data on triglycine sulfate.

(v) The found numerical data confirm the model validity and the possibility of its application to more complex biomolecular systems (biomembrane ionic channels and DNA) using triglycine sulfate as a model object.

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