RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 47, NUMBER 6 JUNE 1993

Solitons and $1/f$ noise in molecular chains

H. Rosu
Instituto de Fisica, Universidad de Guanajuato, León, Mexico

E. Canessa
ICTP-International Centre for Theoretical Physics, Trieste, Italy
(Received 21 December 1992)

Davydov's model of solitons in α-helix protein chains is shown to display features of self-organized criticality (SOC), i.e., power-law behavior 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 obtaining flicker noise in α-helix protein chains and to predicting 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)].

PACS number(s): 02.50.−r, 05.60.+w, 87.10.+e, 72.70+m

The concept of solitons has found a fascinating novel application to biological phenomena since Davydov [1] introduced a cubic nonlinear 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 *adenosine triphosphate* molecule [2].

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

To this end the recent proposal by Voss [11] (see also [12,13]) 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 β. The idea that nucleotide bases in strands of DNA may be correlated over several thousands of base positions opens the way to exploring how, and to what extent, solitons might be useful for gaining physical insight into Voss's relevant finding on DNA. It is tempting to analyze this phenomenon from a first-principles formalism based on soliton physics and, from this, to understand that class of nonlinear dynamical systems that drives itself into a statistically stationary critical state, the so-called self-organized criticality (SOC) [14], with no intrinsic length or time scale, where the systems exhibit power-law (fractal) behavior and generate flicker noise [15].

In this work we shall make a small step towards such a theory to show that Davydov solitons in quasi-1D α-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 for understanding SOC from an *ab initio* basis in terms of interactions. In addition, our work complements recent ideas put forward by one of us [16], regarding an analytical continuous probability theory for SOC, in that we propose here that random peptide group displacements might be one possible mechanism for generating $1/f$ noise in macromolecular chains.

We start considering the simplest Davydov 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 (~ 114 amu) placed at positions: $x_n = nR + u_n$, where n is an index that counts unit cells (in the hydrogen-bonded direction), and $u_n (\ll R)$ are small displacements from the equilibrium positions nR caused by internal molecular motion. The molecular groups are taken as the peptide subunits of α-helix protein polymers and R as the length of the amide's hydrogen bond (~ 3 Å).

The Hamiltonian operator H for the collective degrees of freedom (DOF) resulting from the interaction of intramolecular amide-I modes (C=O stretching) and the

lattice motion of such a chain is

$$H = H_{\rm vib} + H_{\rm ph} + H_{\rm int} \quad . \tag{1}$$

In the above,

$$H_{\rm vib} = \sum_n \{\varepsilon_0 B_n^\dagger B_n - J(B_n^\dagger B_{n+1} + B_{n+1}^\dagger B_n)\} \quad , \tag{2}$$

where $B_n^\dagger$ and B_n are boson creation and annihilation operators for the vibrational excitation at the nth site associated with the amide-I dipolar oscillator—having the quantum energy $\varepsilon_0 \sim 0.205$ eV. The dipolar resonant interaction is only considered between the nearest-neighbor molecules, i.e., $J = 2d^2/R^3$ ($= 9.67 \times 10^{-4}$ eV from infrared spectra), where d ($= 0.29$ 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,

$$H_{\rm ph} = \sum_q \hbar\Omega_q (b_q^\dagger b_q + \tfrac{1}{2}) \quad , \tag{3}$$

where $b_q^\dagger$ and b_q are phonon creation and annihilation operators. Ω_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 (~ 76 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,

$$H_{\rm int} = \frac{1}{\sqrt{N}} \sum_{q,n} \chi(q) e^{iqnR} B_n^\dagger B_n (b_q + b_{-q}^\dagger) \quad , \tag{4}$$

where $\chi(q) = \chi^*(-q) = i\chi(\frac{\hbar}{2M\Omega_q})^{1/2}\sin(qR)$. The physical meaning of the nonlinear coupling parameter χ is to characterize change effects of the amide-I bond energy per some unit extension of the hydrogen bond. This parameter is expressed as $\chi = \partial\epsilon_0/\partial R$, whose numerical value lies in the interval: $\chi = (3\text{–}6.2) \times 10^{-11}$ N.

For the wave function of the above Schrödinger equation, Davydov wrote

$$||\psi_D(t)\rangle\rangle = \sum_n \alpha_n(t) \exp[\sigma(t)] B_n^\dagger \, ||0\rangle\rangle \quad , \tag{5}$$

where $||0\rangle\rangle$ 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 [17]. There also exists a classical displaced oscillator ansatz (or D_2) as well as a modified $m - D_1$ state [18].

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 β, the function $\rho(\zeta) = -R\frac{\partial\beta(\zeta)}{\partial\zeta}$ is also defined as characterizing the (infinitesimal) difference of displacements of nearest-neighbor 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:

$$\alpha(\zeta) = \sqrt{\mu/2} e^{[\frac{i}{\hbar}(\frac{\hbar^2 v_s x}{2JR^2} - E_s t)]} \cosh^{-1}\left(\frac{\mu}{R}\zeta\right) \quad , \tag{6}$$

$$\rho(\zeta) = \frac{\chi}{w(1-s^2)} \mathrm{sech}^{-2}\left(\frac{\mu}{R}\zeta\right) \quad , \tag{7}$$

$$\beta(\zeta) = \frac{\chi}{w(1-s^2)}[1 - \tanh(Q\zeta)] \quad , \tag{8}$$

where $Q = \frac{MR\chi^2}{2w\hbar^2(1-s^2)}$. The quantities μ, E_s, and s are respectively given by $\mu = \chi^2/Jw(1-s^2)$, $E_s = \varepsilon_0 - 2J + \frac{\hbar^2 v_s^2}{4JR^2} - J\mu^2/3$, 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/μ, propagating with velocity v_s and transferring vibrational energy ε_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 that still presents an open problem. Of special interest to us here is the K_1 solution, which might be considered as a spatial continuous representation of the 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 [19].

Let us next attach, 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 later on. In the ζ-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 β of Eq. (8) at the time scale $0 < t < \tau \approx 1/f$ by [11]

$$S_\beta(f) \propto \frac{1}{\tau}\left|\int_0^\tau \beta(\zeta) e^{2\pi i f t}\, dt\right|^2 \quad , \tag{9}$$

where $\tau \to \infty$ and $\zeta(x,t)$ is the random variable. Figure 1 shows the results obtained for the spectral density S_β when using $x \to x_0 \pm \Delta x$, such that we set $x_0 = 0$ and choose Δx to vary randomly between ± 1 for simplicity. These results have been computed using a standard fast-Fourier-transform algorithm. On averaging over thou-

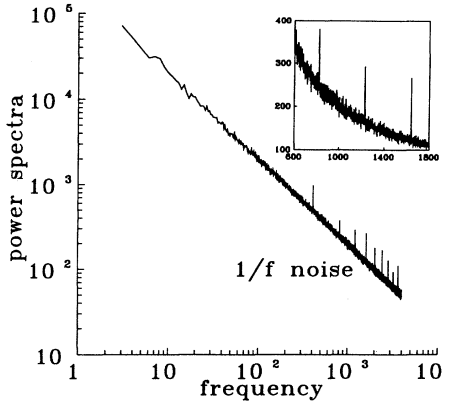

FIG. 1. Noise power spectrum for the temporal evolution of the random fluctuations in $\beta(\zeta^*)$, including periodical resetting.

sands of ensembles, 2^{13} (unit) time steps within the interval $0 < t < 10^4$ are found to suffice in achieving less than a 5% error in calculations. As revealed from this figure the noise power spectrum of the Davydov β displacement, when assumed to be a function of random ζ, shows a clear manifestation of $1/f$ noise. We believe this treatment of flicker noise to be somehow of relevance to the findings of Voss on DNA [11]. In particular, we have superposed a peaked structure in the $1/f$ power spectrum of β by periodically resetting Δx 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., $t_0 = 0$, $x_0 = 0$) conditions. According to such complex dynamics, the physics behind this phenomenon, i.e., the existence of time correlations, is due to the random disorder we have introduced and whose possible cause will be analyzed below.

Let us first also investigate the space domain by fixing the time scale (i.e., by now assuming static solutions). We consider once more the random variable ζ to characterize random disorder of the peptide group displacements from their equilibrium positions with a density probability ϕ proportional to $\beta(\zeta)$ [16]. Since the uniform *probability distribution function* of having random events can be written as

$$\mathcal{G}(\zeta_2) - \mathcal{G}(\zeta_1) = \mathcal{P}\{\zeta_1 < \zeta \leq \zeta_2\} \approx \int_{\zeta_1}^{\zeta_2} \phi(\zeta')\, d\zeta' \quad , \quad (10)$$

where $\{\}$ indicates the function interval; then, this integral over the limits $\zeta_2 \equiv \lambda_1\zeta_0 \geq \zeta + \lambda_2\zeta_0 \equiv \zeta_1$ gives

$$\mathcal{G}(\lambda_1\zeta_0) - \mathcal{G}(\zeta + \lambda_2\zeta_0) = \int_{\zeta+\lambda_2\zeta_0}^{\lambda_1\zeta_0} \beta(\zeta')\, d\zeta' \equiv -\tau(\zeta) \quad , \quad (11)$$

with β given in Eq. (8) and ζ_0 being a constant. The minus implies that the functions $\mathcal{G}$ are here assumed to satisfy the condition $\mathcal{G}(\zeta + \lambda_2\zeta_0) > \mathcal{G}(\lambda_1\zeta_0)$ for $\zeta \neq 0$, which does not need to be defined, whereas the free parameters λ_i (i=1,2) will restrict the range of ζ.

The aforementioned integration limits lead to the condition $\lambda_2 - \lambda_1 + \zeta \leq 0$ and was discussed in our previous work [16]. If $\lambda_2 \neq \lambda_1$, then we get [in terms of $\tau(0)$]

$$\tau(\zeta^*) \approx \left(1 + \frac{\zeta^*}{\lambda_2 - \lambda_1}\right)\{\tau(0) + \zeta_0 \ln\cosh\lambda_2\} - \zeta_0\left(\frac{\zeta^*}{\lambda_2 - \lambda_1}\ln\cosh\lambda_1 + \ln\cosh(\lambda_2 + \zeta^*)\right) \quad . \quad (12)$$

where $\zeta^* = \zeta/\zeta_0$, $\tau(0) = \zeta_0(\lambda_2 - \lambda_1)(1 + \Gamma_\lambda)$, and $\Gamma_\lambda = (\ln\cosh\lambda_1 - \ln\cosh\lambda_2)/(\lambda_2 - \lambda_1)$.

In Fig. 2 we show the dependence of the normalized probability distribution function τ on the reduced variable ζ^* for values of $\lambda_1 = 3$, $\lambda_2 = -8$, and $\tau(0) = 1$, which, in turn, determine the value of ζ_0. In our calculations, i.e., using Eqs. (8) and (12), we have also reduced $\frac{\chi}{w(1-s^2)} \propto 1$ and $Q\zeta_0 \propto 1$ for simplicity. The choice of $\tau(0)$ allows us to normalize $\tau(\zeta^*)$ and to mimic features of SOC, namely, a power-law behavior in space correlations (within the range $0 \leq \zeta^* \leq 8$), provided ζ^* 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 $\ln\cosh(\lambda_2 + \zeta^*) \approx 0$, and hence τ of Eq. (12) depends linearly on ζ^* for values $\zeta^* \leq -\lambda_2$.

To see more clearly possible power-law features in the behavior of τ 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 ζ^* this function converges to a constant negative value, revealing in this way the constant nature of the negative slopes in the (τ-ζ^*) curves. In view of these features of the derivative of τ, the second derivative has also been included in Fig. 2. It presents a sharp peak around the inflection point of $\frac{\partial\tau}{\partial\zeta^*}$, thus indicating the range of validity of such a power-law behavior. The cutoff in the ζ^* axis for the τ 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 β as a

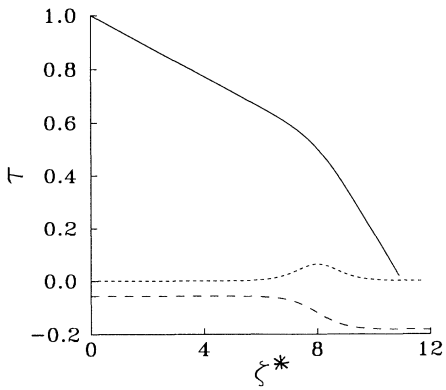

FIG. 2. (Full line) probability distribution function τ of having random events vs reduced variable ζ^* using $\lambda_1 > \lambda_2$, such that $\lambda_2 < 0$ and $\tau(0) = 1$. (Dotted lines) first and (smallest dotted lines) second derivative of τ with respect to ζ^*.

nonequilibrium order parameter of a transition from the D_1 phase of the chain to the Fröhlich phase [20]; 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, which have usually been neglected when taking a continuous limit within the framework of the Davydov theory, but which, in our opinion, may become important as the source for generating randomness. These effects include radiation chaos and disorder. Radiation effects were first discovered in the context of lattice topological solitons (dislocations), and subsequently proved to exist also in the case of dynamical solitons [21]. 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 [21]. Chaotic effects, due to lattice discreteness have been discussed in Ref. [22] 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 [23]. Considering the 20 different natural amino acids in real peptide chains, each of different mass, one may think of a sequence of random masses as having important effects on soliton propagation. This has been observed by Förner [24] in investigating sequences of masses, spring constants, nonlinear coupling constants, heat baths, 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 [25]. We believe all of these phenonomena to generate (a sort of intrinsic) randomness for the displacements β 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 in understanding long-range correlations in biological systems [26] and flicker noise, possibly including DNA [11]. 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 β, which has been analyzed 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 as heuristic. But, in view of the obtained results, this can be considered as one of the simplest, most reasonable ways to relate local properties to macroscopic behavior. To this end, note that a relation of this kind has also been used within the context of pattern formation [27].

The authors thank Dr. J. Langowski (EMBL–Grenoble) for a valuable discussion and Professor Yu Lu (ICTP–Trieste) for encouragement.

[1] A.S. Davydov, J. Theor. Biol. **38**, 559 (1973); see also *Solitons in Molecular Systems* (Reidel, Dordrecht, 1985).
[2] F.L. Hock, *Energy Transformations in Mammals: Regularity Mechanisms* (Saunders, Philadelphia, 1971), pp.1–5.
[3] V. Muto, A.C. Scott, and P.L. Christiansen, Physica D **44**, 75 (1990).
[4] S. Takeno, Prog. Theor. Phys. **69**, 1689 (1983); J. Phys. Soc. Jpn. **59**, 3127 (1990).
[5] S. Yomosa, Phys. Rev. A **32**, 1752 (1985).
[6] Lj.M. Ristowski, Z. Nestorovič, and G.S. Davidovič, Z. Phys. B **88**, 145 (1992).
[7] H. Bolterauer, J.A. Tuszyński, and M.V. Satarič, Phys. Rev. A **44**, 1366 (1991).
[8] L. Cruzeiro-Hansson, Phys. Rev. A **45**, 4111 (1992).
[9] W. Fann *et al.*, Phys. Rev. Lett. **64**, 607 (1990).
[10] A.C. Scott, Physica D **51**, 333 (1991).
[11] R.F. Voss, Phys. Rev. Lett. **68**, 3805 (1992).
[12] C.-K. Peng *et al.*, Nature (London) **356**, 168 (1992).
[13] W. Li and K. Kaneko, Europhys. Lett. **17**, 655 (1992).
[14] P. Bak, C. Tang, and K. Weisenfeld, Phys. Rev. Lett **59**, 381 (1987).
[15] It has been found that discrete (sandpile) models for SOC result in $1/f^2$, whereas their continuous counterparts may exhibit $1/f$ instead. Accordingly, we obtain here the continuous limiting behavior. For a discussion see H.F. Chau and K.S. Cheng, Phys. Rev. A **46** R2981 (1992).
[16] E. Canessa, Phys. Rev. E **47**, R5 (1993).
[17] D.W. Brown, B.J. West, and K. Lindenberg, Phys. Rev. A **33**, 4104 (1986); **33**, 4110 (1986).
[18] D.W. Brown and Z. Ivic, Phys. Rev. B **40**, 9876 (1989).
[19] D.W. Brown, K. Lindenberg, and B.J. West, Phys. Rev. Lett. **57**, 2341 (1986).
[20] H. Fröhlich, Int. J. Quantum Chem. **2**, 641 (1968).
[21] M. Peyrard, S. Pnevmatikos, and N. Flytzanis, Physica D **19**, 268 (1986).
[22] S. Takeno, Prog. Teor. Phys. **73**, 853 (1985).
[23] S.R. Phillipot *et al.*, Phys. Rev. B **35**, 7533 (1987).
[24] W. Förner, Phys. Rev. A **44**, 2694 (1991), and references therein.
[25] Z. Fei, Y.S. Kivshar, and L. Vázquez, Phys. Rev. A **46**, 5214 (1992); **46**, 6019 (1992).
[26] G.S. Mani, J. Theor. Biol. **158**, 447 (1992).
[27] W. Wei and E. Canessa, Phys. Rev. E **47**, 1243 (1993).