International Journal of Theoretical Physics, Vol. 42, No. 12, December 2003 (© 2003)

Two-Component Solitary Waves in Hydrogen-Bonded Molecular Systems

Yuan-Fa Cheng[1]

Received July 31, 2003

The dynamics of two-component solitary waves in hydrogen-bonded chains in an external force and damping is investigated. The influence of the motion and the optical mode of the heavy ion sublattice on the portion sublattice is discussed. It will increase the soliton width and decrease the soliton mobility. The general expression for the kink soliton soliton is obtained. The velocity, the mobility and conductivity of the kink soliton are calculated. The results are in good agreement with the experimental data.

KEY WORDS: two-component solitary waves; optical mode; hydrogen-bonded chain.

1. INTRODUCTION

There is a large number of hydrogen-bonded condensed matter, organic and biological systems that are characterized by the formation of hydrogen-bonded molecular chains. The motion of the proton plays an important role in the phase transition of hydrogen bonded ferroelectrics and the conductivity of ice. Proton conductivity in hydrogen-bonded substances has attracted attention because of the observed protonic conductivity along the chain being about 10^3–10^4 times larger than that in the perpendicular direction (Gorden, 1987; Pang and Muller-Kirsten, 2000). The one-component soliton model for proton transport in a hydrogen-bonded chain in the presence of a constant external force is investigated by Gordon (1987). Considering the influence of motion of the heavy-ion sublattice on the proton sublattice, the two-component soliton model was suggested by a number of authors (Cheng, 2000; Xu and Huang, 1995). However, the heavy-ion sublattice is not an ideal simplex atomic lattice. The heavy ion has an internal vibration, as, e.g. the amide-I vibration in the peptide group of α-helical protein (Xu, 2000). Therefore, in this paper, we discuss the influence of the motion and the optical mode of the heavy-ion sublattice on the proton sublattice, in the presence of an external force and damping, based on the two-component soliton model. In Section 2 we present the model Hamiltonian and derive the equations of motion of the system.

[1] Department of Physics, Hubei University, Wuhan 43002, People's Republic of China.

0020-7748/03/1200-2983/0

In Section 3 we give the corresponding soliton solution. In Section 4 we investigate soliton velocity and conductivity. Finally in Section 5, we discuss the results and conclusions.

2. MODEL AND EQUATION OF MOTION

We assume that the coupling between the proton sublattice and the heave-ion sublattice is nonlinear in the model of the two-component soliton of hydrogen-bonded chains. The Hamiltonian of the system may be written as a sum of three terms

$$H = H_{\mathrm{p}} + H_{\mathrm{h}} + H_{\mathrm{int}} \tag{1}$$

where

$$H_{\mathrm{p}} = \sum_{j} \left\{ \frac{1}{2} m_1 \left[\dot{u}_i^2 + \omega_1^2 (u_{i+1} - u_j)^2 \right] + V(u_i) \right\} \tag{2}$$

is the Hamiltonian of the proton sublattice, m_1 is the mass of the proton, ω_1 is the characteristic frequency of the proton sublattice and

$$V(u_i) = -\frac{A}{2} u_i^2 + \frac{B}{4} u_i^4 \tag{3}$$

is the proton anharmonic potential in each hydrogen bond, and coefficients A, $B > 0$.

H_{h} in the Eq. (1) is the Hamiltonian of the heavy-ion sublattice.

$$H_{\mathrm{h}} = \sum_{i} \frac{1}{2} m_2 \left[\dot{\eta}_i^2 + \omega_2^2 (\eta_{i+1} - \eta_i)^2 + \Omega_{\mathrm{o}}^2 \eta_i^2 \right] \tag{4}$$

where m_2 is the mass of heavy ion ω_2 is the characteristic frequency of the heavy ions sublattice, and Ω_{o} is the frequency of the optical mode of the heavy-ion sublattice (Peyrard *et al.*, 1987).

$\mathrm{H}_{\mathrm{int}}$ in the Eq. (1) is the Hamiltonian of the proton–ion interaction.

$$H_{\mathrm{int}} = \sum_{i} \frac{\chi}{u_{\mathrm{o}}^2} \eta_i \left(u_i^2 - u_{\mathrm{o}}^2 \right) \tag{5}$$

where χ is coupling constant between the proton and the heavy sublattice.

In the continuum approximation model, the Hamiltonian can be written as (Cheng, 2003; Davydov, 1991).

$$H = \frac{1}{l}\int\left[\frac{1}{2}m_1\left(u_t^2 + c_o^2u_x^2\right) + \frac{1}{2}m_2\left(\eta_t^2 + \upsilon_o^2\eta_x^2 + \Omega_o^2\eta^2\right) + V(u) + \frac{k}{u_o^2}\eta\left(u^2 - u_o^2\right)\right]dx \tag{6}$$

where

$$V(u) = -\frac{A}{2}u^2 + \frac{B}{4}u^4 \tag{7}$$

Here, $u(x, t)$ and $\eta(x, t)$ are the displacement fields of the proton (mass m_1) and the heavy ion (mass m_2), respectively. l is the lattice spacing, $C_o = \omega_1 l$ and $\upsilon_o = \omega_2 l$ are the characteristic velocities of the proton and the heavy-ion sublattices, respectively. $k = \chi l^2$ is the coupling constant between the two sublattices. The Lagrange density of the system corresponding to Eq. (6) can be written as

$$L = T - U = \frac{1}{2}m_1u_t^2 + \frac{1}{2}m_2\eta_t^2 - \frac{1}{2}m_1c_o^2u_x^2 - \frac{1}{2}m_2\upsilon_o^2\eta_x^2 - \frac{1}{2}m_2\Omega_o^2\eta^2 - V(u) - \frac{k}{u_o^2}\eta\left(u^2 - u_o^2\right) \tag{8}$$

The Euler–Lagrange equations of motion from (6) and (8) are

$$u_{tt} - c_o^2u_{xx} + \frac{2k}{m_1u_o^2}\eta u + \frac{1}{m_1}\frac{dV(u)}{du} = 0 \tag{9}$$

$$\eta_{tt} - \upsilon_o^2\eta_{xx} + \frac{k}{m_2u_o^2}\left(u^2 - u_o^2\right) + \Omega_o^2\eta = 0 \tag{10}$$

3. SOLITON SOLUTION

In the presence of external force and damping, because of the fact that response of the heavy ions to the force and damping are very much less than for the protons, the force and the damping terms are only introduced in the equation of motion for the protons [6]. The equations of motion (9) and (10) are replaced by the following equations.

$$u_{tt} - c_o^2u_{xx} + \frac{2k}{m_1u_o^2}\eta u + \Gamma_1\frac{\partial u}{\partial t} + \frac{1}{m_1}\frac{dV(u)}{du} = F \tag{11}$$

$$\eta_{tt} - \upsilon_o^2\eta_{xx} + \frac{k}{m_2u_o^2}\left(u^2 - u_o^2\right) + \Omega_o^2\eta = 0 \tag{12}$$

where Γ_1 is the damping coefficient for the proton and F is the external force on the proton.

The partial differential Eqs. (11) and (12) in the independent variables x and t can be reduced to ordinary differential equations in the variable ξ by the substitution.

$$\xi = x - \upsilon t \tag{13}$$

where υ is the velocity of the moving frame, after the transformation (13), Eq. (12) can be written as

$$\upsilon^2 \eta_{\xi\xi} - \upsilon_o^2 \eta_{\xi\xi} + \frac{k}{m_2 u_o^2}\left(u^2 - u_o^2\right) + \Omega_o^2 \eta = 0$$

when $\upsilon = \upsilon_o$, we get

$$\eta = -\frac{k\left(u^2 - u_o^2\right)}{m_2 u_o^2 \Omega_o^2} \tag{14}$$

Equation (11) becomes

$$\upsilon_o^2 u_{\xi\xi} - c_o^2 u_{\xi\xi} + \frac{2k}{m_1 u_o^2}\eta u - \Gamma_1 \upsilon_o u_\xi + \frac{1}{m_1}\frac{dV(u)}{du} = F \tag{15}$$

Substituting Eq. (14) into Eq. (15), we obtain

$$\begin{aligned}\left(\upsilon_o^2 - c_o^2\right)u_{\xi\xi} - \Gamma_1 \upsilon_o u_\xi - \left(\frac{A}{m_1} - \frac{2k^2}{m_1 m_2 u_o^2 \Omega_o^2}\right)u \\ + \left(\frac{B}{m_1} - \frac{2k^2}{m_1 m_2 u_o^4 \Omega_o^2}\right)u^3 - \frac{e^* E}{m_1} = 0\end{aligned} \tag{16}$$

Where e^* is the effective charge of the soliton, E is the external electric field. Usually, $\upsilon_o^2 \ll c_o^2$, we have

$$-c_o^2 u_{\xi\xi} - \lambda u_\xi - \gamma u + g u^3 - \frac{e^* E}{m_1} = 0 \tag{17}$$

Here

$$\lambda = \Gamma_1 \upsilon_o,\ \gamma = \frac{A}{m_1} - \frac{2k^2}{m_1 m_2 u_o^2 \Omega_o^2},\quad g = \frac{B}{m_1} - \frac{2k^2}{m_1 m_2 u_o^4 \Omega_o^2} \tag{18}$$

Using the phase-plane method (Garden, 1987) we shall obtain the kink solution, For this reason we introduce the following notation:

$$\frac{du}{d\xi} = \rho \tag{19}$$

Equation (17) can be written as

$$c_o^2 \rho_\xi + \lambda \rho - g(u - u_1)(u - u_2)(u - u_3) = 0 \tag{20}$$

where

$$u_1 = 2\left(\frac{\gamma}{3g}\right)^{1/2}\cos\left\{\frac{1}{3}\arccos\left[\frac{3e^*E}{2m_1\gamma}\left(\frac{3g}{\gamma}\right)^{1/2}\right]\right\} \tag{21}$$

$$u_2 = -2\left(\frac{\gamma}{3g}\right)^{1/2}\cos\left\{\frac{\pi}{3}-\frac{1}{3}\arccos\left[\frac{3e^*E}{2m_1\gamma}\left(\frac{3g}{\gamma}\right)^{1/2}\right]\right\} \tag{22}$$

$$u_3 = -2\left(\frac{\gamma}{3g}\right)^{1/2}\cos\left\{\frac{\pi}{3}+\frac{1}{3}\arccos\left[\frac{3e^*E}{2m_1\gamma}\left(\frac{3g}{\gamma}\right)^{1/2}\right]\right\} \tag{23}$$

are the roots of the equation.

Therefore the kink-type solution which we seek corresponds to a trajectory in the (ρ, u) phase Plane of the system of Eqs. (19) and (20). From (19) and (20) we obtain a differential equation for solution trajectory as

$$c_{\mathrm{o}}^2\rho\frac{\partial\rho}{du} + \lambda\rho - g(u-u_1)(u-u_2)(u-u_3) = 0 \tag{24}$$

Equation (24) can be satisfied by a trajectory of the form

$$\rho = \rho_{\mathrm{o}}(u-u_1)(u-u_2) \tag{25}$$

Inserting Eq. (25) into (24), we have

$$\rho_{\mathrm{o}} = \frac{1}{c_{\mathrm{o}}}\sqrt{\frac{g}{2}} = \frac{1}{\sqrt{2}c_{\mathrm{o}}}\left(\frac{B}{m_1} - \frac{2k^2}{m_1m_2u_{\mathrm{o}}^4\Omega_{\mathrm{o}}^2}\right)^{1/2} \tag{26}$$

The substituting Eq. (25) into (19) and integrating (19), we get kink soliton solution

$$u = u_2 + (u_1 - u_2)(1 - e^{\xi/W_{\mathrm{k}}})^{-1} \tag{27}$$

Here W_{k} is the width of the soliton

$$W_{\mathrm{k}} = \frac{1}{\rho_{\mathrm{o}}(u_1-u_2)} = \frac{\sqrt{2}c_{\mathrm{o}}}{u_1-u_2}\left(\frac{B}{m_1} - \frac{2k^2}{m_1m_2u_{\mathrm{o}}^4\Omega_{\mathrm{o}}^2}\right)^{-1/2} \tag{28}$$

we see that the width of the soliton increase as interaction between the two sublattices and the influence of the optical mode of the heavy-ion sublattice, The kink soliton describes ion-type nonlinear defect because the charge density depends directly on $\delta_{\mathrm{e}} = (-\frac{\partial u}{\partial x})$ (Xu and Huang, 1995) Eq. (27) show that the motion of this kink describes the propagation of the charge, According to the theory of charge transport by solitons (Xu, 1993), the kink defect can capture and carry the electron, i.e., it transports charge and energy along hydrogen-bonded molecular chains.

4. VELOCITY AND CONDUCTIVITY

The substitution of (25) into (24) gives kink soliton velocity along hydrogen bonded molecular chains

$$\upsilon_o = \frac{3c_o}{\Gamma_1}\sqrt{\frac{g}{2}}u_3 = \frac{c_o}{\Gamma_1}(6\gamma)^{1/2}\cos\left\{\frac{\pi}{3} + \frac{1}{3}\arccos\left[\frac{3e^*E}{2m_1\gamma}\left(\frac{3g}{\gamma}\right)^{1/2}\right]\right\} \quad (29)$$

From (29) we obtain soliton velocity for a small external applied electric field

$$E \ll \frac{2m_1\gamma}{3e^*}\left(\frac{\gamma}{3g}\right)^{1/2}, \quad \upsilon_o = \frac{3c_o e^* E}{m_1\gamma\Gamma_1}\left(\frac{g}{2}\right)^{1/2}$$
$$= \frac{3c_o e^* E}{\Gamma_1\left(A - \frac{2k^2}{m_2 u_o^2\Omega_o^2}\right)}\left(\frac{B}{2m_1} - \frac{k^2}{m_1 m_2 u_o^4 \Omega_o^2}\right)^{1/2} \quad (30)$$

If we define the mobility of the kink soliton as

$$\upsilon_o = \mu E \quad (31)$$

where υ_o is qiven by (30), the mobility of the kink soliton is equal to

$$\mu = \frac{3c_o e^*}{\Gamma_1\left(A - \frac{2k^2}{m_2 u_o^2\Omega_o^2}\right)}\left(\frac{B}{2m_1} - \frac{k^2}{m_1 m_2 u_o^4 \Omega_o^2}\right)^{1/2} \quad (32)$$

This equation imply that influence of the coupling between two sublattices and optical mode of the heavy-ion sublattice is to reduce the mobility, when $k = 0$, Eq. (32) becomes mobility of soliton in one-component mode (Gorden, 1987).

If the density N of the kink soliton is small enough to neglect kink–kink interactions, Then we obtain the expression for the conductivity.

$$\sigma = Ne^*\mu = \frac{3Nc_o e^{*2}}{\Gamma_1\left(A - \frac{2k^2}{m_2 u_o^2\Omega_o^2}\right)}\left(\frac{B}{2m_1} - \frac{k^2}{m_1 m_2 u_o^4 \Omega_o^2}\right)^{1/2} \quad (33)$$

We have chosen the following set of model parameters in ice at -10°C (Gorden, 1987; Xu, 1996), $\Gamma_1 = 6 \times 10^{13}$ s^{-1}, $\Omega_o = 600$ cm^{-1}, $c_o = 1.1 \times 10^6$ cm s^{-1}, $m_2 = 17\,\mathrm{m}_1$, $k = 0.1$ eV Å^{-1}, $A = 4.92 \times 10^5$ gs^{-2}, $B = 14.6 \times 10^{23}$ gcm^{-2} s^{-2}, $N = 8 \times 10^{10}$ cm^{-3}, $u_o = 0.183$ Å. Taking $e^* = 1.2$ e, here e is the protonic charge. The calculations according to Eqs. (32) and 33 give $\mu = 4.5 \times 10^{-2}$ cm^2 V^{-1} s^{-1} and $\sigma = 6.9 \times 10^{-10}$ Ω^{-1} cm^{-1}. These values are close to observed one $\sigma = 6.6 \times 10^{-10}$ Ω^{-1} cm^{-1} (Geicke, 1984).

5. DISCUSSION AND CONCLUSIONS

Finally, we discuss the following two problems:

1. In the preceding discussion, approximation condition is written as

$$E \Big/ \frac{2m_1\gamma}{3e^*}\left(\frac{\gamma}{3g}\right)^{1/2} \ll 1 \tag{34}$$

We use the date for ice and obtain

$$\frac{2m_1\gamma}{3e^*}\left(\frac{\gamma}{3g}\right)^{1/2} = 1.9 \times 10^8 \text{ V cm}^{-1} \tag{35}$$

Taking $E_{\max} = 180$ KV cm^{-1}, we get

$$E_{\max} \Big/ \frac{2m_1 r}{3e^*}\left(\frac{\gamma}{3g}\right)^{1/2} = 0.94 \times 10^{-3} \ll 1 \tag{36}$$

This shows that the Eq. (34) usually can be satisfied.

2. Now we can check the above-mentioned approximation:

$$\upsilon_{\text{o}}^2/c_{\text{o}}^2 \ll 1 \tag{37}$$

From the data for ice and taking $E = 180 \times 10^3$ V cm^{-1}, we have

$$\upsilon_{\text{o}}^2 \big/ c_{\text{o}}^2 = \upsilon_{\max}^2 \big/ c_{\text{o}}^2 = \left[\frac{3e^* E}{m_1 \gamma \Gamma_1}\left(\frac{B}{2m_1}\right)^{1/2}\right]^2 = 0.57 \times 10^{-4} \ll 1 \tag{38}$$

Therefore, the Eq. (37) can easily be satisfied.

In conclusion, we have studied influence of the motion and the optical mode of the heavy ion sublattice on the proton sublattice in hydrogen-bonded chains in presence of an external force and damping, based on the two-component soliton model, and show that it will increase the width of the soliton and decrease the mobility. The solutions of the kink soliton is obtained. The velocity, the mobility and the conductivity of the kink soliton are calculated. The calculated conductivity is in satisfactory agreement with the experiment.

ACKNOWLEDGMENT

The author is grateful to Prof J. Z. Xu for helpful discussions.

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