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Dynamics of an Orientational-Kink Pair in a Hydrogen-Bonded Chain in an External Field

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We discuss dynamic properties of an orientational-kink pair in hydrogen-bonded chains in the presence of an external force and damping, based on a new two-component soliton model. We study the scattering of an electromagnetic wave by an orientational-kink pair. Finally, we find the expressions of the scattering cross-section of an orientational-kink pair for an electromagnetic wave and the mobility of the orientational-kink pair.

KEY WORDS: hydrogen-bonded chain; two-component model; orientational kink pair.

The hydrogen bridge exists in many biological molecular chains and solid state systems. The conduction mechanism of a soliton in hydrogen-bonded chains is an extremely important and interesting scientific problem. The motion of the protons may result in ionic and orientational (Bjerrum or bonding) defects, which correspond to the exchange and rotation of bonds in hydrogen-bonded chains, respectively (Sergienko, 1988, 1990). The former involve an intrabond motion of the (unique) binding proton, while the latter result from interbond or intermolecular motion of the protons due to rotations of molecules (e.g., the water molecules in ice) (Davydov, 1991; Pang and Müller-Kirsten, 2000). Thus the transfer of protons along the hydrogen-bonded chains is caused by the transport of two types of defects. Many authors have proposed a variety of soliton models to study the formation and the transport of defects in hydrogen-bonded chains (Pnevmatikos *et al.*, 1991; Xu and Huang, 1995). But they all suffer from the same defect, namely, they take into account only one or the other of the two possible types of defects. This is rather limited, especially since there exists an abundance of experimental evidence that clearly suggests that both types of defects participate in the transfer of charge across the hydrogen-bonded network (Tsironis and Pnevmatikos, 1989). The one-component soliton for proton transport in hydrogen-bonded chains was introduced by Pnevmatikos *et al.* (1991), considering the influence of motion of the heavy ions sublattice on the proton sublattice, and the two-component soliton

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model was suggested by Xu and Huang (1995). Recently Pang proposed a new two-component soliton model that can describe simultaneously the formation and propagation of ionic and orientational defects (Pang and Müller-Kirsten, 2000). Utilizing this model we have studied the motion of ionic defect in hydrogen-bonded chains in the presence of an external force (Cheng, 2001). In this paper, on the basis of Pang's model (Pang and Müller-Kirsten, 2000), we further discuss the motion of orientational defect in the presence of an external force and damping. We investigate the scattering of an electromagnetic wave by an orientational-kink pair and obtain the scattering cross-section of the orientational-kink pair for an electromagnetic wave. The mobility of the orientational-kink pair is also found.

Considering a new model Hamiltonian of the hydrogen-bonded molecular chain (Pang and Müller-Kirsten, 2000)

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

where

$$H_{\mathrm{p}} = \sum_i \left\{ \frac{1}{2m} p_i^2 + \frac{1}{2} m\omega_0^2 u_i^2 - \frac{1}{2} m\omega_1^2 u_i u_{i+1} + U(u_i) \right\} \tag{2}$$

and

$$U(u_i) = U_0 \left(1 - \left(\frac{u_1}{u_0} \right)^2 \right)^2 \tag{3}$$

$$H_{\mathrm{ion}} = \sum_i \left\{ \frac{1}{2M} P_i^2 + \frac{1}{2} \beta (\eta_i - \eta_{i-1})^2 \right\} \tag{4}$$

$$H_{\mathrm{int}} = \sum_i \left\{ \frac{1}{2} m\chi_1 (\eta_{i+1} - \eta_{i-1}) u_i^2 + m\chi_2 (\eta_{i+1} - \eta_i) u_i u_{i+1} \right\} \tag{5}$$

where the proton displacements and momenta are u_i and $p_i = m\dot{u}_i$ respectively, u_0 is the distance along the chain from the top of the barrier to one of the minima in the double-well potential, $U(u_i)$ is the proton potential energy in each hydrogen bond, and $\Delta = 2u_0$ is the distance between the two minima. The quantity $\frac{1}{2} m\omega_1^2 u_i u_{i+1}$ shows the correlation interaction between neighbouring protons caused by the dipole–dipole interactions. ω_0 and ω_1 are diagonal and nondiagonal elements of the dynamical matrix of the proton respectively, η_i and $P_i = M\dot{\eta}_i$ are the displacement of the heavy ion from its equilibrium position and its conjugate momentum respectively, $c_0 = l(\beta/M)^{1/2}$ is the velocity of sound in the heavy ionic sublattice, l is the lattice constant, and m and M are the masses of the proton and heavy ion respectively. The part H_{p} of H is the Hamiltonian of the protonic sublattice with an onsite double-well potential $U(u_i)$, H_{ion} being the Hamiltonian of the heavy ionic sublattice with low-frequency harmonic vibration and H_{int} being the interaction Hamiltonian between the protonic and the heavy ionic sublattices.

In the continuum approximation with the long-wavelength limit, the Euler–Lagrange equations of motion corresponding to Eq. (1) are (Cheng, 2001)

$$u_{tt} = \upsilon_1^2 u_{xx} - 2(\chi_1 + \chi_2) l \eta_x u + \frac{4U_0 u}{m u_0^2}\left[1 + \frac{m u_0^2\left(\omega_1^2 - \omega_0^2\right)}{4U_0} - \left(\frac{u}{u_0}\right)^2\right] \quad (6)$$

$$\eta_{tt} = c_0^2 \eta_{xx} + \frac{2m}{M}(\chi_1 + \chi_2) l u u_x \quad (7)$$

Here υ_1 and c_0 are the characteristic velocities of the proton and the heavy-ion sublattices, respectively.

Using the variable transformation $y = x - \upsilon t$, we let

$$\bar{\varepsilon} = \omega_0^2 - \omega_1^2 + 2g(\chi_1 + \chi_2) l - \frac{4U_0}{m u_0^2} \quad (8)$$

$$\bar{G} = \frac{2(\chi_1 + \chi_2)^2 m l^2}{m c_0^2 (1 - s^2)} - \frac{4U_0}{m u_0^4} \quad \text{and} \quad s = \frac{\upsilon}{c_0} \quad (9)$$

Integrating Eq. (7), we may reduce Eqs. (6) and (7) to the following equation (Cheng, 2000, 2001):

$$u_{yy} + \frac{\bar{\varepsilon}}{\upsilon^2 - \upsilon_1^2} u - \frac{\bar{G}}{\upsilon^2 - \upsilon_1^2} u^3 = 0 \quad (10)$$

When $\bar{\varepsilon} > 0$, $\bar{G} > 0$, and $0 < \upsilon < c_0$, $0 < \upsilon_1 < \upsilon$, Eq. (10) have kink soliton solution (Cheng, 2000, 2001)

$$u = \pm\left(\frac{\bar{\varepsilon}}{\bar{G}}\right)^{1/2} \tanh\left[\left(\frac{\bar{\varepsilon}}{2\left(\upsilon^2 - \upsilon_1^2\right)}\right)^{1/2} (x - \upsilon t)\right] \quad (11)$$

From (7) and (11) we get

$$\eta = \bar{D} u \quad (12)$$

Here we choose integration constant $g = \frac{m(\chi_1+\chi_2) l u_0^2}{M c_0^2 (1-s^2)}$, and we further set

$$\bar{D} = -\frac{\sqrt{2}(\chi_1 + \chi_2) m l}{M c_0^2 (1 - s^2)}\left(\frac{\upsilon^2 - \upsilon_1^2}{\bar{G}}\right)^{1/2} \quad (13)$$

Equation (11) describes orientational defect (Pang and Müller-Kirsten, 2000), the plus sign of $u\ (x, t)$ in (11) applies to the L orientational defect, which amounts to creation of a negative effective charge corresponding to a kink soliton, and the minus sign in $u\ (x, t)$ applies in the case of the D orientational defect, which amounts to creation of a positive effective charge corresponding to an antikink soliton (Davydov, 1991; Pang and Müller-Kirsten, 2000).

Equations (11) and (12) show that if the nonlinear excitation in the proton sublattice is an orientational-kink (or antikink), then the nonlinear excitation in the heavy-ion sublattice is an orientational antikink (or kink). They propagate along the chains with the same velocity in pairs, i.e. they form an orientational-kink pair.

From Eqs. (6) and (7) and considering the boundary conditions, we obtain the constant of the motion as follows:

$$\begin{aligned} P &= -\frac{1}{l}\int (m u_t u_x + M\eta_t\eta_x)\,dx \\ &= P_{\mathrm{k}} + P_{\mathrm{ak}} = \bar{M}^*_{\mathrm{sol}}\upsilon \end{aligned} \tag{14}$$

This is the momentum of an orientational-kink pair (Xu and Huang, 1995), where

$$P_{\mathrm{k}} = -\frac{m}{l}\int u_x u_t\,dx = \bar{m}^*\upsilon \tag{15}$$

$$\bar{m}^* = \frac{2\sqrt{2}m\bar{\varepsilon}^{3/2}}{3\left(\upsilon^2 - \upsilon_1^2\right)^{1/2}\bar{G}l} = Im \tag{16}$$

P_{k} and $\bar{m}^*$ are the momentum and the effective mass of the orientational-kink in the proton sublattice respectively.

$$P_{\mathrm{ak}} = -\frac{M}{l}\int \eta_x\eta_t\,dx = \bar{M}^*\upsilon \tag{17}$$

$$\bar{M}^* = \frac{2\sqrt{2}M\bar{D}^2\bar{\varepsilon}^{3/2}}{3\left(\upsilon^2 - \upsilon_1^2\right)^{1/2}\bar{G}l} = I\bar{D}^2 M \tag{18}$$

P_{ak} and $\bar{M}^*$ are the momentum and the effective mass of the orientational antikink in the heavy-ion sublattice respectively.

$$\bar{M}^*_{\mathrm{sol}} = \bar{m}^* + \bar{M}^* = I(m + \bar{D}^2 M) \tag{19}$$

$\bar{M}^*_{\mathrm{sol}}$ is the effective mass of the orientational-kink pair, where

$$I = \frac{2\sqrt{2}\bar{\varepsilon}^{3/2}}{3\left(\upsilon^2 - \upsilon_1^2\right)^{1/2}\bar{G}l} \tag{20}$$

In the presence of an external force and damping, the equations of motion ((6) and (7)) are replaced by the following equations (Peyrared *et al.*, 1987):

$$\begin{aligned} & u_{tt} - \upsilon_1^2 u_{xx} + 2(\chi_1 + \chi_2) l u \eta_x - \frac{4U_0 u}{m u_0^2} \\ & \quad \times \left[1 + \frac{m u_0^2\left(\omega_1^2 - \omega_0^2\right)}{4U_0} - \left(\frac{u}{u_0}\right)^2\right] = -\lambda_1 u_t + f_1 \end{aligned} \tag{21}$$

$$\eta_{tt} - c_0^2\eta_{xx} - \frac{2m}{M}(\chi_1 + \chi_2) l u u_x = -\lambda_2\eta_t + f_2 \tag{22}$$

Here $f_1 = -F_1/m,\ f_2 = -F_2/M$, F_1 and F_2 are the external forces on the proton and the heavy ion respectively, and λ_1 and λ_2 are the damping coefficients respectively for the proton and heavy ion motion. The right hand sides of Eqs. (21) and (22) are the perturbations.

Usually the perturbation is small and it is considered that the effect of an external force and damping on a kink will only lead to a little variation of the velocity of the kink but the waveform of the kink will not be changed. From Eqs. (11)–(13), (14), (21), and (22), and considering the boundary conditions, we find the equation of motion of an orientational-kink pair to be

$$\frac{dp}{dt} = -\lambda_1 P_{\mathrm{k}} - \lambda_2 P_{\mathrm{ak}} + \frac{2\bar{F}}{l}\left(\frac{\bar{\varepsilon}}{\bar{G}}\right)^{1/2} \tag{23}$$

Substituting Eqs. (15)–(20) into Eq. (23), we finally obtain the equation of motion of an orientational-kink pair in the presence of an external force and damping:

$$\frac{d\upsilon}{dt} + \bar{\Lambda}\upsilon = \frac{2\bar{F}}{M^*_{\mathrm{sol}} l}\left(\frac{\bar{\varepsilon}}{\bar{G}}\right)^{1/2} \tag{24}$$

where

$$\bar{F} = F_1 + \bar{D}F_2 \tag{25}$$

$$\bar{\Lambda} = \frac{1}{M^*_{\mathrm{sol}}}(\lambda_1 \bar{m}^* + \lambda_2 \bar{M}^*) \tag{26}$$

It is difficult to solve Eq. (24), and we discuss only the case where $\upsilon_1 < \upsilon \ll c_0$. Under this approximation, $\bar{G}$, $\bar{\varepsilon}$, $\bar{D}$, $\bar{\Lambda}\,M^*_{\mathrm{sol}}$ can be regarded as constants and be written as $\bar{G}_0$, $\bar{\varepsilon}_0$, $\bar{D}_0$, $\bar{\Lambda}_0$, M^{0*}_{sol}, e.g.

$$\bar{G}_0 = \frac{2(\chi_1 + \chi_2)^2 m l^2}{M c_0^2} - \frac{4U_0}{m u_0^4} \tag{27}$$

$$\bar{\varepsilon}_0 = \omega_0^2 - \omega_1^2 + \frac{2ml^2(\chi_1 + \chi_2)^2 u_0^2}{M c_0^2} - \frac{4U_0}{m u_0^2} \tag{28}$$

$$\bar{\Lambda}_0 = \frac{\lambda_1 m + \lambda_2 \bar{D}_0^2 M}{m + \bar{D}_0^2 M} \tag{29}$$

Equation (24) becomes

$$\frac{d\upsilon}{dt} + \bar{\Lambda}_0\upsilon = \frac{2\bar{F}}{M^{0*}_{\mathrm{sol}} l}\left(\frac{\bar{\varepsilon}_0}{\bar{G}_0}\right)^{1/2} \tag{30}$$

We here discuss the scattering of an orientational-kink pair for an electromagnetic wave. We assume that the system is affected by an electromagnetic wave, the velocity and displacement of the kink pair are very much less than the speed of light and the wavelength of the incident electromagnetic wave respectively, and the incident electrical field is given by $E = E_{\mathrm{m}} \exp(-i\Omega t)$, where E_{m} and Ω are the amplitude and the frequency of the incident electrical field respectively. In this case, the influence of the incident magnetic field on the kink pair can be neglected. Thus Eq. (30) becomes

$$\frac{d\upsilon}{dt} + \bar{\Lambda}_0 \upsilon = \frac{2\bar{e}^* E_{\mathrm{m}}}{\bar{M}^{0*}_{\mathrm{sol}} l} \left(\frac{\bar{\varepsilon}_0}{G_0} \right)^{1/2} \exp(-i\Omega t) \tag{31}$$

Here $\bar{F} = \bar{e}^* E_{\mathrm{m}} \exp(-i\Omega t) = (e_1 + \bar{D}_0 e_2) E_{\mathrm{m}} \exp(-i\Omega t)$; e_1 and e_2 are the effective charges of the kink in the proton and in the heavy ion sublattice respectively. From Eq. (31), we find the acceleration of an orientational-kink pair,

$$a = \frac{d\upsilon}{dt} = \frac{2\bar{e}^* E_{\mathrm{m}} \Omega}{\bar{M}^{0*}_{\mathrm{sol}} l (\bar{\Lambda}_0 + \Omega^2)^{1/2}} \left(\frac{\bar{\varepsilon}_0}{G_0} \right)^{1/2} \exp\left[-i \left(\Omega t - \varphi + \frac{\pi}{2} \right) \right] \tag{32}$$

where

$$\tan \varphi = \Omega / \bar{\Lambda}_0 \tag{33}$$

The accelerated orientational-kink pair will produce electromagnetic radiation. Therefore, we can get the average power of the electromagnetic wave scattered by an orientational-kink pair from Eq. (32),

$$W = \frac{2\Omega^2 \bar{e}^{*4} I_0}{3\pi \varepsilon^2 c^4 \bar{M}^{0*2}_{\mathrm{sol}} l^2 \left(\bar{\Lambda}_0^2 + \Omega^2 \right)} \left(\frac{\bar{\varepsilon}_0}{G_0} \right) \tag{34}$$

Here c is the speed of light, ε is the dielectric constant, and $I_0 = \frac{1}{2} \varepsilon c E_{\mathrm{m}}^2$ is the average energy flow of the incident electromagnetic wave. Thus we find the scattering cross-section of an orientational-kink pair for an electromagnetic wave,

$$\sigma = \frac{W}{I_0} = \frac{2\Omega^2 \bar{e}^{*4}}{3\pi \varepsilon^2 c^4 \bar{M}^{0*2}_{\mathrm{sol}} l^2 \left(\bar{\Lambda}_0^2 + \Omega^2 \right)} \left(\frac{\bar{\varepsilon}_0}{G_0} \right) \tag{35}$$

In the limit of low frequency, i.e., $\Omega \ll \bar{\Lambda}_0$, Eq. (35) becomes

$$\sigma = \frac{2\Omega^2 \bar{e}^{*4}}{3\pi \varepsilon^2 c^4 \bar{M}^{0*2}_{\mathrm{sol}} l^2 \bar{\Lambda}_0^2} \left(\frac{\bar{\varepsilon}_0}{G_0} \right) \tag{36}$$

i.e., the scattering cross-section is directly proportional to Ω^2.

In the limit of high frequency, i.e., $\Omega \gg \bar{\Lambda}_0$, Eq. (35) is given by

$$\sigma = \frac{2\bar{e}^{*4}}{3\pi \varepsilon^2 c^4 \bar{M}^{0*2}_{\mathrm{sol}} l^2} \left(\frac{\bar{\varepsilon}_0}{G_0} \right) = \frac{8}{3} \pi r_{\mathrm{s}}^2 \tag{37}$$

This is just the Thomson scattering cross-section. Here

$$r_s = \frac{2\bar{e}^{*2}}{4\pi\varepsilon c^2 \bar{M}^{0*}_{\rm sol} l}\left(\frac{\bar{\varepsilon}_0}{\bar{G}_0}\right)^{1/2} \tag{38}$$

is the effective scattering radius of the orientational-kink pair. Therefore, the orientational-kink pair is much like the free electron for the case of scattering of an electromagnetic wave with high frequency.

When the frequency of the external electrical field is equal to the zero, namely the system is subjected to a constant electrical field with strength $E_{\rm m}$, $\bar{F} = \bar{e}^* E_{\rm m} = (e_1 + \bar{D}_0 e_2) E_{\rm m}$. Solving Eq. (30), we obtain the mobility of the orientational-kink pair (Cheng, 2001),

$$\bar{\mu} = \frac{2e_1\left(1 + \bar{D}_0 \frac{e_2}{e_1}\right)}{(\lambda_1 \bar{m}^* + \lambda_2 M^*) l}\left(\frac{\bar{\varepsilon}_0}{\bar{G}_0}\right)^{1/2} \tag{39}$$

Equation (39) can be written as

$$\bar{\mu} = \bar{\mu}_0 \bar{Q}\left(1 + \bar{D}_0 \frac{e_2}{e_1}\right) \tag{40}$$

Here

$$\bar{Q} = \left(1 + \bar{D}_0^2 \frac{\lambda_2 M}{\lambda_1 m}\right)^{-1}\left[\frac{m u_0^2}{4U_0}\left(\omega_0^2 - \omega_1^2\right) + \frac{2g(\chi_1 + \chi_2) m l u_0^2}{4U_0} - 1\right]^{-1/2} \tag{41}$$

$$\bar{\mu}_0 = \frac{3e_1\left(\upsilon^2 - \upsilon_1^2\right)^{1/2}}{\lambda_1 m \omega_{\rm H}}\left(\frac{\bar{G}_0}{\bar{\varepsilon}_0}\right)^{1/2} \tag{42}$$

where $\omega_{\rm H}$ is the frequency of the O—H stretching vibration and $\bar{\mu}_0$ is the mobility of the kink in the one-component soliton model (Xu, 1990). Equations (40)–(42) imply that the influence of motion of the heavy ions and the coupling between the two sublattices is to decrease the mobility.

We have chosen the following set of model parameters for ice (Gordon, 1987; Pang and Müller-Kirsten, 2000; Xu, 1990): $m = m_{\rm p}$, $M = 100 m_{\rm p}$, $U_0 = 10$ ev, $\Delta = 2u_0$, $\Delta = 0.367$–0.780 Å, $l = 5$ Å, $\upsilon_1 = 10^3$ m s^{-1}, $c_0 = 10^4$ m s^{-1}, $\lambda_1 = 6 \times 10^{13}$ s^{-1}, $\chi_1 = 3 \times 10^{47}$ m s^{-2}, $\chi_2 = 0.2 \times 10^{44}$ m s^{-2}, $\nu_{\rm H} = 3250$ cm^{-1}, $e_1 = 0.36e$, where e is the protonic charge. Taking $\upsilon = 1.1 \times 10^3$ m s^{-1}. The calculations according to Eqs. (40)–(42) give $\mu = (3.2 \sim 6.9) \times 10^{-4}$ cm^2 V^{-1} s^{-1}. This result agrees with that of orientational defect accounts for 10^{-4} cm^2 V^{-1} s^{-1} by Jaccard (Davydov, 1991).

In conclusion, we have studied the motion of an orientational-kink pair in hydrogen-bonded chains in the presence of an external force and damping, on the basis of a new two-component soliton model. Furthermore, we investigated the scattering of an electromagnetic wave by an orientational-kink pair and show that scattering of an electromagnetic wave by an orientational-kink pair of high frequency is similar to Thomson scattering of a free electron. The scattering cross-section of the orientational-kink pair for an electromagnetic wave and mobility of the orientational-kink pair have also been found. The calculated mobility agrees with that of Jaccard.

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