A model for the nonlinear transfer of vibrational energy in molecular chains is derived at temperatures of realistic interest for transport in proteins. The study includes the influence of the fluctuations of polarization in the chain. This theory exhibits a new form of temperature-dependence in intrinsic parameters of alpha-helix, and consequently in the coefficients of the nonlinear Schrödinger equation governing the system and in the solitons’ parameters. Thermal fluctuations are analysed in the basis of the non-Gaussian approximation and the total free-energy of the alpha-helix is determined to elucidate the denaturation process of the protein.
1 Introduction

The understanding of the mechanism of the transport of energy, charge or information along one-dimensional protein is a long-standing problem that remains of great interest. It is well-known that protein is a molecular system built by very stable and regular features such as alpha-helix, beta sheets and loops. In the biological context, the mechanism for transport along proteins of free energy released by hydrolysis of adenosinetriphosphate (ATP) (≈ 0.42eV 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 alpha-helix structure. In 1973 [1], Davydov proposed a soliton model for energy transport in biological molecules. As a specific context for the development of this idea, Davydov concentrated upon the alpha-helical structure of protein; being primarily interested in the conformational changes responsible for muscle contraction, where the trigger and the energy donating reaction is the hydrolysis of ATP. The basic point of Davydov’s proposal is that the energy from ATP could be trapped and transported in proteins as quanta of the intramolecular C=O stretching mode with excitation energy ≈ 1650 cm\(^{-1}\).

Following this original suggestion, the concept of Davydov soliton has been utilized in many studies. So, the idea about the soliton mechanism of bioenergy transport in protein molecules has been subject of large body of works. The references [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19], produced by Davydov and his colleagues and others imminent investigators, deal with this crucial problem of biological motilities. Recently, within the frame of this theory, we have investigated modulational instabilities in acetanilide, ACN (CH\(_3\)COH NC\(_6\)H\(_5\)), taking into account both the N-H and the C=O vibrational self-trappings [20]. There has been much speculation in the literature, with no concrete confirmation, on the existence of the localized excitations predicted by the Davydov model. Fortunately, the application of this theory to ACN is a firm confirmation of the validity of the Davydov approach to an organic solid close to a biological molecule.

Most studies in this field of research have been done at zero temperature, and little attention has been given to Davydov’s soliton at physiological relevant temperatures (T ≈ 300K). While the zero temperature results allow for the existence of soliton states in proteins, an important question is whether these states are stables at biological temperatures and, if not, how long they last.

To introduce the temperature in the system, Davydov [6] calculated the Hamiltonian function by averaging over all possible phonon occupation numbers, and applying the random-phase approximation. Kapor et al. [21] formulated Davydov’s soliton theory for finite temperature by generating the simple product trial function in order to estimate the temperature stability of the soliton. They evaluated the relative displacement of the molecule at a certain temperature T and arrived at the conclusion that the displacement due to the thermal fluctuations is not sufficient
to destroy the soliton localization. Cruzeiro et al. [22] examined temperature effects on the Davydov’s soliton assuming an anisotropic model with different values of the left- and right-sides exciton-phonon coupling constant. They derived, quantum mechanically without approximation, the basic equations of the system from Davydov’s original theory. Their calculations showed that the Davydov soliton is stable at 310 K. Other simulations also showed that the Davydov soliton is stable at 300 K [27, 9, 28, 29, 30, 19].

The first evidence of Davydov-like state was obtained in ACN, a crystal which includes hydrogen-bonded chains identical to those found in proteins as indicated above. An anomalous line, red-shifted by 15 cm$^{-1}$ with respect to the amide-I vibration was found in that crystal [23]. Its interpretation in terms of an interaction of an amide excitation with optical phonons provided good fits of the variation of its intensity with temperature.

An early objection of the role of vibrational excited states in proteins was their short lifetime, which was supposed to be in the subpicosecond range. Scott [10] and Hyman et al. [24] performed intensive numerical calculations to verify Davydov’s results derived from the continuum approximation. This numerical treatment showed formation of solitary waves subsequent to excitation of two or three amide-I bonds at the end of a long molecule. 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 [25, 26] in full agreement with the prediction of the continuum approximation [26]. Recently, the lifetime of amide-I vibrations in myoglobin has been measured and found to be 15 ps [31]. Other significant recent results include the following: the paper by Hamm et al. [32] where they applied nonlinear spectroscopy to the study of ACN taking into consideration the amide-I band [33] as well as the N-H vibrations [34]. In a pump-probe femtosecond spectroscopy experiment, they obtained that the ground state recovery for N-H at room temperature is 20 ps and for amide-I at 90 K it is 35 ps. Computer simulations prove that vibrational excitations can travel tens of nanometers within the lifetime of these excitations [35].

Our contribution is based on this crucial problem of temperature effects in the dynamics of Davydov’s soliton. Calculations are performed with a proper account for the fluctuation of polarization in molecular chains, which really occurs in biological processes anyway. This phenomenon was ignored in works presented so far in this context. This approach can generate some corrective factors in the master equation of the system, and subsequently on the parameters of the Davydov’s solution. The paper is organized as follows: in the next section, we present the model. In section 3, we examine the changes induced by the temperature in the dynamical structure of protein. The fourth section is reserved to the study of thermal fluctuations, and we end the paper by some concluding remarks.
2 The model

The alpha-helix is a typical example of a molecular system consisting of periodically repeating groups of atoms, weakly interacting with each other. The Hamiltonian operator of such system can be written as a sum of four terms (see for instance reference [10])

\[ H = H_{ex} + H_{ph} + H_{int} + H_i, \]  

where

\[ H_{ex} = \sum_n \left[ J_0 B_n^+ B_n + M_0 B_n^+ (B_{n-1} + B_{n+1}) \right], \]

\[ H_{ph} = \sum_n \left[ \frac{p_n^2}{2M} + \frac{1}{2} \chi (u_n - u_{n-1})^2 \right], \]

\[ H_{int} = -J_1 \sum_n (u_{n+1} - u_{n-1}) B_n^+ B_n, \]

\[ H_i = \sum_n U(r_{n,l}) B_n^+ B_n. \]

\( H_{ex} \) is the energy operator of intramolecular excitations with molecules fixed at nodes na, \( a \) being the equilibrium distance between molecules of the chain. \( H_{ph} \) is the operator of the longitudinal deformation energy of the chain, \( H_{int} \) is the energy operator of short-range deformation interaction of a quasi-particle with the displacements in linear approximation. \( H_i \) is the energy operator of the polarization fluctuation with the intramolecular excitation in the alpha-helix.

In these expressions \( B_n \) and \( B_n^+ \) are operators corresponding to the absence and presence of intramolecular excitations of the molecule \( n \), satisfying Bose Commutation relations; \( J_0 \) is the energy of the bottom of the excitons zone; \( M_0 \) is the energy of the resonant dipole-dipole interaction between neighboring molecules. In the phonon part of the Hamiltonian, (3), \( \chi \) is the longitudinal elasticity of the chain; \( p_n \) denotes the conjugal momentum to the displacement \( u_n \) of molecule \( n \) with mass \( M \),

\[ [u_n, p_n] = i\hbar \delta_{nm}. \]

The interaction of excitons with phonon is described by (4), where \( J_1 \) is the exciton-phonon coupling constant.

When the solitary wave travels along the chain, it generates an electric dipole due to an intramolecular excitation. Let us represent by \( P_1 \) the intrinsic moment of each molecule and by \( P_2 \) the dipole that emerges resulting from the intramolecular excitation. The interaction energy between the exciton-induced dipole at the site \( n \) and the dipole of the molecule at site \( l \) is expressed by (5). The dipoles have a tendency to be directed along the x-axis in an anti-parallel
manner or end to end. The energy of the orientational interaction between dipoles is inversely proportional to the third power of the distance, \( r_{nl} \), between these dipoles,

\[
U (r_{l,n}) = \frac{1}{r_{l,n}^5} \left[ \left( \vec{P}_1 \cdot \vec{r}_{l,n} \right)^2 - 3 \left( \vec{P}_1 \cdot \vec{r}_{l,n} \right) \left( \vec{P}_2 \cdot \vec{r}_{l,n} \right) \right], \quad r_{l,n} = u_l - u_n
\]  

(7)

When the dipoles are directed end to end, expression (7) is simplified to

\[
U (r_{l,n}) = \frac{-2P_1P_2}{r_{l,n}^3}
\]  

(8)

The probability that the molecule at site \( n \) acquires this energy (8) is given by

\[
P_n = C \exp \left[ -\frac{U (r_{l,n})}{K_BT} \right]
\]  

(9)

\( C \) being the normalization constant. The probability involving all the molecules of the chain is

\[
P = \sum_n P_n \equiv \sum_n C \exp \left[ -\frac{U (r_{l,n})}{K_BT} \right] = 1.
\]  

(10)

The normalization constant shall be determined latter.

The basic assumption in this study is that the protein molecules are submitted to thermal vibrations in a gas or liquid. The molecular chain being in thermal equilibrium with a reservoir at biologically relevant temperature \( (T \sim 300K) \). In this sense, we take an average of the formula (8) according to all reciprocal orientations of the dipoles, taking into account the Boltzmann factor \( \exp (-U/K_BT) \). At 300K, the inequality, \( U \ll K_BT \), holds and the averaging process gives

\[
U (r_{l,n}) = -C \left[ \frac{2P_1P_2}{r_{l,n}^3} + \frac{4P_1^2P_2^2}{K_BT r_{l,n}^6} \right]
\]  

(11)

The interactions between molecules are limited only to nearest-neighbor molecules which is a good approximation in alpha-helix. Then, the Hamiltonian (5) can be rewritten approximately as

\[
H_i = -C \left[ \frac{4P_1P_2}{a^3} + \frac{8P_1^2P_2^2}{K_BT a^6} \right] \sum_n B_n^+ B_n + C \left[ \frac{12P_1P_2}{a^4} + \frac{48P_1^2P_2^2}{K_BT a^7} \right] \sum_n (u_{n+1} - u_n) B_n^+ B_n.
\]  

(12)

We shall assume that the chain contains a large number \( N \) of molecules. In this framework, end effects can be neglected. To establish the equations of motion of the intramolecular excitations and the longitudinal vibrations of the protein alpha-helices from (1), we express the displacements, \( u_n \), and the momentum operator, \( p_n \), in terms of the creation \( b_q^+ \) and annihilation \( b_q \) operators for phonons with wave numbers \( q \),

\[
u_n = \sum_q \left( \frac{\hbar}{2MN\Omega_q} \right)^{1/2} (b_q + b_q^+) \exp (imq),
\]  

(13)
\[ P_n = -i \sum_q \left( \frac{2M\Omega_q\hbar}{N} \right)^{1/2} (b_q - b_{-q}^\dagger) \exp(inqa) , \]  

where the phonon frequency is

\[ \Omega_q = |q| V_0; \quad V_0 = a (\chi/M) , \]

\( V_0 \) is the velocity of the longitudinal sound in the chain and \( q \), the phonon wave number, which takes \( N \) different values in the reciprocal cells. By doing so, thermal effects will be well-exhibited.

Substituting (13-15) into (1) yields

\[ H = \sum_q \hbar \Omega_q b_q^\dagger b_q + \sum_n \left[ \tilde{J}_0 (T) B_n^+ B_n + M_0 B_n^+ (B_{n-1} + B_{n+1}) \right] + \sum_q N^{-1/2} [F(q) + F_1(q)] B_n^+ B_n (b_q + b_{-q}^\dagger) \exp(inqa) \]  

with

\[ \tilde{J}_0 (T) = J_0 - J_0^i (T) , \]

\[ J_0^i (T) = \frac{4p_1p_2C}{a^3} \left( 1 + \frac{2p_1p_2}{K_B T a^3} \right) , \]

\[ F(q) = -2iJ_1 \left( \frac{\hbar}{2M\Omega_q} \right)^{1/2} \sin(qa) , \]

\[ F_1(q) = -2iJ_1^i (T) \left( \frac{\hbar}{2M\Omega_q} \right)^{1/2} \left[ 1 - \exp(iqa) \right] , \]

\[ J_1^i (T) = \frac{12p_1p_2C}{a^4} \left( 1 + \frac{4p_1p_2}{K_B T a^3} \right) . \]

For the sake of simplicity, the zero-point energy of the lattice has been neglected.

Now, we introduce the thermalization scheme proposed by Davydov [9]. To begin with these calculations, we define the collective states of the chain by the functions

\[ | \Phi_\nu(t) > = \sum_n \varphi_n(t) B_n^+ | 0 >_{ex} U_n(t) | \nu > . \]

The unitary operator, incoming in (21), is expressed as

\[ U_n(t) = \exp \left[ \sum_q \left( \beta_{nq}^* (t) b_q - \beta_{nq} (t) b_{-q}^\dagger \right) \right] . \]

The squares of the moduli of the unknown wave functions \( \varphi_n(t) \) represent the probability distribution of the intramolecular excitation. They satisfy the normalization condition. The functions \( \beta_{nq}(t) \), in turn, stand for the average displacements of the equilibrium positions of the molecules in the state \( U_n(t) | \nu > \), while \( | 0 >_{ex} \) is the excitonic vacuum state. Finally

\[ | \nu > = \prod_q \left( b_{q}^\dagger \right)^{\nu_q} / \sqrt{\nu_q} | 0 >_{ph} \]
is the phonon complete set.

Let us now form the statistical expectation value of the Hamiltonian operator in the state (21) (the reader can refer to paper [6])

\[ \mathcal{H} = \sum_{\nu} \rho_{\nu \nu} H_{\nu \nu}, \tag{24} \]

with

\[ \rho_{\nu \nu} = \frac{\langle \nu | \exp(-H_{ph}/K_B T) | \nu \rangle}{\sum_{\nu} | \langle \nu | \exp(-H_{ph}/K_B T) | \nu \rangle |}. \tag{25} \]

\( \rho_{\nu \nu} \) are the diagonal elements of the density matrix of phonon states, \((\nu_q)\) represents a particular phonon state and

\[ H_{\nu \nu} = \langle \Phi_{\nu}(t) | H_{ex} + H_{int} + H_{i} | \Phi_{\nu}(t) \rangle + \sum_{n} \langle \nu | U^+_n H_{ph} U_n | \nu \rangle > \tag{26} \]

are the diagonal matrix elements of the Hamiltonian. With the help of (21) and (26), (24) becomes

\[ \mathcal{H}_{\nu \nu} = \sum_{n} \left[ \tilde{J}_0 (T) | \varphi_n |^2 + M_0 \exp \left( - \tilde{W}_n \right) \varphi_n^* (\varphi_{n-1} + \varphi_{n+1}) \right. \]

\[ \left. - N^{-1/2} \sum_{q} \left[ F(q) + F_1(q) \right] | \varphi_n |^2 (\beta_{nq} + \beta_{nq}^*) \exp(i qa) + \sum_{q} \hbar \Omega_q \left( \tilde{\beta}_q + | \beta_{nq} |^2 \right) \right] \tag{27} \]

where

\[ \tilde{W}_n = 2 \sum_{q} \left( 2 \tilde{\beta}_q + 1 \right) | \beta_{nq} |^2 \sin^2 \left( aq/2 \right); \tilde{\beta}_q = \left[ \exp \left( h\Omega_q/K_BT \right) - 1 \right]^{-1}. \tag{28} \]

We interpret \( \varphi_n(t) \) and \( \beta_n(t) \) as generalized coordinates, and \( i\hbar \varphi_n^*(t) \) and \( i\hbar \beta_{nq}^*(t) \) as corresponding generalized momentums, respectively. The equations of motion for these dynamical variables are taken to be the classical Hamilton equations in which the expectation value of the quantum Hamiltonian appears as the Hamiltonian function. Then, one obtains the following system of equations governing the alpha-helix for a particular choice of occupation number \((\nu_q)\)

\[ i\hbar \frac{\partial \varphi_n}{\partial t} = \tilde{J}_0 (T) \varphi_n + M_0 \exp \left( - \tilde{W}_n \right) (\varphi_{n-1} + \varphi_{n+1}) \]

\[ + N^{-1/2} \sum_{q} \left[ F(q) + F_1(q) \right] | \varphi_n |^2 (\beta_{nq} + \beta_{nq}^*) \exp(i qa) \] \hspace{1cm} \tag{29}

\[ i\hbar \frac{\partial \beta_{nq}}{\partial t} = h\Omega_q \beta_{nq} - N^{-1/2} \left[ F^*(q) + F^*_1(q) \right] | \varphi_n |^2 \exp(-i qa) \]

\[ i\hbar \frac{\partial \beta_{nq}^*}{\partial t} = - h\Omega_q \beta_{nq}^* + N^{-1/2} \left[ F(-q) + F_1^*(-q) \right] | \varphi_n |^2 \exp(-i qa) \] \hspace{1cm} \tag{30}
3 Temperature-induced changes in the dynamics of the protein

In order to solve the set of equations (29-31), we start from equations (30) and (31), by introducing a new ansatz

$$u_{nq} = \left( \frac{\hbar}{2M\Omega_q} \right)^{1/2} \left[ 1 - \exp (-iqa) \right] (\beta_{nq} + \beta^*_{-qn}). \quad (32)$$

The function (32) is related with deformational displacement in direct lattice by corresponding Fourier-transform

$$u_n (t) = \sum_q Q_{nq} \exp (iqa). \quad (33)$$

In this sense, we arrive at the new equation of motion

$$\frac{d^2u_{nq}}{dt^2} = -\Omega^2 q u_{nq} - 2N^{-1/2} \tilde{J}_1 (T) \frac{q^2a^2}{M} | \varphi_n |^2 \exp (-iqa) \quad (34)$$

with

$$\tilde{J}_1 (T) = J_1 + J_1^i (T). \quad (35)$$

We also rewrite (29) as

$$i\hbar \frac{\partial \varphi_n}{\partial t} = \tilde{J}_0 (T) \varphi_n + M_0 \exp \left( -\tilde{W}_n \right) (\varphi_{n-1} + \varphi_{n+1}) + 2 \tilde{J}_1 (T) u_n (t) \varphi_n. \quad (36)$$

The inertia-free approximation (34) leads us to

$$u_n (t) = -2 N \sum_q \tilde{J}_2^2 (T) \frac{q^2a^2}{M\Omega_q^2} | \varphi_n |^2. \quad (37)$$

$$u_n (t)$$ describes an effective decrease of the distance between neighboring molecules in the region of the lattice covered by the excitation. Eq. (37) upon substitution into Eq. (36) yields the discrete nonlinear equation

$$i\hbar \frac{\partial \varphi_n}{\partial t} = \tilde{J}_0 (T) \varphi_n + M_0 \exp \left( -\tilde{W}_n \right) (\varphi_{n-1} + \varphi_{n+1})$$

$$-4 N \sum_q \tilde{J}_2^2 (T) \frac{q^2a^2}{M\Omega_q^2} | \varphi_n |^2 \varphi_n. \quad (38)$$

Then, the explicit value of the Debye-Waller factor, (28), taking into account (32) and (37) is transformed into

$$W_n = \frac{2a^2 \tilde{J}_2^2 (T)}{\hbar MV_0^3 (1 + \cos(\theta))} \sum_q | q | \left( 2 \tilde{\nu}_q + 1 \right) | \varphi_n |^4, \quad (39)$$

$\theta$ being the phase shift between the two functions $\beta_{nq}$ and $\beta_{-qn}$.

In the continuum approximation, we sum over the wave number by using the long wavelength limit, so that Eq. (38) may be rewritten as follows
\[ i\hbar \frac{\partial \varphi (x, t)}{\partial t} = \left[ J_0 (T) + 2M_0 \exp (-W) \right] \varphi (x, t) + M_0 a^2 \exp (-W) \frac{\partial^2 \varphi (x, t)}{\partial x^2} \]

\[ - \frac{4a^2}{MV_0^2} J_1 (T) | \varphi (x, t) |^2 \varphi (x, t). \] (40)

To solve this nonlinear equation, we use the following values relevant for alpha helical protein molecules [3], for the different estimates:

\[ J_0 = 0.205 \text{ eV}; M_0 = -7.8 \text{ cm}^{-1}; J_1 = -3.4 \times 10^{-11} \text{ N}; P \sim 0.3 \text{ D}; \]

\[ M = 114 m_p; V = 4.5 \times 10^3 \text{ m/s}; a = 4.5 \text{ \AA}. \] (41)

The main problem in (40) results from the presence of the products \( \exp (-W) \varphi \) and \( \exp (-W) \varphi_{xx} \), where

\[ W = B f (T) | \varphi (x, t) |^4 \] (42)

with

\[ B = \frac{2a^4}{\hbar MV_0^3 (1 + \cos(\theta))}; \quad f (T) = \left( \frac{1}{2} + \frac{2kB T}{\hbar \Omega_0} \right) J_1^2 (T). \] (43)

Following Davydov [9], we are interested in states in which the quasi-particle localization region considerably exceeds the distances between the molecules. In this case, \( | \varphi (x, t) |^2 \ll 1 \). Then, we can adopt the following simplification

\[ \exp (-W) \varphi (x, t) \approx \left[ 1 - B f (T) g | \varphi (x, t) |^2 \right] \varphi (x, t); \] (44)

g represents the average value of the function \(| \varphi (x, t) |^2 \) in the region where it differs greatly from zero. Taking into consideration the smoothness of \( \varphi (x, t) \), in the product \( \exp (-W) \varphi_{xx} \), we make the substitution

\[ \exp (-W) \varphi_{xx} \approx \exp \left[ -B f (T) g^2 \right] \varphi_{xx}. \] (45)

According to these simplifications we arrive at the cubic nonlinear Schrödinger equation

\[ i\hbar \frac{\partial \varphi (x, t)}{\partial t} = \left[ \tilde{J}_0 (T) + 2M_0 \right] \varphi (x, t) - \frac{\hbar^2}{2m_{ex} (T)} \frac{\partial^2 \varphi (x, t)}{\partial x^2} \]

\[ + G (T) | \varphi (x, t) |^2 \varphi (x, t). \] (46)

Here,

\[ m_{ex} (T) = m_{ex} \exp \left[ B f (T) g^2 \right]; \quad m_{ex} = - \frac{\hbar^2}{2M_0 a^2}; \] (47)

\[ G (T) = \frac{4a^2}{MV_0^2} J_1^2 (T) \left[ 1 + \frac{M_0 a^2 f_D (T) g}{\hbar V_0 (1 + \cos(\theta))} \right]; \quad f_D (T) = \frac{1}{2} + \frac{2kB T}{\hbar \Omega_0} \] (48)

\( m_{ex} \) being the effective mass of the exciton.
The normalized solution of (46) has the form

$$\varphi (x, t) = \left[ \frac{aQ(T)}{2} \right]^{1/2} \text{Sech} [Q(T)(x - Vt)] \exp [i(kx - \omega t)]; \quad (49)$$

with

$$Q(T) = \frac{am_{ex}(T)G(T)}{2\hbar^2}; \quad k = \frac{m_{ex}V}{\hbar} \quad (50)$$

$$\hbar \omega = \tilde{\omega}_0(T) + 2M_0 - \frac{1}{2}m_{ex}V^2 + M_0a^2Q^2(T) \quad (51)$$

In the interval $\Delta x = \frac{\pi}{Q(T)}$, the quantity $g$ is defined as

$$g = \frac{a^2m_{ex}(T)G(T)}{2\pi\hbar^2} \quad (52)$$

Therefore, (49) becomes

$$G(T) = \frac{4a^2}{MV_0^2} \left[ 1 + \frac{Bf(T)m_{ex}(T)}{2\pi m_{ex}} \right]^{-1} \sim \frac{J_1(T)}{J_1(T)}. \quad (53)$$

Next, we consider the continuum limit of equation (10). Making use of equations (37) and (49), we determine the normalization constant, $C$. After some algebra we obtain

$$C = \left[ \frac{1}{\left( \sum_q \frac{q^2}{12} \right)^3} \frac{p_1p_2\exp[-Q(T)Vt]}{a^7K_BTQ(T)J_1(T)} \right]^{-1} \quad (54)$$

It is straightforward to verify that Eq. (46) can be derived from Hamilton's canonical equations for the Hamiltonian density,

$$\mathcal{H}(x) = \left[ \tilde{\omega}_0(T) + 2M_0 \right] |\varphi|^2 + \frac{\hbar^2}{2m_{ex}(T)} |\varphi_x|^2 - \frac{1}{2}G(T) |\varphi|^4. \quad (55)$$

Then, the exact solution of the energy per pulse is defined as [36]

$$E_p = \int_{-\infty}^{\infty} \mathcal{H}(s) ds; \quad s = x - vt. \quad (56)$$

The integration leads to

$$E_p = \tilde{\omega}_0(T) + 2M_0 - \frac{M_0m_{ex}a^2}{2m_{ex}(T)} \left[ Q^2(T) + \frac{\hbar^2V^2m_{ex}^2(T)}{2a^4M_0^2m_{ex}^2} \right]$$

$$- \frac{4a^2Q(T)}{3MV_0^2} \frac{\tilde{J}_1(T)}{J_1(T)} \left[ 1 + \frac{M_0f_D(T)ga^2}{\hbar V_0(1 + \cos(\theta))} \right]. \quad (57)$$

In the case of interest, the sech-soliton solution is concerned and the energy per pulse is approximately equal to the total energy of the system.

Our calculations show that, because of the fluctuation of polarization, intrinsic parameters of the protein molecule in real physiological conditions must be reconsidered. New temperature-dependent factors appear in different expressions in addition to the well-known Davydov's thermal factors; see for instance (17) and (35) with additional terms $J^i_0$ and $J^i_1$, respectively. In
comparison with Davydov’s results, the effective mass of the exciton, \( m_{\text{ex}}(T) \), contains a corrective term, say \( f(T) \). The nonlinearity parameter, \( G(T) \), also exhibits corrective terms through the coupling constant \( \tilde{J}_1(T) \). Otherwise, \( \tilde{J}_1(T) \) has two terms: a negative term an a positive one. As a bid of explanation, we can say that the negative contribution, \( J_1 \), accounts for excitation states lying near the bottom of the vibrational excitation band, while the positive contribution, \( J_1^+(T) \), involves other excitations generated by the temperature and situated far from the bottom. Considering alpha-helix parameters, one can easily demonstrate that the nonlinearity coefficient (53) is always positive in the physiological temperature range. This remark confirms the existence and propagation of localized waves (solitons) at biological temperatures.

4 Thermal fluctuations: Total free energy

The type of excitations underlined in this section do not minimize the energy functional. Consequently, they cannot be considered as solutions of the nonlinear Schrödinger equation (46). However, they play an important role in the realm of biology because they represent states that the system may reside in at a low enough energy cost.

In a warm environment, hygrogen bonds absorb thermal energy, the potential energy between molecules varies and strong anharmonicities appear in the system. The calculations are performed using the celebrated non-Gaussian approach proposed by Tuszynski and Wierzbicki [37]. We adopt such an approach to properly account for the nonlinearities resulting from the fluctuations. To begin, we decompose the fluctuations, \( \varphi(x) \) into its Fourier-components \( \varphi_k \) according to

\[
\varphi(x) = \frac{1}{\sqrt{L}} \sum_{|k|<\lambda} \varphi_k \exp(ikx)
\]

with

\[
\lambda = \frac{2\pi}{a}
\]

being the cutoff value of the wave number \( k \), and \( L \), the length of the protein.

The Fourier-transformed Hamiltonian considered here is derived from (56). The basic principle of this method is to involve only paired-up modes (\( k \) and \( -k \)) in the calculations. The asymmetric combinations are neglected as they are expected to lead to numerous cancellations, we obtain

\[
H_F = \sum_{|k|<\lambda} H_k = \sum_{|k|<\lambda} \left[ -\frac{1}{2L} \left( \tilde{J}_0(T) + 2M_0 + \frac{M_0 m_{\text{ex}} a^2}{m_{\text{ex}}(T) k^2} \right) |\varphi_k|^2 + \frac{3G(T)}{2L^2} |\varphi_k|^4 \right]
\]

according to which the partition function factorizes into

\[
Z = \sum_{|k|<\lambda} Z_k
\]

with

\[
Z_k = \int_{-\infty}^{\infty} d\varphi_k \exp\left( -\frac{H_k}{k_B T} \right) = \sqrt{\pi} (32 f)^{-\frac{1}{4}} D_{-\frac{1}{2}}(y) \exp\left( y^2 \right)
\]
where $D_{-\frac{1}{2}}(y)$ is a parabolic cylinder function. For the sake of convenience, we have set

$$f(T) = \frac{3G(T)}{2K_BTL^2},$$

$$y = \frac{\tilde{J}_0(T) + 2M_0 + \left(M_0 m_{ex} a^2/m_{ex}(T)\right) k^2}{2\sqrt{3K_B T G(T)}}.$$  \hspace{1cm} (63)

Then, the total free energy of alpha-helix is defined as

$$F_\alpha = -K_B T \sum_{|k|<\lambda} \lg (Z_k).$$  \hspace{1cm} (64)

Making the transition to continuum limit, $F_\alpha$ becomes

$$F_\alpha = -K_B T \frac{L}{2\pi} \int_{-\pi/2}^{\pi/2} \left[ \frac{1}{2} \lg \left( \frac{\pi}{\sqrt{32T}} \right) + \lg \left( D_{-\frac{1}{2}}(y) \right) + y^2 \right] dk.$$  \hspace{1cm} (65)

After lengthy but straightforward calculations, we arrive at

$$F_\alpha = -K_B T \frac{L}{a} \left[ \frac{\lg \left( \sqrt{\pi} W_2(T) \right)}{4} - \frac{1}{4} \lg (32 f(T)) + \frac{3}{4} W_1^2(T) + \frac{W_1(T) W_2(T) \pi^2}{2a^2} \right].$$  \hspace{1cm} (66)

where

$$W_1(T) = \frac{\tilde{J}_0(T) + 2M_0}{2\sqrt{3K_B T G(T)}}, \quad W_2(T) = \frac{M_0 m_{ex} a^2/m_{ex}(T)}{2\sqrt{3K_B T G(T)}}.$$  \hspace{1cm} (67)

The calculated total free energy (66) is responsible of the inner structure of the alpha-helix. The conformational structure of polypeptide chains are stabilized by H-bonds of the peptide groups. The denaturant process of the alpha-helix is released by the dislocation of H-bonds. This dislocation being accompanied by an energy lost. The greater the number of freed unit cells the lower is the total free energy of the system. So, in proportion, as the peptide groups are freed following the breaking of H-bonds, $F_\alpha$ decreases gradually and reaches the critical value $F_P$: the energy at which the alpha-helix is thoroughly denatured and turns into a grope. This transition takes place at a specific temperature.

Denaturation refers to a process in which a protein shape is altered through some form of external stress such as heat absorption, in such a way that it will no longer be able to carry out its cellular function. Generally speaking, proteins lose their biological function when denatured. To have an idea of what happens, let’s present some concrete situations: (i) enzymes lose their catalytic activity, because the substrates can no longer bind to the active site, and because amino acid residues are involved in stabilizing substrates, transition rates are no longer positioned to be able to do so. (ii) In the secondary structure denaturation, the regular repeating patterns (alpha-helix, beta-sheets) disappear and adopt a random coil. On the other hand, the denaturation of deoxyribose nucleic acid (DNA) due to the temperatures manifests itself by the separation of a double strand into two single strands. This situation occurs when the H-bonds between the strands are broken. Such a phenomenon may occur during polymerase chain reaction. Finally, one should mention that denaturation occurs in an abnormal situation and alters the protein molecule.
5 Conclusion

Since Davydov’s proposal for energy transfer in proteins, according to which the energy liberated in an enzymatic reaction can be stored and transported in the form of a soliton, many studies have been carried out using the Davydov’s idea, much of which ignored the influence of the temperature. This is obviously a serious omission because biological organisms function at a temperature of 300K rather than absolute zero. In this model, we have introduced the effects of ambient temperature taking into consideration the fluctuation nature of the polarization of the protein. We have shown that the dynamics of the system is described by a nonlinear equation which can be approximated as a nonlinear Schrödinger equation. The coefficients of the latter as well as the parameters of the soliton have been reconsidered in our formalism. When studying thermal fluctuations, we have used the non-Gaussian approach, and the total free energy of alpha-helix has been determined. The denaturation process of the protein, due to an increase of the temperature, has been outlined. Such an abnormal situation leads to an alteration of the protein molecule.

The molecular mechanism of energy transport in biosystems is one of the more exciting topics at the end of the twentieth century. We hope that this contribution will help for a better understanding of certain dysfunctions of our organism. This remains our main objective. The topic is more complex, indeed, because of the complexity of the functional structure of living organisms. More and more needs to be done to definitely embrace the reality of such systems. It is with this humble thought in mind that we conclude this paper.

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