Dynamics of the Davydov model in α -helical proteins: Effects of the coupling parameter and temperature

Albert F. Lawrence

Molecular Electronics Center, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213 and Industrial Electronics Group Technology Center, Hughes Aircraft Company, 6155 El Camino Real, Carlsbad, California 92008

James C. McDaniel, David B. Chang, and Brian M. Pierce Support Systems Organization, Hughes Aircraft Company, P.O. Box 9399, Long Beach, California 90810

Robert R. Birge

Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213 (Received 25 April 1985; revised manuscript received 15 October 1985)

A model incorporating exciton-phonon interactions has been proposed as a mechanism for localizing and stabilizing energy transport in long-chain proteins. Previous analytical and numerical studies have not adequately addressed the effects of thermal phonons, which may act to disperse exciton energy. We have performed numerical calculations which indicate that excitons are strongly dispersed at biologically relevant temperatures. Furthermore, the propagation of the excitonphonon system at low temperatures makes a transition from a solitary-wave mode to a stationary, self-trapped mode as the coupling between excitons and phonons is increased. We also report new calculations of exciton—normal-mode coupling in the formamide dimer, which indicate that more sophisticated models are necessary to yield the true coupling constant in proteins.

I. INTRODUCTION

One of the central problems of bioenergetics is determining the mechanism or mechanisms by which energy is transferred from site to site in large protein molecules.¹ Exchange of energy from site to site along the protein backbone via amide-I excitation has been proposed as a possible vehicle for energy propagation in enzymes and other protein molecules.²⁻⁶ Because the excitation energy of an amide-I bond is slightly less than one-half of the energy released by hydrolysis of one molecule of adenosine triphosphate, Davydov has proposed a model in which two quanta of amide-I excitation energy are stabilized by phonons in a combined excitation which propagates as a solitary wave along a long α -helical molecule.³ Details of this model, which treats the amide-I vibration as a molecular exciton, have been presented in a number of papers by Davydov, $^{2-4}$ Scott, $^{6-8}$ and others. $^{9-11}$ In essence, the model is one dimensional, requires a nonlinear interaction between excitons and acoustic phonons, and in the continuum approximation predicts the stabilization of two or three quanta of amide-I excitation energy in a solitarywave state.

Numerical calculations by Scott^7 and Hyman *et al.*⁹ have tended to verify the results derived from the continuum approximation. The numerical models exhibit formation of solitary waves subsequent to excitation of two or three amide-I bonds at the end of a long molecule. As predicted from the continuum approximation,³ these localized disturbances are dynamically stable and persist for times which are much longer than the estimated time for dispersion of an amide-I excitation^{1,3} which does not in-

teract with phonons.

Several issues need to be resolved before Davydov's model can be applied to proteins in a living cell. Among these are the effects of thermal vibrations and the nature (and strength) of the coupling between acoustic phonons and amide-I vibrations. Although the bulk of the work on the dynamics of the Davydov model is based on the assumption that the temperature is absolute zero, Davydov has derived equations for a long chain in thermal equilibrium with a heat bath.⁵ His main result is that thermalization decreases the effective exciton-phonon coupling and increases the exciton mass. Derivation of simple closed expressions for the magnitudes of thermal effects requires adopting several simplifying assumptions in addition to the continuum approximation. Furthermore, for biologically relevant temperatures, the lattice energy contributed by thermal phonons will exceed the energy contributed by exciton-induced phonons.¹² This should lead to qualitatively different effects of thermalization at different exciton-phonon coupling strengths.

II. DAVYDOV MODEL

Our computational model is given in previous papers^{12,13} and by Hyman *et al.*⁹ The Hamiltonian for phonons and excitons interacting in the protein α helix is given as⁷

$$H_{\rm sol} = H_{\rm ex} + H_{\rm ph} + H_{\rm int} , \qquad (1)$$

where H_{ex} is the contribution of the unperturbed excitons, H_{ph} is the contribution of the unperturbed phonons, and H_{int} is the contribution of the interaction between exci-

tons and phonons.

Before presenting an explicit formula for H_{sol} , some explanation of the structure of the protein α helix is necessary. The protein backbone is a covalently bonded chain

The helical structure is given by a series of hydrogen bonds between C=O units and H-N units. Because the number of peptide bonds per turn of the helix is approximately 2.7, the hydrogen-bonded chains form three spines circling the helix in the opposite direction to the backbone.⁵ The sequence of bonds in a spine is given as

Thus in the Davydov model each amide-I bond is in a cell (n,i) where n is determined by the position along the backbone (counting by groups of three residues) and i is determined by the spine.

The exciton Hamiltonian is given by

$$H_{ex} = \sum_{(n,i)} H_{n,i} + \frac{1}{2} \sum_{\substack{(n,i) \\ (m,j)}} V_{(n,i),(m,j)} , \qquad (2)$$

where the first sum is over the Hamiltonian operator for isolated group and the second sum is over all cells such that $(n,i) \neq (m,j)$. (See Ref. 14.) The wave function is given by the product

$$\Phi = \prod_{(n,i)} \phi_{(n,i)f} , \qquad (3)$$

where the $\phi_{(n,i)f}$ are eigenfunctions of the operator $H_{n,i}$. (We are assuming that the overlap integral $\int \phi^*_{(n,i)f} \phi_{(m,j)f'}$ may be neglected.)

The Davydov model is generally presented in the second quantization. Following Davydov, $b_{(n,i)f}^{\dagger}$ and $b_{(n,i)f}$ denote the creation and annihilation operators of the state f in the cell (n,i). The operators associated with the same cell (n,i) and state satisfy the Fermi commutation rules; if the state or cell is different, the operators satisfy Bose commutation rules. In the second quantization representation

$$H_{ex} = \sum \epsilon_f b^{\dagger}_{(n,i)f} b_{(n,i)f} + \frac{1}{2} \sum b^{\dagger}_{(n,i)f'} b^{\dagger}_{(m,j)g'} b_{(m,j)g} b_{(n,i)f} \times \langle f'g' | V_{(n,i)(m,j)} | gf \rangle , \qquad (4)$$

where ϵ_f is the energy of state f and the second sum is over all combinations such that $n \neq m$. (See Ref. 14.) We write

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$$P_{(n,i)f} = b_{(n,i)0}^{\dagger} b_{(n,i)f}^{\dagger} ,$$

$$P_{(n,i)f}^{\dagger} = b_{(n,i)f}^{\dagger} b_{(n,i)0} .$$
(5)

We adopt a two-level model, so we may suppress the third

index in Eq. (5). Furthermore, we neglect all terms except those arising from nearest-neighbor interactions in the Heitler-London approximation.¹⁴ We may then write the contribution due to unperturbed excitons:

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$$H_{ex} = \Delta \sum_{n,i} P_{n,i}^{\dagger} - J \sum_{n,i} (P_{n+1,i}^{\dagger} P_{n,i} + P_{n,i}^{\dagger} P_{n+1,i}) + L \sum_{n,i} (P_{n,i+1}^{\dagger} P_{n,i} + P_{n,i}^{\dagger} P_{n,i+1}) .$$
(6)

The parameters Δ , J, and L are given as the excitation energy of an amide-I bond in the protein, the resonant coupling energy between a particular amide-I bond and its nearest neighbors along the hydrogen-bonded spine, and the resonant coupling between a particular amide-I bond and the nearest neighbors along the helix.¹⁴

The phonon Hamiltonian is given as a one-dimensional chain of harmonic oscillators:

$$H_{\rm ph} = (1/2M) \sum_{n,i} p_{n,i}^2 + (w/2) \sum_{n,i} (u_{n,i} - u_{n-1,i})^2 .$$
(7)

(See Ref. 15.) In Eq. (7) the parameters M and wrepresent the mass of a peptide unit and the spring constant of the helix.

The interaction between excitons and phonons is given by

$$H_{\text{int}} = \chi_1 \sum_{n,i} P_{n,i}^{\dagger} P_{n,i} (u_{n+1,i} - u_{n,i}) + \chi_2 \sum_{n,i} (P_{n,i}^{\dagger} P_{n+1,i} + P_{n+1,i}^{\dagger} P_{n,i}) \times (u_{n+1,i} - u_{n,i}) , \qquad (8)$$

where χ_1 gives the coupling originating from a change of amide-I excitation energy and χ_2 gives the coupling originating from the change of exchange energy due to stretching of the helix between groups n + 1 and n. (See Refs. 5 and 7.) Various estimates of χ_1 and χ_2 have appeared in the literature. Hyman *et al.*⁹ employed the estimate $\chi_1 = \chi_2 = \chi$ where χ was taken to be in the range $2 \times 10^{-11} - 6 \times 10^{-11}$ N. Scott, in a later publication,⁷ estimated χ_2 by the following formula:

$$\chi^2 = \frac{3J}{d} , \qquad (9)$$

where $J = 7.8 \text{ cm}^{-1}$ and d = 4.5 Å. This gives $\chi_2 = 10^{-12}$ N. Scott also assigned χ_1 a value of 3.4×10^{-11} N. Our calculations have thrown this estimate into question. As discussed in Appendix A, we obtain much lower values. Also, as may be seen from examination of the dynamical equations in Appendix B [Eq. (B10)], the effects of χ_1 and χ_2 are indistinguishable in energy transfer from excitons to phonons and thus in the formation of solitary waves or self-trapped states.

III. DYNAMICAL EQUATIONS

We define a wave function

$$|\phi_{\rm sol}\rangle = \sum C_{n,i}(t)P_{n,i}^{\dagger}\exp[\sigma(t)]|0\rangle , \qquad (10)$$

where

$$|0\rangle = \pi \phi_{(n,i)0} \tag{11}$$

is the ground state and

$$\sigma(t) = -(i/\hbar) \sum_{n,i} \left[\beta_{n,i}(t)p - \pi_{n,i}(t)u_{n,i} \right].$$
(12)

(See Refs. 5 and 7.)

The equations of motion for the $C_{n,i}(t)$ and $\beta_{n,i}(t)$ are derived in Appendix B. We assign the same numerical values to the parameters of the model as in Hyman *et al.*⁹ This gives the following coupled system of second-order equations:

$$idC_{n,i}/dt = (1.41)C_{n,i} \sum_{n,i} \left[(d\beta_{n,i}/dt)^2 + (\beta_{n+1,i} - \beta_{n,i})^2 \right] - 0.058(C_{n-1,i} + C_{n+1,i}) + 0.092(C_{n,i+1} + C_{n,i-1}) + 0.372(10^{10}\chi) \left[(1 - \delta_N^n)(\beta_{n+1,i} - \beta_{n,i})C_{n,i} + (1 - \delta_0^n)(\beta_{n,i} - \beta_{n-1,i})C_{n,i} \right]$$

$$+(1-\delta_{N}^{n})C_{n+1,i}(\beta_{n+1,i}-\beta_{n,i})+(1-\delta_{0}^{n})C_{n-1,i}(\beta_{n,i}-\beta_{n-1,i})], \qquad (13a)$$

$$d^{2}\beta_{n,i}/dt^{2} = (1 - \delta_{N}^{n})(-\beta_{n-1,i} + \beta_{n,i}) + (1 - \delta_{0}^{n})(\beta_{n,i} - \beta_{n-1,i}) + 0.132(10^{10}\chi)[(1 - \delta_{N}^{n})(1 - \delta_{0}^{n})(|C_{n+1,i}|^{2} - |C_{n-1,i}|^{2}) + \delta_{0}^{n}(|C_{n+1,i}|^{2} + |C_{n,i}|^{2}) - \delta_{N}^{n}(|C_{n-1,i}|^{2} + |C_{n,i}|^{2}) + C_{n,i}^{*}(C_{n+1,i} - C_{n-1,i}) + (C_{n+1,i}^{*} - C_{n-1,i}^{*})C_{n,i}].$$
(13b)

The time variable in these equations has been normalized by factoring out $(w/M)^{1/2}$. The delta functions δ_0^n and δ_N^n account for the boundary conditions at the n=0 and N ends of the helix, respectively.

During our computations we used values of 0.5×10^{-10} , 1.0×10^{-10} , 1.5×10^{-10} , and 3.0×10^{-10} N for the nonlinear coupling constant. Chain length was set to 200 residues. Various initial conditions were employed, to generate the effects of various levels of excitation and the effects of thermal phonons. We permitted the chain to relax for 20 psec before introducing amide-I excitations. The potential energy, which was introduced by chain distortion, corresponded for each temperature to the total phonon energy expected at that temperature.

IV. THERMAL FLUCTUATIONS

In this treatment of the interaction of excitons and phonons in a thermalized linear chain, Davydov⁵ calculates the function

$$H = \sum_{(\mathbf{v}_q)} \rho_{\mathbf{v}\mathbf{v}} H_{\mathbf{v}\mathbf{v}} , \qquad (14)$$

where q is a wave number, (v_q) represents a particular phonon state of the chain

$$|v\rangle = |(v_q)\rangle = \prod_{q} |v_q\rangle , \qquad (15)$$

the $\rho_{\nu\nu}$ are the diagonal elements of the density matrix of phonon states, and

$$H_{\gamma\gamma} = \langle \psi_{\text{sol},\gamma} | H | \psi_{\text{sol},\gamma} \rangle . \tag{16}$$

Furthermore, H is the operator H_{sol} for a linear chain and

$$\psi_{\text{sol},\nu} = \sum C_n(t) P_n^{\dagger} | 0 \rangle U_n(t) | P \rangle , \qquad (17)$$

that is, $\psi_{sol,v}$ denotes the thermalized wave function corresponding to the wave function ψ_{sol} defined in Eq. (10). Given these definitions for H_{vv} and $\psi_{sol,v}$ it is possible to calculate the dynamics of the chain for a particular choice of occupation numbers (v_q) . Davydov, in calculating the function H by averaging over all possible phonon occupation numbers, applies the random-phase approximation, which neglects correlations among the phonons.

Because numerical studies have shown formation and propagation of a Davydov soliton only over a narrow range of coupling parameters (Refs. 7-9) one might expect that the random fluctuations in distances between adjacent peptide residue would have strong effects upon the propagation of excitons along the protein α helix. Application of the random-phase approximation smooths out these fluctuations by neglecting the correlations. Furthermore, it would be extremely difficult to predict the behavior of a three-spine helix from analysis of a linear chain, were correlations significant. Our approach, therefore, is to assign random phonon occupation numbers consistent with the prescription of the fluctuationdissipation theorem and calculate the dynamics of the chain for each specific assignment. Analysis of chain dynamics for several specific assignments of phonon occupation number establishes whether a soliton is likely to form and thus whether Davydov's averaging procedure is valid.

We turn now to a discussion of the phonon spectrum. The fluctuation-dissipation theorem gives the expected phonon energy. We assume classical dynamics for the acoustic phonons. In this model the system observables q are driven by external forces $f_i^Q(t)$.¹⁶ The Hamiltonian may be written¹⁶⁻¹⁸

$$H = H_0 + \sum_{i} F_i^{Q}(t)Q_i \; ; \tag{18}$$

the spectra $G_{ij}(\omega)$ of the Q_i 's in thermal equilibrium may be expressed in terms of the admittance functions of the system. Specifically, assume the Fourier transforms of $\langle dQ/dt \rangle$ and $F_i^Q(t)$,

$$\alpha_j(\omega) = \left[1/(2\pi)^{1/2}\right] \int_{-\infty}^{\infty} dt \, e^{-j\omega t} \langle dQ_i/dt \rangle , \quad (19a)$$

$$\gamma_i(\omega) = [1/(2\pi)^{1/2}] \int_{-\infty}^{\infty} dt \, e^{-j\omega t} F_i^Q(t) ,$$
 (19b)

are related by the admittance functions $Y_{ij}(\omega)$:

$$\alpha_j(\omega) = \sum_i \gamma_i(\omega) Y_{ij}(\omega) .$$
⁽²⁰⁾

Then the power spectra G_{ij} defined as the Fourier transforms of the correlation functions $\frac{1}{2} \{Q_i, Q_j(t)\}_+$ in thermal equilibrium,

$$G_{ij}(\omega) = [1/(2\pi)^{1/2}] \int_{-\infty}^{\infty} dt \, e^{-i\omega t \frac{1}{2}} \langle \{Q_i, Q_j(t)\}_+ \rangle ,$$
(21)

are given in terms of the blackbody function

$$E(\omega,\beta) = (\hbar\omega/2) \coth(h\beta\omega/2)$$
(22)

and the admittance functions $Y_{ij}(\omega)$:

$$\operatorname{Re}^{(s)}G_{ij}(\omega) = -(2/\pi)^{1/2} [E(\omega,\beta)/\omega^{2}] \operatorname{Re}^{(s)}Y_{ij}(\omega) ,$$
(23a)
$$\operatorname{Im}^{(a)}G_{ij}(\omega) = -i(2/\pi)^{1/2} [E(\omega,\beta)/\omega^{2}] \operatorname{Im}^{(a)}Y_{ij}(\omega) .$$
(23b)

In these equations the superscripts (s) and (a) of an expression denote the portions of the function which are symmetrical and antisymmetrical in the subscripts *i* and *j*, respectively. The quantity β is defined in terms of temperature *T* and Boltzmann's constant k_B :

$$\beta = 1/k_B T . \tag{24}$$

In order to apply this theorem to acoustic phonons in an α helix, we treat the system as three uncoupled onedimensional lattices of point masses coupled by linear restoring forces. The equation of motion for the classical case may be written

$$M\ddot{u}_{n} = K(u_{n+1} - u_{n}) - K(u_{n} - u_{n-1}) - vM\dot{u}_{n} + F_{n} , \quad (25)$$

where v is a disspation term [not to be confused with the use of v in Eq. (14)], F_n is the forcing function, K is the restoring force, and u_n is the displacement of the *n*th mass.¹⁶

Assuming that a is the equilibrium distance between units, this system may be decomposed into its normal modes,

$$u_n = u_k(t) \exp(ikan) , \qquad (26a)$$

$$F_n = F_k(t) \exp(ikan) , \qquad (26b)$$

where k is the kth normal mode, and rewritten as a series of uncoupled equations in the time-varying amplitudes $u_k(t)$:

$$M\ddot{u}_{k} = Ku_{k}[2\cos(ka)-2] + \nu M\dot{u}_{k} + F_{k}$$
 (27)

The solution to this equation is well known:¹⁶

$$u_{k}(t) = Y_{k}(t)\dot{u}_{n}(0) + W_{k}(t)u_{k}(0) + \int_{0}^{t} Y_{k}(t)F_{k}(t-\tau)d\tau .$$
(28)

This gives the transfer function

$$Y_{k}(\omega) = (1/M)[i\omega/(-\omega^{2} + \omega_{0}^{2} - \omega i\nu)], \qquad (29)$$

where

$$\omega_0^2 = (2K/M)[1 - \cos(ka)] > 0.$$
(30)

The function $Y_k(w)$ can be taken as an admittance function because of the relation of the force term $F_k(t)$ and the normal mode (observable) in Eq. (28).

By Eq. (29),

Re
$$Y = -\frac{1}{M} \frac{\omega^2 v}{(\omega^2 - \omega^2)^2 + \omega^2 v^2}$$
. (31)

The power in the kth normal mode may be calculated by insertion of Eq. (31) in Eq. (23) and integrating over ω . If v is assumed to be small, this leads to

$$G(\omega_0) = \int G(\omega) d\omega$$

= $(2/\pi)^{1/2} E(\omega_0, \beta) (\pi/2\omega_0^2 M)$. (32)

This corresponds to the power in the kth normal mode which would be obtained in the $\nu \rightarrow 0$ limit on applying the usual Landau $\omega \rightarrow \omega + i\epsilon$ prescription for the treatment of susceptibilities. In applying this approximation we are assuming that the clamping time constant is less than the time constants given by the frequencies of interest.

The average value of the square of the phonon displacements $\langle |B|^2 \rangle$ may be written as

$$\langle |B|^2 \rangle = \sum_{k=\pi/Na}^{\pi/a} \frac{\hbar}{2MN\omega_k} \coth(\hbar\beta\omega_k) , \qquad (33)$$

$$k = \pi/Na, 2\pi/Na, \dots, \pi/a,$$

$$\beta = 1/k_BT, \text{ and } \omega_k^2 = V_0^2/a^2[1 - \cos(ka)].$$
(34)

The following constants were used in our calculations: $V_0 = 1.15 \times 10^4$ m/sec=phonon velocity, $\dot{M} = 3(1.17 \times 10^{-25} \text{ kg}) = 3 \times \text{mass}$ of peptide unit, N = 66 = number of cells (3 peptide units), $a = 4.5 \times 10^{-10}$ m=distance between adjacent turns of helix.

The differential equations (6) were solved on a VAX 11/780, using double-precision arithmetic. A third-order Adam-Bashford-Moulton method was used to perform the integrations. The code was set to maintain a relative error of 0.000001 during each time step. This was sufficient to maintain $\sum_{n,i} |C_{n,i}|^2 - I$ at a value less than 0.0001 during the computation, where I=the number of amide-I bonds initially excited and $C_{n,i}$ describes the exciton probability amplitude along the *i*th chain.

V. RESULTS

The results of our calculations are represented in Figs. 1-11. With the exception of Fig. 7(b) each of the plots depicts the evolution of the probability amplitudes $|C_{n,i}(t)|$. The horizontal axis of each plot is the residue number. The vertical axis represents a superposition of

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FIG. 1. Exciton propagation. Horizontal axis: residue number. Vertical axis: probability amplitude modulus and time superimposed. Traces are at 4×10^{-13} -sec intervals. Coupling constant is 0.5×10^{-10} N, initial excitation is one quantum of amide-I bond energy in first residue, temperature is 0 K. The bulk of the energy is in dispersive wave. The small disturbance which propagates at about half the velocity of the dispersive wave is a solitary wave. Note interference between solitary wave and reflected dispersive wave.

time and amplitude. The time increment from each horizontal plot to the next is 0.4 psec.

In general, variation of the nonlinear coupling constant, initial conditions, and nominal temperature all have profound effects on the dynamics of the system. The general effects are as follows.

FIG. 2. Exciton propagation. Axes, coupling constant, and temperature are as in Fig. 1. Initial excitation is two quanta (in first two residues of chain). Both a large-amplitude solitary wave and a dispersive wave form. Dispersive wave develops strong interference patterns at the chain boundary. The solitary wave may be seen to have trailing disturbances, which propagate at a slightly slower velocity. These also exhibit interactions with the reflected dispersive wave. Solitary wave has complex dynamical structure, exhibiting internal oscillations which propagate as small wavelets running counter to the motion of the main wave for 3 or 4 psec before dispersing. This produces an oscillation of the energy between spines, as observed by Scott (Ref. 7).

(1) Nonlinear coupling constant. Transport changes qualitatively between values of χ equal to 0.5×10^{-10} and 1.0×10^{-10} N. Another change was observed between 1.5×10^{-10} and 3.0×10^{-10} N. Both solitary waves and



FIG. 3. Exciton propagation. Axes, etc., are as in Fig. 1. Initial excitation is three quanta, one each in the first three residues of the chain. The probability amplitude of the solitary wave increases in Figs. 1-3 while the amplitude of the dispersive wave remains constant.

dispersive waves were observed for χ equal to 0.5×10^{-10} N, solitary-wave propagation alone at 1.0 and 1.5×10^{-10} N, and a localized disturbance at 3.0×10^{-10} N. In the latter case the propagation appeared to be by a hopping motion.

(2) Initial condition. Soliton formation requires two or three quanta excitation at 0.5×10^{-10} N, while a single quantum is sufficient to produce a localized wave at higher values. Multiple quantum excitation at 3.0×10^{-10} N gives a localized excitation which is attracted to the end



FIG. 4. Exciton propagation. Axes are as in Fig. 1. Coupling constant is 1.5×10^{-10} N, with one quantum initial excitation. Solitary wave forms, in contrast with the case of coupling constant of 0.5×10^{-10} N. Solitary wave decelerates and radiates a dispersive wave.

of the chain.

(3) Thermalization. Solitary waves are strongly dispersed by introduction of thermal phonons at a nominal temperature of 240 K or higher. Although a localized wave begins to propagate under some conditions for coupling constants of 0.5, 1.0, and 1.5×10^{-10} N, it is dispersed before traveling more than ten residues along a spine. In the case of a coupling constant of 3.0×10^{-10} N, no localized disturbance appears at all, and motion of the exciton appears to be diffusive.



FIG. 5. Exciton propagation. Axes are as in Fig. 1. Coupling constant is as in Fig. 4, two quanta initial excitation. Dispersive wave forms as well as solitary wave. Solitary wave persists after reflection.

Energy propagation under nonthermal conditions occurs in three modes, phonons, excitons and a boundstate combination of phonons and amide-I excitation. Figures 1-3 show the dynamics for the lowest value chosen for the nonlinear coupling, and Figs. 4-7(a) show the dynamics for the other values chosen during our study. In general, the bound state propagates as a solitary wave, while the phonons and excitons propagate dispersively. The equations for free exciton and phonon propa-



FIG. 6. Exciton propagation. Axes are in Fig. 1. Coupling constant is 3.0×10^{-10} N, with one quantum initial excitation. Solitary wave forms and decelerates to zero velocity. The exciton then oscillates between adjacent sites on the same spine, then hops randomly to an adjacent site on the spine.

gation may be obtained by setting the coupling constant equal to zero:

$$ih (dC_{n,i}/dt) = -J(C_{n+1,i} + C_{n-1,i}) + L(C_{n,i+1} + C_{n,i-1}) + WC_{n,i}, \quad (35)$$

$$M(d^{2}\beta_{n,i}/dt^{2}) = w(\beta_{n+1,i} - 2\beta_{n,i} + \beta_{n-1,i}) .$$
 (36)

Equation (35) may be taken to describe the dispersive ex-



FIG. 7. (a) Exciton propagation. Axes and chain parameters are the same as in Fig. 6, initial excitation is two quanta. Some radiation of exciton probability is apparent, especially during initial deceleration of disturbance. (b) Phonon propagation. Horizontal axis is residue number, vertical axis is time and displacement superimposed. Solitary-wave disturbance is associated with large-amplitude displacement. Note scattering of phonons during formation of the solitary disturbance.

citon propagating ahead of the solitary wave in Figs. 1–3. Phonons (not shown) were also seen to propagate freely in the records corresponding to these figures during the first hundred picoseconds. Exciton velocity is seen to be twice the velocity of the exciton-phonon bound state for coupling constant 0.5×10^{-10} , phonon velocity about five times that of the bound state.

Interaction between propagating phonons and the dispersive exciton in Figs. 1-3 was seen to be negligible.

The interaction between phonons and the solitary wave is also minor, but as may be seen from the figures, the interaction between the reflected exciton and the solitary wave is quite strong. Although the solitary wave is seen to begin reforming after interacting with the reflected exciton, the completion of the process was interrupted by the solitary wave colliding with the end of the chain.

The ratio of the probability amplitude of the exciton and the bound states depends both upon the initial excitation and the nonlinear coupling constant. A solitary wave forms for a one quantum initial excitation at coupling constant 1.0×10^{-10} N. At higher values for the coupling constant the amide-I excitation is trapped at a single site and appears to propagate by a random hopping motion. The probability for formation of a free exciton appears to be negligible at coupling constants greater than or equal to 1.5×10^{-10} N.

The motion of the exciton at the highest value of the nonlinear coupling constant, 3.0×10^{-10} N, more resem-

bles that of a small polaron than a freely propagating exciton. This is also verified through comparison of Figs. 7(a) and 7(b). Figure 7(b) shows the evolution of the coherent phonon states on the same time scale as Fig. 7(a). The amide-I excitation is seen to make hopping transitions when it interacts with phonons reflecting between the ends of the chain. This is not an accident, because as Davydov has shown, a Hamiltonian very similar to that presented in Eqs. (1) and (2) describes the interaction of an electron interacting with phonons along a one-dimensional



200 All conditions. Axes ¹⁰ N, initial excita-FIG. 9. Exciton propagation. Same conditions.

FIG. 8. Exciton propagation under thermal conditions. Axes as in Fig. 1. Coupling constant is 1.0×10^{-10} N, initial excitation is three quanta, thermal phonons correspond to 240 K. Exciton is dispersed rapidly over wide region of the chain.

FIG. 9. Exciton propagation. Same conditions as in Fig. 8, except initial excitation is two quanta. Dispersion is more rapid than shown in Fig. 8.

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chain. In the case of a small polaron, a self-trapped electron, the electron may tunnel to an adjacent site when lattice vibrations prepare a potential well near the polaron which is equivalent to the energy of the well already occupied by the electron. The tendency of the amide-I excitation to go to the end of the chain as in Figs. 6 and 7(a) may also be explained by this model. Because the phonon wave train interacts with itself when it is reflected from the end of the chain, the density of sites available for hopping transitions increases toward the ends the chain. Furthermore, as observed by Hyman *et al.*, free boundaries make the ends of the chain most favorable energeti-

Propagation of amide-I excitation energy seems also to exhibit qualitative changes in behavior under thermal conditions. Although some degree of localization is apparent for coupling constants of 0.5 and 1.0×10^{-10} N, as in Figs. 8–10 we did not observe any evidence of a stable solitary wave. The wave system in Fig. 10 preserves some of the features of the corresponding zero-temperature case, but the wave which should correspond to the solitonlike entity of Fig. 3 continues to spread, so it is not dynamically stable. Propagation of excitation at the highest coupling constant in our calculations, 3.0×10^{-10} , was always completely random, as in Fig. 11.

cally for exciton occupation.



FIG. 10. Exciton propagation. Coupling constant is 0.5×10^{-10} N, initial excitation is three quanta, thermal phonons are at temperature of 300 K. Dispersive wave is visible as in Figs. 1–3 but solitary wave does not form.



FIG. 11. Exciton propagation. Coupling constant is 3.0×10^{-10} N, two quanta excitation, temperature is 240 K. Propagation appears as a purely diffusion process.

VI. DISCUSSION

Although the dynamics exhibited by the Davydov model at biologically relevant temperatures casts some doubt on the existence of amide-I solitons in the proteins of living cells, the model is still of interest because it shows a wide range of behavior at low temperature. We have observed at least two bifurcations in the lowtemperature dynamics as the nonlinear coupling constant is increased from 0.5 to 3.0×10^{-10} N. The model exhibits transitions from coherent (single excitation, low coupling) to solitonic (multiple excitation, low coupling) propagation and from solitonic to highly localized, incoherent (high coupling) propagation. Both coherent and incoherent propagation of excitons have been treated extensively in the literature: In particular, our calculations recover the dynamics described by Agronovich and Gala- nin^{19} for excitons and by $Emin^{20-22}$ for the formally similar case of small polarons.

The continuum limit for the dynamical equations (B9) and (B10) has been given by Scott in normalized space and time coordinates:

$$i\frac{\partial A}{\partial \tau} + \frac{\partial^2 A}{\partial \xi^2} = \frac{k_1 k_2 \chi}{(1 - s^2)c^6} |A|^2 A , \qquad (37)$$

where $|A|^2$ is the longitudinal density of amide-I excitation energy $\chi = \chi_1 + \chi_2$, c is the longitudinal sound speed, and sc is the speed of propagation of a solitary wave. Further, k_1 and k_2 may be calculated from the parameters of the model by noting Eqs. (B9) and (B10) reduce to

$$i\frac{\partial A}{\partial t} + \frac{\partial^2 A}{\partial x^2} = -k_1 \chi \rho A ,$$

$$\frac{\partial^2 \rho}{\partial x^2} - \frac{1}{c^2} \frac{\partial^2 \rho}{\partial t^2} = k_2 \chi \frac{\partial^2}{\partial x^2} (|A|^2) ,$$
(38)

where

 $\rho = \partial \beta / \partial \chi$.

There are two interesting limiting cases for Eq. (37). The first, obtained by setting $\chi = 0$ in Eq. (38), corresponds to the continuum limit of Eqs. (35). This might be denoted a coherent exciton and corresponds to the situation in Fig. 1. The second, obtained by setting the time derivative equal to zero in Eq. (37), corresponds to the situation in Figs. 6 and 7. It is interesting to note that the equation specified by Emin,²²

$$\left[\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2}-\frac{z^2}{s}|\phi(x)|^2\right]\phi(x)=E\phi(x),\qquad(39)$$

is formally similar to the stationary case of Eq. (37). This inspection of the continuum equation for a Davydov soliton shows that it is an intermediate state between a coherent exciton and a polaronlike state or an incoherent exciton. Thus, the existence of a Davydov soliton in a molecular crystal at low temperatures depends on the value of the nonlinear coupling parameter being within the correct range and the material being sufficiently anisotropic to permit exciton propagation only in a preferred direction.

Given that such materials exist, a further question is how this intermediate state may be observed. One suggested approach is via measurement of Raman lines.^{7,23} Our previous calculations indicate that the phonons generated by the nonlinear coupling are difficult to distinguish from the normal modes of short protein segments.¹³ Another approach would be to consider the optical properties. The recent development of femtosecond pulse light sources makes possible measurement of transient perturbations of the optical properties of crystals. One such experiment, demonstrating the existence of an inverse electro-optical effect, has recently been reported by Auston *et al.*²⁴ In this experiment a Cherenkov cone of electromagnetic radiation produced by a pulse is detected by a second probe pulse. An analogous experiment may determine whether there is a nonlinear coupling between excitons and phonons generating a self-trapped state in a molecular crystal.

The microscopic model for the experimental system involves photons, excitons, and phonons. This would seem to be a hopelessly complex many-body problem, but considerable simplification is possible. One may treat the phonons classically as time-varying perturbations in a polariton model. This treatment has the advantage that the crystal-field Hamiltonian (exciton, phonon, and interaction terms) may be diagonalized in terms of Bose operators representing annihilation and creation of polaritons.²⁵

In particular, we may write

$$H = \sum_{l} (\Delta E_l + E_l \xi_l^{\dagger} \xi_l) + \cdots , \qquad (40)$$

where the ellipsis denotes phonon terms, and where ΔE_l and E_1 are (slowly) time-varying functions dependent on the phonon-perturbed interatomic distances in the molecular crystal and ξ_l^{\dagger} and ξ_l are polariton annihilation and creation operators. The calculations are a straightforward modification of those presented by Turlet et al.²⁴ In particular, this model gives time- and space-varying dispersions for photons in the neighborhood of a system of propagating solitary waves. In this region, small shifts in resonance frequency such as those induced by changes in intermolecular distances would produce large changes in propagation of a second probe pulse. In particular, a pump pulse near resonance would generate excitons. The probe pulse would interact with the phonons generated via the phonon-exciton coupling. The phonons would produce time- and wavelength-dependent changes in the propagation of the probe pulse.

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APPENDIX A: CALCULATION OF EXCITON-PHONON COUPLING CONSTANTS

According to Kuprievich and Kudritskaya,^{26,27} the exciton-phonon interaction parameter consists of a resonance component (χ_2) and two nonresonance components (χ_1^+, χ_1^-) . The χ_2 term can be obtained from the known magnitude of the resonance interaction between the transition dipoles associated with the amide-I vibration in α -helical polypeptides. The nonresonance components are best determined from a theoretical treatment of exciton-phonon coupling at the microscopic level. This treatment involves the use of quantum-mechanical self-consistent-field molecular-orbital (SCFMO) procedure.

The Hamiltonian for the interaction of vibrational excitons with acoustical phonons in a discrete chain of Nmolecular units forming a regular one-dimensional lattice was derived by Kuprievich and Kudritskaya^{26,27} in a form differing slightly from that reported by Davydov:⁵ In this expression χ_1^+ and χ_1^- are the parameters defining nonresonance interaction of a unit with its neighbors and χ_2 is the parameter defining the resonance interaction between neighboring units.

The explicit formulations of χ_1^+ , χ_1^- , and χ_2 for a dimeric group consisting of peptide groups m and m + 1 are as follows:^{26,27}

$$\chi_1^+ = (\hbar/2\omega)\partial(\partial^2 E_{m,m+1}/\partial Q_m^2)/\partial R_{m,m+1} , \qquad (A2)$$

$$\chi_1^- = (\hbar/2\omega)\partial(\partial^2 E_{m,m+1}/\partial Q_{m+1}^2)/\partial R_{m,m+1} , \qquad (A3)$$

$$\chi_2 = (\hbar/2\omega)\partial(\partial^2 E_{m,m+1}/\partial Q_m\partial Q_{m+1})/\partial R_{m,m+1}, \quad (A4)$$

where ω is the intramolecular amide-I vibrational frequency, $R_{m,m+1}$ is the distance or hydrogen-bond length between groups m and m + 1, $E_{m,m+1}$ is the interaction energy (or total energy in the Born-Oppenheimer approximation²⁸) of groups m and m + 1, and Q_i is the normalmode coordinate for the amide-I vibrations in groups mand m + 1. Since the second derivatives of the total energy of the dimer with respect to its vibrational normal coordinates are proportional to the harmonic force constants for these modes, the coupling parameters in Eqs. (A2)-(A4) can be viewed as the first derivatives of the harmonic force constants for the amide-I vibrations in the dimer with respect to the intermolecular distance $R_{m,m+1}$. Thus, the acoustical phonons of the α helix which are defined principally by changes in $R_{m,m+1}$ (i.e., changes in the pitch of the α helix^{26,27}) are coupled to the amide-I vibrational excitons.

A value of 10^{-12} N for χ_2 can be derived from the known magnitude of the resonance interaction between the amide-I vibrational transition dipoles. Kuprievich and Kudritskaya²⁶ argue that χ_1^- is negligible with respect to χ_1^+ . The principal reason is that the dominant contribution to the amide-I vibrational normal mode in a peptide group is the C=O bond stretching motion.^{26,29,30} As a result, the amide-I vibration of group *m* will be much more perturbed than that of group m + 1 by changes in $R_{m,m+1}$.

The calculation of the interaction energy $E_{m,m+1}$ of the two peptide groups as a function of the intra- and intermolecular coordinates is fundamental to the determination of χ_1^+ . In the Born-Oppenheimer or adiabatic approximation,²⁸ the interaction energy is equivalent to the total energy E for the system, which is calculatable using quantum-mechanical *ab initio* SCFMO procedures (Schaefer, Ref. 31).

The mapping of the *E* surface for a dipeptide system as a function of its intra- and intermolecular coordinates is a formidable task. However, as outlined by Kuprievich and Kudritskaya,²⁶ one can obtain a crude estimate of χ_1 by investigating the simplest system that contains two peptide groups connected by a hydrogen bond, i.e., the formamide dimer. To do this, we determined an equilibrium geometry for the dimer and approximated the amide-I vibrational normal mode as a C=O bond stretching motion.

Both Kuprievich and Kudritskaya's and our SCFMO calculations of the total energy of the formamide dimer were performed with the minimal atomic-orbital basis set composed of 36 Slater-type orbitals (STO), each being approximated by three Gaussian functions (3G) (Ref. 32). The STO-3G basis set is good only for qualitative analyses of the geometries of amide compounds.^{30,31} For example, an energy-minimized geometry of the formamide monomer calculated using the STO-3G basis set was not in complete agreement with the experimentally determined geometry for the molecule.³⁰ The major differences were that the calculated geometry was slightly nonplanar, while the observed one was planar, and that the calculated C—N bond length was 0.1 Å longer than the observed one.³⁰

The specific differences between Kuprievich and Kudritskaya's²⁶ and our approaches to the calculation of χ_1^+ are the determination of an equilibrium geometry for the dimer and the manner in which the C=O distance was changed. Our equilibrium geometry was derived from an energy minimization of the complete geometry of the dimer. This was accomplished by utilizing energy gradient and optimization routines. The only constraint on the geometry optimization was that the dimer had to be planar. This constraint was implemented because the observed geometry of the formamide monomer is planar.³³

TABLE I. Calculated values of the nonresonance excitonphonon coupling parameter for different diagonal force constants for the C=O bond in the formamide dimer and monomer.

	$\chi_1^+(N \times 10^{11})^b$	
$k (N/m)^a$	Present work ^c	Ref. 26
1150	-0.27	- 3.64
(monomer, Ref. 33) ^e 1380 (monomer, Ref. 30) ^f	-0.22	-3.03
1540	-0.20	-2.72
1473	-0.21	-2.84
dimer, present work) ⁱ	-0.20	-2.65

^aThe diagonal force constant for the stretching of the C(1) = O(1) bond.

^bThe nonresonance exciton-phonon coupling parameter. $\chi_1^+ = (\hbar\omega/2K)(\partial K/\partial R) = (\hbar\omega/2K)(\Delta K/\Delta R)$, where $\hbar\omega =$ the experimental mean frequency of the amide-I vibration (1660 cm⁻¹ = 3.297 × 10⁻²⁰ J). K as defined in e. $K = \Delta(\Delta E)/\Delta\xi$, where ξ reflects the carbonyl bond length.

"The value of χ_1^+ determined using $\Delta K / \Delta R$ calculated in the present work.

^dThe value of χ_1^+ determined using $\Delta K / \Delta R$ calculated by Kuprievich and Kudritskaya.

^eDerived from spectroscopic data.

^fCalculated using the *ab initio* SCFMO method with the 4-31G split-valence basis set.

 g^{-i} Calculated using the *ab initio* SCFMO method with the STO-3G basis set.

The change in C=O distances should correspond to the motion of the carbon and oxygen atoms in the C(1)= O(1) bond stretching motion. We elected to move both the C(1) and O(1) atoms in increments of 0.01 bohr, so that *E* was calculated at 0.0, 0.02, and 0.04 bohr.

Table I lists Kuprievich and Kudritskaya's and our calculated values of χ_1^+ for different harmonic force constants for the C=O bond stretching vibration in the formamide dimer and monomer. The disagreement between Kuprievich and Kudritskaya's calculated value for χ_1^+ and ours was disturbing, so we recalculated value for χ_1^+ using the exact procedure of Kuprievich and Kudritskaya,²⁶ obtaining a calculated magnitude of 0.7×10^{-11} N for χ_1^+ . Although this is larger than our original calculated magnitude of 0.2×10^{-11} N, it still is less than the minimum value of 3.5×10^{-11} N predicted by Scott to sustain a Davydov soliton.⁷

A more sophisticated ab initio SCFMO calculation employing the 4-31G basis set³⁴ yielded a magnitude of 1.3×10^{-11} N for χ_1^+ . This magnitude is less than Scott's minimum value, but it has increased relative to the one calculated using the STO-3G basis set. Therefore, as one improves the sophistication of the SCFMO calculation, one would expect χ_1^+ to increase. Because χ_1^+ is proportional to the hydrogen-bond binding energy, the stronger the hydrogen bond, the greater the value of χ_1^+ . There is no doubt that the hydrogen bond for the formamide dimer is stronger than what we have calculated using the 4-31G basis set, because we have neglected the van der Waals forces. Furthermore, the strength of hydrogen bonds between molecular units in a hydrogen-bonded polymer chain can be double that of the hydrogen bond in a dimer.³⁵ By including van der Waals forces in our theoretical formalism and by increasing the number of formamide monomer units in our model of the polypeptide, we would expect the calculated χ_1^+ to increase to a value perhaps greater than 0.35×10^{-11} N. From the perspective of the quantum-mechanical calculation of χ_1^+ , the presence of Davydov solitons in α -helical polypeptides is still not resolved.

APPENDIX B: DERIVATION OF THE DYNAMICAL EQUATIONS

By Eqs. (10) and (12),

$$\beta_{n,i}(t) = \langle \phi_{\text{sol}}(t) | u_{n,i} | \phi_{\text{sol}}(t) \rangle , \qquad (B1)$$

$$\pi_{n,i}(t) = \langle \phi_{\text{sol}}(t) | P_{n,i} | \phi_{\text{sol}}(t) \rangle .$$
(B2)

Furthermore, if M is the mass of each oscillator and N is the chain length,¹⁵

$$u_{n,i} = \sum_{q} \left(\hbar/2MN\Omega_{q,i} \right) \left(b_{q,i} + b_{-q,i}^{\dagger} \right) \exp(jnq) , \qquad (B3)$$

$$p_{n,i} = -j \sum_{q} (h \Omega_{q,i} M/2N)^{1/2} \times (b_{q,i} - b^{\dagger}_{-q,i}) \exp(jnq) .$$
(B4)

Substitution of these identities into the expression for $\sigma(t)$ gives

$$\sigma(t) = \exp\left[\sum_{j \neq n} \left[\Omega_{q,i} z_{q,i}(t) b_{q,i} + z_{q,i}^{*}(t) b_{q,i}^{\dagger}\right]\right],$$
(B5)

where

$$z_{q,i} = (\hbar/2MN\Omega_{q,i})^{1/2} \sum_{i} \pi_{n,i} \exp(jnq) + j\hbar\Omega_{q,i}M/2N \sum_{n} \beta_{n,i} \exp(jnq) .$$
(B6)

(We have used the notation j for $\sqrt{-1}$.) This shows that the functions $\beta_{n,i}(t)$ and $\pi_{n,i}(t)$ represent coherent phonon states.¹⁵ The canonical Hamiltonian equations hold in this case, so

$$\pi_{n,i}(t) = \frac{\partial F}{\partial \beta_{n,i}}, \quad \dot{\beta}_{n,i}(t) = \pi_{n,i}(t) , \qquad (B7)$$

where

$$F = \langle H_{\rm sol} \rangle = \langle \phi_{\rm sol} | H_{\rm sol} | \phi_{\rm sol} \rangle \; .$$

Furthermore,

$$i\hbar \frac{\partial C_{n,i}(t)}{\partial t} = \frac{\partial F}{\partial C_{n,i}} .$$
 (B8)

Writing F explicitly, we obtain

$$i\hbar \frac{dC_{N,i}}{dt} = [E_0 + w + \chi_1(\beta_{n+1,i} - \beta_{n-1,i})]C_{N,i}$$
$$-J(C_{n+1,i} + C_{n-1,i}) + L(C_{n,i+1} + C_{n,i-1})$$
$$+ \chi_2[(\beta_{n+1,i} - \beta_{n,i})C_{n+1,i}$$
$$+ (\beta_{n,i} - \beta_{n-1,i})C_{n-1,i}]$$
(B9)

from Eq. (B8) and

$$M \frac{d^{2}\beta_{n,i}}{dt^{2}} - w(\beta_{n+1,i} - 2\beta_{n,i} + \beta_{n-1,i})$$

$$= \chi_{1}(|C_{n+1,i}|^{2} - |C_{n-1,i}|^{2})$$

$$+ \chi_{2}[C_{n,i}^{*}(C_{n+1,i} - C_{n-1,i})]$$

$$+ (C_{n+1,i}^{*} - C_{n-1,i}^{*})C_{n,i}] \qquad (B10)$$

from Eqs. (B7), where

$$w = \frac{1}{2} \sum_{n,i} \left[M \left[\frac{d\beta_{n,i}}{dt} \right]^2 + w \left(\beta_{n,i} - \beta_{n-1,i} \right)^2 \right].$$

To obtain the explicit form used in the calculations we make the following assignments: $M = 1.17 \times 10^{-25}$ kg (peptide group + CH₃), w = 76 N/cm, J = 7.8 cm⁻¹, L = 12.4 cm⁻¹, $\chi_1 = \chi_2 = \chi$ (a variable parameter).

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FIG. 1. Exciton propagation. Horizontal axis: residue number. Vertical axis: probability amplitude modulus and time superimposed. Traces are at 4×10^{-13} -sec intervals. Coupling constant is 0.5×10^{-10} N, initial excitation is one quantum of amide-I bond energy in first residue, temperature is 0 K. The bulk of the energy is in dispersive wave. The small disturbance which propagates at about half the velocity of the dispersive wave is a solitary wave. Note interference between solitary wave and reflected dispersive wave.



FIG. 10. Exciton propagation. Coupling constant is 0.5×10^{-10} N, initial excitation is three quanta, thermal phonons are at temperature of 300 K. Dispersive wave is visible as in Figs. 1–3 but solitary wave does not form.



FIG. 11. Exciton propagation. Coupling constant is 3.0×10^{-10} N, two quanta excitation, temperature is 240 K. Propagation appears as a purely diffusion process.



FIG. 2. Exciton propagation. Axes, coupling constant, and temperature are as in Fig. 1. Initial excitation is two quanta (in first two residues of chain). Both a large-amplitude solitary wave and a dispersive wave form. Dispersive wave develops strong interference patterns at the chain boundary. The solitary wave may be seen to have trailing disturbances, which propagate at a slightly slower velocity. These also exhibit interactions with the reflected dispersive wave. Solitary wave has complex dynamical structure, exhibiting internal oscillations which propagate as small wavelets running counter to the motion of the main wave for 3 or 4 psec before dispersing. This produces an oscillation of the energy between spines, as observed by Scott (Ref. 7).



FIG. 3. Exciton propagation. Axes, etc., are as in Fig. 1. Initial excitation is three quanta, one each in the first three residues of the chain. The probability amplitude of the solitary wave increases in Figs. 1-3 while the amplitude of the dispersive wave remains constant.



FIG. 4. Exciton propagation. Axes are as in Fig. 1. Coupling constant is 1.5×10^{-10} N, with one quantum initial excitation. Solitary wave forms, in contrast with the case of coupling constant of 0.5×10^{-10} N. Solitary wave decelerates and radiates a dispersive wave.



FIG. 5. Exciton propagation. Axes are as in Fig. 1. Coupling constant is as in Fig. 4, two quanta initial excitation. Dispersive wave forms as well as solitary wave. Solitary wave persists after reflection.



FIG. 6. Exciton propagation. Axes are in Fig. 1. Coupling constant is 3.0×10^{-10} N, with one quantum initial excitation. Solitary wave forms and decelerates to zero velocity. The exciton then oscillates between adjacent sites on the same spine, then hops randomly to an adjacent site on the spine.



FIG. 7. (a) Exciton propagation. Axes and chain parameters are the same as in Fig. 6, initial excitation is two quanta. Some radiation of exciton probability is apparent, especially during initial deceleration of disturbance. (b) Phonon propagation. Horizontal axis is residue number, vertical axis is time and displacement superimposed. Solitary-wave disturbance is associated with large-amplitude displacement. Note scattering of phonons during formation of the solitary disturbance.



FIG. 8. Exciton propagation under thermal conditions. Axes as in Fig. 1. Coupling constant is 1.0×10^{-10} N, initial excitation is three quanta, thermal phonons correspond to 240 K. Exciton is dispersed rapidly over wide region of the chain.



FIG. 9. Exciton propagation. Same conditions as in Fig. 8, except initial excitation is two quanta. Dispersion is more rapid than shown in Fig. 8.