Do Davydov Solitons Exist at 300 K?

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The Davydov model for a one-dimensional protein, coupling the high-frequency amide-I vibration to longitudinal-acoustic phonons, is investigated by use of finite-temperature molecular dynamics. Soliton dynamics is studied in both equilibrium and nonequilibrium situations. The random thermal motions prevent self-trapping from occurring at temperatures of interest for transport in real proteins.

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The understanding of energy transport along linear-chain molecules is a long-standing problem that remains of great interest. In the biological context, the mechanism for transport along proteins of the free energy released by hydrolysis of adenosine triphosphate (ATP) (≈ 0.42 eV or 3350 cm^{-1}) continues to be investigated. Proteins consist of chains of hydrogen-bonded peptide (H—N—C=O) groups; three such chains in a helical arrangement define the α-helix structure. In 1973 Davydov[1] proposed a mechanism whereby the energy from ATP could be trapped and transported in proteins as quanta of the intramolecular C=O stretching mode (amide-I vibration) with excitation energy ≈ 1650 cm^{-1}. His proposal was that amide-I vibrational energy might become self-trapped through an interaction with low-frequency longitudinal acoustic phonons which arises because the amide-I energy depends on the length of the hydrogen bond between the peptide groups. Because of this interaction, displacements of peptide groups in a small region of the chain cause a reduction in the energy of the intramolecular amide-I vibration in that region. For certain ranges of parameters, Davydov finds that this effect leads to self-trapping of amide-I energy, which otherwise would be dispersed by dipole-dipole coupling between neighboring molecules along the chain. The localized spatial region where the energy is trapped can propagate, and thus a solitonlike mechanism for energy transport is possible. Since then considerable work has been done on the Davydov soliton theory.[2] Most studies have been done at zero temperature, and little attention has been given to soliton properties at biologically relevant temperatures ($T \approx 300$ K).

Our purpose here is to report how the properties of the Davydov model are affected by having the system at finite temperature. We have added external damping and noise forces to Davydov's equations to describe coupling the system to a thermal reservoir at temperature T, thereby obtaining Langevin equations. Our essential result is the following: *At temperatures of realistic interest for transport in proteins, the random noise forces prevent Davydov self-trapping from occurring.* Our evidence for this assertion follows.

Davydov's Hamiltonian is[3]

$$H=\sum_n E_0 B_n^\dagger B_n - J\sum_n (B_{n+1}^\dagger B_n + B_n^\dagger B_{n+1}) + \sum_n [p_n^2/2m + \tfrac{1}{2}w(u_{n+1}-u_n)^2] + \chi_1 \sum_n (u_{n+1}-u_{n-1}) B_n^\dagger B_n. \quad (1)$$

Here, $B_n^\dagger$ and B_n are creation and annihilation operators for quanta of intramolecular vibrations with energy E_0 at site n (the C=O stretch mode), u_n and p_n are the molecular displacement and momentum operators for the molecule at site n, m and w are the molecular mass and intermolecular force constant, and J is the intersite transfer energy produced by dipole-dipole interactions. The nonlinear coupling constant χ_1 arises from modulation of the on-site energy by the molecular displacements.[4]

To understand the dynamics arising from this Hamiltonian, Davydov[3] makes the *Ansatz* for the state vector

$$|\psi(t)\rangle = \sum_n a_n(t) B_n^\dagger \exp\{-(i/\hbar)\sum_j [\beta_j(t)p_j - \pi_j(t)u_j]\}|0\rangle, \quad (2)$$

where $|0\rangle$ is the ground-state vector. Since the part of $|\psi\rangle$ which depends upon the displacement and momentum operators is a coherent state, one shows that

$$\langle\psi(t)|u_n|\psi(t)\rangle = \beta_n(t), \quad \langle\psi(t)|p_n|\psi(t)\rangle = \pi_n(t). \quad (3)$$

By requiring that $|\psi(t)\rangle$ satisfy the time-dependent Schrödinger equation, one shows that a_n and β_n must satisfy[3]

$$i\hbar\dot{a}_n = -J(a_{n+1}+a_{n-1}) + \chi_1(\beta_{n+1}-\beta_{n-1})a_n, \quad (4a)$$

$$m\ddot{\beta}_n = w(\beta_{n+1}-2\beta_n+\beta_{n-1}) + \chi_1(|a_{n+1}|^2 - |a_{n-1}|^2). \quad (4b)$$

To describe the interaction of the system with a thermal reservoir at temperature T, we have added a damping force and a noise force,

$$F_n = -m\Gamma\dot{\beta}_n + \eta_n(t), \tag{5}$$

to (4b) for the molecular displacements. We have chosen the correlation function of the random force to be

$$\langle \eta_n(t)\eta_{n'}(t')\rangle = 2m\Gamma k_B T\delta_{nn'}\delta(t-t'), \tag{6}$$

and have verified numerically to high accuracy that over sufficiently long time intervals this gives for the mean kinetic energy

$$\langle \textstyle\sum_n \frac{1}{2}m\dot{\beta}_n^2(t)\rangle = \frac{1}{2}Nk_B T. \tag{7}$$

Even with the damping and noise forces included, Eqs. (4) have a conserved quantity, $\sum_n |a_n(t)|^2 = \text{const}$. The interpretation of $a_n(t)$ from (2) as a probability amplitude requires that within Davydov's theory the value of this constant is unity:

$$\textstyle\sum_n |a_n(t)|^2 = \langle\psi(t)|\psi(t)\rangle = 1.$$

Our equations involve the combination of (6) and (7), which are the classical fluctuation-dissipation relation,[5] with (4), which are obtained quantum mechanically. The justification for doing this is that for parameter values near those appropriate for the α helix (see below and Table I) a quantum of the highest-frequency acoustic mode $\hbar\omega_{\max}$ is around 100 K. If we solve the equations at 300 K, then the occupation numbers of *all* phonon modes are rather accurately given by the classical distribution, and in that situation (7) is valid. The use of (7) for temperatures below, say, 200 K would not be valid because of quantum corrections to the phonon occupation numbers, but such temperatures are not biologically relevant.

Davydov analyzes[1-3] (4) by making approximations which reduce it to the cubic nonlinear Schrödinger equation. The self-trapped state of vibrational energy and lattice displacements is described by the well-known hyperbolic secant solution of this equation. He has also extended the theory to account for thermal effects.[6] Again a nonlinear Schrödinger equation is obtained, but now with a temperature-dependent coefficient for the nonlinear term. Soliton solutions should then exist for temperatures where this coefficient is positive. Using parameters for the α helix (Table I), we calculate from this theory that solitons should exist up to $T = 370$ K.

We have solved the set of stochastic differential equations in (4)–(6) using techniques developed by Greenside and Helfand.[7] In our calculations, the norm of the state vector is conserved to at least 5 parts in 1000. The simulations were done for a chain of 100 sites with periodic boundary conditions. The parameters used in the results here are given in Table I. The mass m was always taken to be 114 proton masses[2] ($m = 1.904\times10^{-25}$ kG). The rate of spatial variation of the variables is determined by the ratio χ_1^2/wJ, as given in the table. The quantity t_0 in the table is $(m/w)^{1/2}$ and is the time unit used to nondimensionalize the equations. The dimensionless value of Γ used for most runs was 0.005.[8] We varied Γ from 0.0025 to 0.05 and found no qualitative change in the results described below.

Our results are presented by certain diagnostics. One is "wave form" graphs: plots of $|a_n|^2$ and the "discrete gradient" $\beta_{n+1}-\beta_{n-1}$ as functions of n at a given t. A soliton is recognized as a maximum in $|a_n|^2$ and a minimum in $\beta_{n+1}-\beta_{n-1}$ occurring together. The second diagnostic is a "soliton detector": On the (t,n) plane, we mark those times and positions where both $|a_n|^2$ exceeds a certain level (chosen to be 0.02) and $\beta_{n+1}-\beta_{n-1}$ is negative. The temporal extent of the marked regions shows how long solitonlike entities can exist.

First, in Fig. 1 we show an example which verifies that the equations without noise do possess the coherent, localized, propagating solutions Davydov has described. Fig. 1(a) shows the soliton-detector results at a very low temperature, $T = 0.01$ K, with the parameters labeled "Discrete" in Table I and with random initial conditions. One sees in Fig. 1(a) that several solitons are nucleated, move along the chain, collide, and coalesce so that eventually only one remains, and it becomes pinned. The wave-form graphs in Fig. 1(b) show the correlation of the maximum in $|a_n|^2$ and the minimum in $\beta_{n+1}-\beta_{n-1}$ which characterizes the Davydov soliton. This is clear evidence that solitons can form in this system at zero temperature. Similar results are obtained with the "continuum" parameters in Table I, but the peaks are broader since the soliton spreads over more lattice sites. (We note that the pinning is sensitive to the value of χ_1; decreasing it by 20% eliminates the pinning but still leads to soliton formation.)

Fig. 2(a) shows the result of raising the temperature to 300 K, with other parameters remaining the same as for Fig. 1 and with random initial conditions. Forma-

TABLE I. Parameter values.

	w (N/m)	J (cm^{-1})	χ_1 (10^{10} N)	χ_1^2/wJ	t_0 (10^{-13} s)
Discrete	5.0	20.0	0.75	2.83	1.95
Continuum	13.0	31.2	0.48	0.29	1.21
α-helix[a]	13.0	7.8	0.62	1.91	1.21

[a]Reference 2.

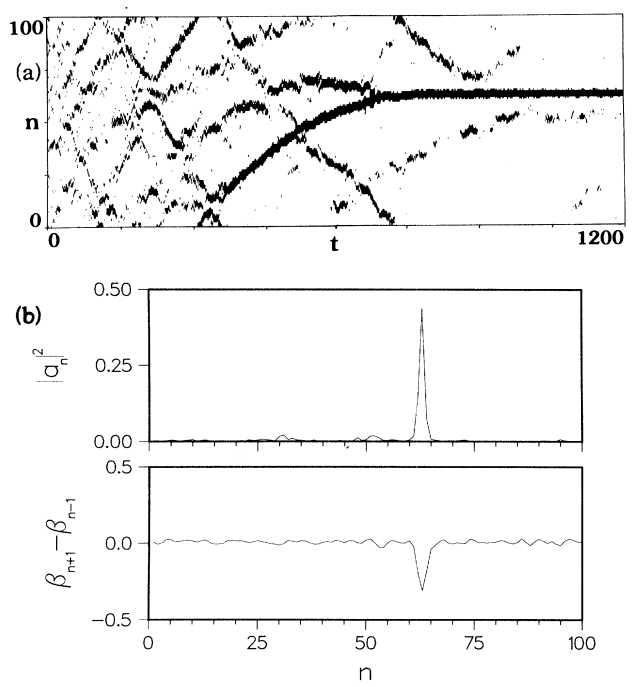

FIG. 1. Simulations at essentially zero temperature. (a) Soliton-detector plot (see text for description). Time values are in the dimensionless units given in Table I. Soliton nucleation and propagation as predicted by Davydov's theory (Ref. 3). The parameters are those labeled "Discrete" in Table I, and the initial conditions are random. (b) Wave form graph (see text for description) at $t=1200$ time units in the evolution shown in part (a).

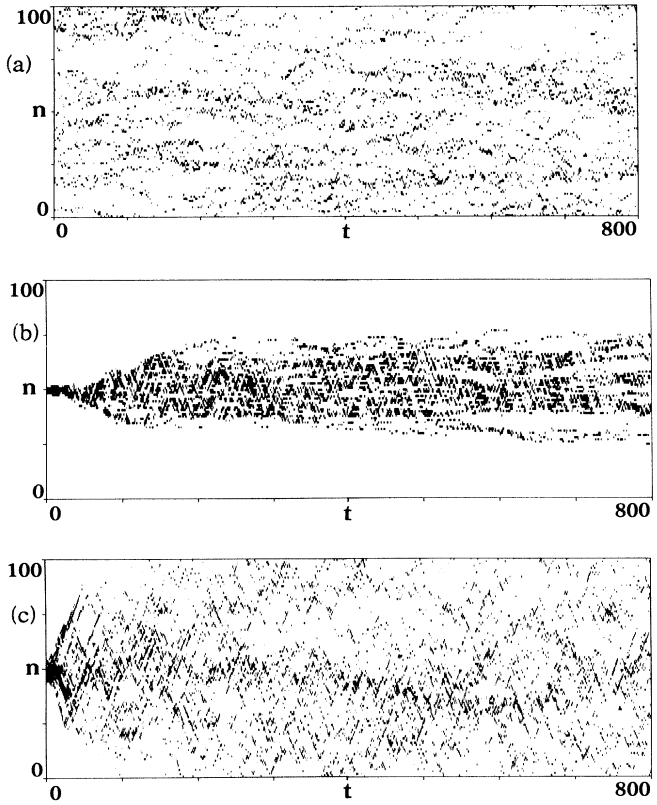

FIG. 2. Soliton-detector plots for simulations at $T=300$ K. (a) Parameters other than temperature same as in Fig. 2(a). (b) α-helix parameters, Davydov-soliton initial condition (Ref. 3). (c) Continuum parameters, Davydov-soliton initial condition.

tion and propagation of solitons is now seen not to occur; the random forces prevent the necessary correlations between the two fields from occurring.

The spontaneous formation of solitons discussed above may not be the correct process to consider. For example the release of energy by ATP hydrolysis may nucleate a soliton, and it could then propagate. To check this possibility, we did nonequilibrium simulations in which the Davydov soliton[3] is the initial condition. It is then allowed to evolve under the influence of the random noise forces. Soliton-detector results from two such simulations are shown here; Fig. 2(b) is done with α-helix parameters and Fig. 2(c) with continuum parameters. In both cases the noise forces correspond to a temperature of 300 K. For both sets of parameters the initial soliton is seen to disappear in a few picoseconds. The filamentary black regions in Figs. 2(b) and 2(c) have a certain slope, which corresponds to the sound velocity in the units used for the calculation. This observation shows that the two sets of excitations are propagating independently of each other.

To be sure that our results do not depend on the method of introducing temperature, we have carried out another type of simulation. We use the equations with the noise and damping terms included to prepare the system close to the desired temperature. Then we turn off the noise and damping, introduce a Davydov soliton at the center of the chain, and continue the evolution deterministically, using just (4) without (5). We find that the evolution of the soliton is the same without the random forces as it is with them; it disappears within a few picoseconds.

To see how these results depend on the value of the nonlinear coupling χ_1, we have done calculations using values 10 times larger than the accepted value for the α helix (Table I). For $T=300$ K, a soliton present in the initial state then lives for a time of 100–150 ps, which is still a short time for biological purposes. In addition, for these χ_1 values it is so tightly pinned to the lattice that its usefulness for energy transport is doubtful.

There is an alternative classical derivation of (4) in which the sum $\sum_n |a_n(t)|^2$ can have any value, deter-

mined from the intensity of the amide-I vibration.[9] Semiclassical quantization then restricts it to integer values. While we feel that the interpretation of $a_n(t)$ as a probability amplitude is lost in this derivation, we have carried out simulations in which the sum has values up to ten. This does not change the nature of the results; a soliton present in the initial state still disappears in a few picoseconds.

Finally we emphasize that these results are not sensitive to the precise temperature value. $T=300$ K has been used because that is close to biologically relevant temperatures. Even though quantum effects would make our simulations inaccurate at low temperatures (see above) we have noted that noise forces corresponding to $T=10$ K are strong enough to destroy the solitons. Thus, this is not a situation where small changes in the parameters would change the results.

We interpret these results as showing that the original proposal of Davydov, to form solitons by coupling molecular excitations and *acoustic phonons,* does not work at temperatures relevant to biological processes. The random displacements produced by the thermal motions are so much larger than the displacements needed to form the coherent soliton pattern that the solitons cannot be formed at these temperatures.

In spite of our results here, Davydov's fundamental idea of forming solitonlike entities via nonlinear coupling of two spatially extended oscillating systems is still attractive, even though choosing one system to be acoustic phonons is evidently not useful. The α-helix structure is complex enough to provide other candidates for coupling, some of which have sufficiently high frequencies that thermal effects at 300 K would be negligible. These possibilities are under investigation.

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