Abstract

Davydov’s model of solitons in $\alpha$-helix protein chains is shown to display features of self-organized criticality (SOC), i.e., power law behaviour of correlations in space and $1/f$ noise, as a consequence of considering random peptide group displacements from their (periodic) equilibrium positions along a chain. This may shed light on a basic mechanism leading to obtain flicker noise in $\alpha$-helix protein chains and to predict a SOC regime in biomolecular structures from first principles. We believe our treatment of $1/f$ noise to be of some relevance to recent findings due to Voss on DNA [Phys. Rev. Lett. 68, 3805 (1992)].

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Solitons and $1/f$ noise in molecular chains

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The concept of solitons found a fascinating novel application into biological phenomena since Davydov [1] introduced a cubic non-linear Schrödinger equation to describe energy transport in molecular chains such as α-helices. The topological and dynamical stability of Davydov solitons -i.e., conservation of form and velocity after interaction, respectively- is related to the spontaneous (local) symmetry breaking of the protein molecules. A dynamical balance between the dispersion due to the resonance interaction of intrapeptide dipole vibrations and the nonlinearity of the interaction of such vibrations with the (time-dependent) local displacements from the equilibrium positions of the peptide groups -say, β- is believed to play a crucial role for the transport of energy released in the hydrolysis of the \textit{adenosine triphosphate} (ATP) molecule [2].

Because of this, Davydov solitons -as well as alternative soliton models to account for nonlinearity in quasi 1D biomolecular chains (see, e.g., [3, 4, 5])- are an active research field. Recent progress has been directed to relate excitations in Davydov systems to Bose-Fröhlich condensation phenomena [6, 7] and to include more appropriately quantum and temperature effects on the lifetime of the soliton [8, 9]. Even though a large amount of theoretical work has been accumulated in the past two decades following these Davydov’s pioneering ideas, there is still a number of open problems. Firstly, there is as yet no experimental verification of Davydov solitons [10, 11]. Indeed Davydov’s model might look rather unrealistic [3], but from the standpoint of physics it is not unreasonable to study it as an effective way towards achieving better understanding of complex molecular systems. Secondly, to our knowledge, the case of having \textit{random} peptide group displacements β due to \textit{local disorder} has not been fully considered.

To this end the recent proposal by Voss [12] (see also [13, 14]) that long-range correlations and 1/f noise can be detected in DNA sequences when viewed as random
processes, gives one inspiration for carrying out an investigation on random $\beta$. The idea that nucleotide bases in strands of DNA may be correlated over several thousands of base-positions, opens the way to explore how, and to which extent, solitons might be useful to gain physical insight into Voss’s relevant finding on DNA. It is tempting to analyse this phenomenon from a first principle formalism based on soliton physics and, from this, to understand that class of non-linear dynamical systems which drive themselves into a statistically stationary critical state, the so-called self-organized criticality (SOC) [15], with no intrinsic length or time scale, where the systems exhibit power law (fractal) behaviour and generate flicker noise [16].

In this work we shall make a small step towards such a theory to show that Davydov solitons in quasi-1D $\alpha$-helix chains at $0 \, K$, if they exist, might display features of SOC as a consequence of assuming random peptide group displacements from their (periodic) equilibrium positions along a chain. This suggests a possible physical mechanism to understand SOC from an ab-initio basis in terms of interactions. In addition our work complement recent ideas put forward by one of us [17], regarding an analytical continuous probability theory for SOC, in that we propose here that random peptide group displacements might be one possible mechanism to generate $1/f$ noise in macromolecular chains.

We start considering the simplest Davydov’s protein molecule, i.e. $\alpha = 1$ [1], which we briefly describe below for completeness. The basic idea is that the amide-$I$ vibrational energy is coupled through interaction with acoustic phonons. The molecular chain has $N \, (\gg 1)$ molecular units of mass $M \, (\sim 114 \, a.m.u.)$ placed at positions: $x_n = nR + u_n$, where $n$ is an index that counts unit cells (in the hydrogen-bonded direction), $u_n (\ll R)$ are small displacements from the equilibrium positions $nR$ caused by internal molecular
The molecular groups are taken as the peptide subunits of $\alpha$-helix protein polymers and $R$ as the length of the amide’s hydrogen bond ($\sim 3\text{Å}$).

The Hamiltonian operator $H$ for the collective degrees of freedom resulting from the interaction of intramolecular amide-$I$ modes, $(C = O$ stretching$)$, and the lattice motion of such a chain is

$$H = H_{\text{vib}} + H_{\text{ph}} + H_{\text{int}}.$$  \hspace{1cm} (1)

In the above,

$$H_{\text{vib}} = \sum_n \{\epsilon_0 B_n^\dagger B_n - J(B_n^\dagger B_{n+1} + B_{n+1}^\dagger B_n)\},$$  \hspace{1cm} (2)

where $B_n^\dagger$ and $B_n$ are boson creation and annihilation operators for the vibrational excitation at the $n$th site associated with the amide-$I$ dipolar oscillator -having the quantum energy $\epsilon_0 \sim 0.205 \text{ eV}$. The dipolar resonant interaction is only considered between the nearest neighbor molecules, \textit{i.e.}, $J = 2d^2/R^3$ ($= 9.67 \times 10^{-4} \text{ eV}$ from infrared spectra), where $d$ ($= 0.29 \text{ D}$) is the dipolar electric moment aligned along the $C = O$ bond.

The second term of Eq. (1) describes the longitudinal harmonic oscillations (phonons) of the chain, which in second quantized form is written as a sum over the momentum normal modes $q$, namely

$$H_{\text{ph}} = \sum_q \hbar \Omega_q (b_q^\dagger b_q + \frac{1}{2}),$$  \hspace{1cm} (3)

where $b_q^\dagger$ and $b_q$ are phonon creation and annihilation operators. $\Omega_q$ is given by the dispersion equation $\Omega_q^2 = 4(\nu_a^2/R^2)\sin^2(\frac{1}{2}qR)$ with $\nu_a = R\sqrt{w/M}$ and $w$ an elasticity coefficient ($\sim 76 \text{ N/m}$).
The last term in the collective Davydov Hamiltonian is the nonlinear interaction between the vibrational dof’s and the phonon dof’s, namely

\[ H_{\text{int}} = \frac{1}{\sqrt{N}} \sum_{q,n} \chi(q)e^{i\xi}B_n^\dagger B_n(b_q + b_q^\dagger) \]  

(4)

where \( \chi(q) = \chi^*(-q) = i\chi\left(\frac{\hbar}{2M\Omega q}\right)^{1/2}\sin(qR) \). The physical meaning of the nonlinear coupling parameter \( \chi \) is to characterize change effects of the amide-I bond energy per some unit extension of the hydrogen bond. This parameter is expressed as \( \chi = \partial \varepsilon_0 / \partial R \), whose numerical value lies in the interval: \( \chi = 3 - 6.2 \times 10^{-11} \) N.

For the wavefunction of the above Schrödinger equation, Davydov wrote

\[ \left| \psi_D(t) \right\rangle = \sum_n \alpha_n(t) \exp(\sigma(t)) B_n^\dagger \left| 0 \right\rangle \]  

(5)

where \( \left| 0 \right\rangle \) is a generalized vacuum state in the collective space of vibrational-phonon dof’s and \( \alpha_n(t) \) are normalized functions. The quantum-mechanical phase \( \sigma(t) \) is written as \( \sigma(t) = -\frac{i}{\hbar} \sum_q [\beta_{qn}(t)b_q^\dagger - \beta_{qn}^*(t)b_q] \), which is termed the \( D_1 \) ansatz. It is a superposition of tensor products of single-exciton states and coherent phonon states \[18\]. There also exists a classical displaced oscillator ansatz (or \( D_2 \)) as well as a modified \( m - D_1 \) state \[19\].

For the complex functions \( \alpha_n(t) \) and the real functions \( \beta_{qn}(t) \) of Eq.(5) -which characterize the vibrational state and the displacement from equilibrium of a single molecular unit at site \( n \), respectively- Davydov obtained a system of two coupled discrete-differential equations expressing their ‘classical’ Hamiltonian evolution. In the long wavelength approximation such discrete functions are replaced by two continuous limits \( \alpha(\zeta) \) and \( \beta(\zeta) \), where \( \zeta \equiv nR - v_s t \), subject to the constraint that the propagation velocity \( v_s \) is constant (i.e., stationary propagation). A further approximation is to take \( nR \)
as any point \( x \) along the chain axis. Besides \( \beta \), the function \( \rho(\zeta) = -R \frac{\partial \beta(\zeta)}{\partial \zeta} \) is also defined to characterize the (infinitesimal) difference of displacements of nearest neighbour molecules within the chain and modulation of the chain due to vibrational solitons.

Solutions of the energy transport within Davydov’s Hamiltonian treatment in the continuous and subsonic regime (\( i.e., s^2 = v_s^2/v_a^2 \ll 1 \)) are as follows:

\[
\alpha(\zeta) = \sqrt{\mu/2}e^{\left[i/\hbar \frac{\hbar^2 v_s^2}{2J^2 R^2} - E_s t\right]} \cosh^{-1}\left(\frac{\mu}{R} \zeta\right),
\]

(6)

\[
\rho(\zeta) = \frac{\chi}{w(1 - s^2)} \frac{\cosh^{-2}\left(\frac{\mu}{R} \zeta\right)}{\tanh(Q\zeta)},
\]

(7)

\[
\beta(\zeta) = \frac{\chi}{w(1 - s^2)} (1 - \tanh(Q\zeta)),
\]

(8)

where \( Q = \frac{MR_s^2}{2\hbar^2(1-s^2)} \). The quantities \( \mu, E_s, \) and \( s \) are respectively given by \( \mu = \chi^2/Jw(1 - s^2), E_s = \epsilon_0 - 2J + \frac{\hbar^2 v_s^2}{4JR^2} - J\mu^2/3, \) and \( s = v_s/v_a \).

In the above \( \alpha(\zeta) \) is essentially the Davydov vibrational soliton, which is a quasi-localized structure with size of the order \( R/\mu \), propagating with velocity \( v_s \) and transferring vibrational energy \( \epsilon_0 \). Furthermore, \( \rho(\zeta) \) is the hydrogen bond soliton whereas \( \beta(\zeta) \) is a kink soliton of the displacements of the peptide groups from their (periodic) equilibrium positions. During their (constant-\( v_s \)) movement, the three solitons (usually denoted as \( S_1, R_1 \) and \( K_1 \), respectively) strongly influence each other in a way which is still an open problem. Of special interest to us here is the \( K_1 \) solution, which might be considered as a spatial continuous representation of D’Alambert type (\( i.e., \) of the form \( \beta(x - v_s t) \)) of a product of coherent states, that is needed to obtain the nonlinear Schrödinger dynamics [20]).

Let us include next, to the above Davydov model, a special type of random disorder that may result from several sources, such as radiation and others, and that fluctuates in time. We shall come back to this latter on. In the \( \zeta \)-coordinate frame, the central
position of the kink $K_1$ can be fixed as the spatial origin and small time excursions of its origin will be allowed. Then it is straightforward to estimate time correlations via the (dimensionless) noise power spectrum of the temporal evolution of such fluctuations by characterizing random processes in $\beta$ of Eq.(8) at the time scale $0 < t < \tau \approx 1/f$ by

$$S_\beta(f) \propto \frac{1}{\tau} \left| \int_0^\tau \beta(\zeta)e^{2\pi if t} dt \right|^2 ,$$

(9)

where $\tau \to \infty$ and $\zeta(x,t)$ is the random variable. Figure 1 shows the results obtained for the spectral density $S_\beta$ when using $x \to x_o \pm \Delta x$, such that we set $x_o = 0$ and choose $\Delta x$ to vary randomly between $\pm 1$ for simplicity. These results have been computed using a standard fast fourier transform algorithm. On averaging over thousand ensembles, $2^{13}$ (unit-)time steps within the interval $0 < t < 10^4$ are found to suffice in order to achieve less than 5% of error in calculations. As revealed from this figure the noise power spectrum of the Davydov $\beta$ displacement, when assumed to be a function of random $\zeta$, shows a clear manifestation of $1/f$ noise. We believe this treatment of flicker noise to be somehow of relevance to the findings due to Voss on DNA [12]. In particular, we can superpose a peaked structure in the $1/f$ power spectrum of $\beta$ by periodically resetting $\Delta x$ to naught as shown in the high-frequency region of Fig.1.

From these results we can see that the transition to a steady state, is strongly related to the peptide group fluctuations from their initial (i.e., $t_o = 0, x_o = 0$) conditions. According to such complex dynamics, the physics behind this phenomenon (i.e., existence of time correlations) is due to the random disorder we have introduced and whose possible cause will be analysed below.

Let us first also investigate the space domain by fixing the time scale (i.e., by assum-
ing now static solutions). We consider once more the random variable $\zeta$ to characterize random disorder of the peptide group displacements from their equilibrium positions with a density probability $\phi$ proportional to $\beta(\zeta)$ \cite{7}. Since the uniform probability distribution function of having random events can be written as

$$G(\zeta_2) - G(\zeta_1) = P\{\zeta_1 < \zeta \leq \zeta_2\} \approx \int_{\zeta_1}^{\zeta_2} \phi(\zeta')\,d\zeta' \, ,$$

where $\{\}$ indicates the function interval. Then, this integral over the limits $\zeta_2 \equiv \lambda_1 \zeta_o \geq \zeta + \lambda_2 \zeta_o \equiv \zeta_1$ gives

$$G(\lambda_1 \zeta_o) - G(\zeta + \lambda_2 \zeta_o) = \int_{\zeta + \lambda_2 \zeta_o}^{\lambda_1 \zeta_o} \beta(\zeta')\,d\zeta' \equiv -\tau(\zeta) \, ,$$

with $\beta$ given in Eq.\,(8), ($s^2 \ll 1$), and $\zeta_o$ being a constant. The minus implies that the functions $G$ are here assumed to satisfy the condition $G(\zeta + \lambda_2 \zeta_o) > G(\lambda_1 \zeta_o)$ for $\zeta \neq 0$, which do not need to be defined, whereas the free parameters $\lambda_i \,(i=1,2)$ will restrict the range of $\zeta$.

The afore-mentioned integration limits lead to the condition $\lambda_2 - \lambda_1 + \zeta \leq 0$ as discussed in our previous work \cite{7}. If $\lambda_2 \neq \lambda_1$, then we get (in terms of $\tau(0)$)

$$\tau(\zeta^*) \approx (1 + \frac{\zeta^*}{\lambda_2 - \lambda_1})\{\tau(0) + \zeta_o \ln \cosh \lambda_2\}$$

$$-\zeta_o \{\frac{\zeta^*}{\lambda_2 - \lambda_1} \ln \cosh \lambda_1 + \ln \cosh(\lambda_2 + \zeta^*)\} \, .$$

where $\zeta^* = \zeta/\zeta_o$, $\tau(0) = \zeta_o(\lambda_2 - \lambda_1)(1 + \Gamma)$ and $\Gamma = (\ln \cosh \lambda_1 - \ln \cosh \lambda_2)/(\lambda_2 - \lambda_1)$.

In Fig.2 we show the dependence of the normalized probability distribution function $\tau$ on the reduced variable $\zeta^*$ for values of $\lambda_1 = 3$, $\lambda_2 = -8$ and $\tau(0) = 1$ which, in turn, determine the value of $\zeta_o$. In our calculations, \textit{i.e.} using Eqs.\,(8) and Eq.\,(12), we have also reduced $w(1-s^2) \propto 1$ and $Q\zeta_o \propto 1$ for simplicity. The choice of $\tau(0)$ allows to normalize $\tau(\zeta^*)$ and to mimic features of SOC, namely a power-law behaviour in
space correlations (within the range $0 \leq \zeta^* \leq 8$), provided $\zeta^*$ is associated with the log-function of a measured random event. In fact, we have that $\tau(\zeta^* \to 0) \to 1$ and $\tau(\lambda_1 - \lambda_2) \equiv 0$. Whereas if $\lambda_2 + \zeta^* \approx 0$ then $\ln \cosh(\lambda_2 + \zeta^*) \approx 0$, hence $\tau$ of Eq.(12) depends linearly on $\zeta^*$ for values $\zeta^* \leq -\lambda_2$.

To see more clearly possible power-law features in the behaviour of $\tau$ over an extensive range of values of $\zeta^* \leq 8$, we calculate the linear derivative of $\tau(\zeta^*)$ which is also plotted in Fig.2 by dotted lines. For the smallest displayed values of $\zeta^*$ this function converges to a constant negative value, revealing in this way the constant nature of the negative slopes in the ($\tau$-$\zeta^*$) curves. In view of these features of the derivative of $\tau$, the second derivative has also been included in Fig.2. It presents a sharp peak around the inflection point of $\frac{\partial^2 \tau}{\partial \zeta^*}$, thus indicating the range of validity of such a power-law behaviour. The cutoff in the $\zeta^*$-axis for the $\tau$ curve is related to the system size or integration limit ($i.e.$, $\lambda_1 - \lambda_2 \approx 11$). Accordingly, it reflects the range of long-range correlations in the space domain. In view of these results we can interpret $\beta$ as a nonequilibrium order parameter of a transition from the $D_1$ phase of the chain to the Fröhlich phase [21]. That is, a phase transition from the dynamical balance between the intramolecular excitations (and their exchange) and the longitudinal excitations of the linear Davydov chain, to the Fröhlich nonthermal excitations of longitudinal polarization modes arising in a far-from-equilibrium regime supported by the flow of energy.

We focus now on some possible effects that have been usually neglected when taking a continuous limit within the framework of the Davydov theory but which, in our opinion, may become important as being the source for generating randomness. These effects include radiation, discreteness-chaos, and disorder. Radiation effects have been first discovered in the context of lattice topological solitons (dislocations), and subsequently
proved to exist also in the case of dynamical solitons [22]. In fact, subsonic kinks in a monoatomic chain permanently radiate small amplitude oscillations. Besides this, subsonic kinks (as well as supersonic ones) in diatomic chains lose energy in this process [22]. Chaotic effects, due to lattice discreteness have been discussed in Ref. [23] within a vibron model, with on-site potentials, which is very similar to the Davydov model. Such an effect can be understood as a perturbation of an integrable system. It is a chaotic effect that might imply a random spatial arrangement of stationary solitons. The effect of disorder, on the other hand, is a very important feature of many nonlinear chains [24]. Considering the 20 different natural amino acids in real peptide chains, each of different mass, one may think of a sequence of random masses to have important effects on soliton propagation. This has been observed by Förner [25] by investigating sequences of masses, spring constants, nonlinear coupling constants, heat bath, and disorder in the dipole coupling. Another crucial effect to consider when applying the continuous limit is the impurity disorder in which various types of kink-impurity interactions may be possible [26]. We believe all of these phenomena to generate (a sort of intrinsic) randomness for the displacements $\beta$ along a single molecular chain (i.e., $\alpha = 1$), which leads to obtain SOC features as we have discussed in this work. We add that the present ideas may be easily extended to chains with $\alpha > 1$, since the soliton solutions of the Davydov Hamiltonian -i.e., $S_1$, $R_1$, $K_1$- keep their form unchanged [1].

We have thus tried to interpret, within the simplest Davydov soliton theory, randomness by combining features of both discreteness and disorder effects. These considerations may be useful to understand long-range correlations in biological systems [27] and flicker noise, possibly including DNA [12]. We have predicted a SOC dynamical regime in biomolecular systems from first principles. Indeed we have been able to derive
such a SOC regime as a consequence of random $\beta$ which has been interpreted in terms of a nonequilibrium phase transition between the $D_1$ soliton state of the chain and a probable Fröhlich-condensed phase. The present SOC regime might be seen as a proof of the soliton stability against random disorder. In turn, this may be an indication of the nonequilibrium nucleation of Fröhlich domains along a single chain. Of course, to characterize randomness of the peptide group displacements with a density probability $\phi \propto \beta(\zeta)$ may be seen heuristic. But, in view of the results obtained, this can be considered as one of the simplest reasonable ways to relate local properties to macroscopic behaviour. To this end, note that a relation of this kind has also been used within the context of pattern formation [28].

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Figure captions

• **Fig.1**: Noise power spectrum for the temporal evolution of the random fluctuations in $\beta(\zeta^*)$ including periodical resetting.

• **Fig.2**: (Full line) probability distribution function $\tau$ of having random events vs. reduced variable $\zeta^*$ using $\lambda_1 > \lambda_2$, such that $\lambda_2 < 0$, and $\tau(0) = 1$. (Dotted lines) first and (smallest dotted lines) second derivative of $\tau$ with respect to $\zeta^*$. 