

## Amplification of coherent polar vibrations in biopolymers: Fröhlich condensate

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We consider the nonequilibrium and dissipative evolution, and the steady state of the population of vibrational polar modes in a chain of biomolecules. These polar modes are excited through a coupling with a metabolic pumping source and are in anharmonic interaction with an elastic continuum. Groups of polar modes are coupled in this way through nonlinear terms in the kinetic equations. This nonlinearity is shown to be the source of an unexpected phenomenon characterizing complex behavior in this kind of system: after a threshold of intensity of the pumping source is achieved, polar modes with the lowest frequencies increase enormously their population in a way reminiscent of a Bose-Einstein condensation (Fröhlich effect). The transient time for the steady-state condensate to follow is very short (picosecond time scale) and the condensation appears even for weak values of the anharmonic coupling strength responsible for its occurrence. Further, it seemingly requires accessible levels of metabolic pumping power in order to be produced and sustained.

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### I. INTRODUCTION

Nonlinearity is known to be the source of new and unexpected phenomena that characterize complex behavior in physical systems. This is particularly the case in dissipative systems far from equilibrium [1]. The concept that many-body systems sufficiently far away from equilibrium and governed by nonlinear kinetic laws may display self-organized ordered structures at the macroscopic level, as observed in many cases, has been brought under unifying approaches such as dissipative structures [2,3], synergetics [4], and macroconcepts [5]. We may say that, in particular, biological systems are complex systems by antonomasia, which are open, driven far from equilibrium, and display a variety of nonlinear physicochemical processes. Thus, as is the case, they present an enormous number of rich and noticeable phenomena on the morphological, biochemical, biophysical, etc., levels. We emphasize that this is possible in the nonlinear thermodynamic regime far from equilibrium, since in the linear (Onsager's) regime near equilibrium, ordering is inhibited according to Prigogine's theorem of minimum entropy production (e.g., Ref. [3]) that confirms the stability of the thermally chaotic branch of solutions, i.e., the so-called thermodynamic branch that emerges continuously from the equilibrium state with increasing values of the intensity of the external perturbation.

A quite interesting and illustrative example of nonlinearity at work, producing what can be very relevant biological effects, is a model of a biophysical system proposed by Fröhlich [6,7] that may describe membranes or large chains of macromolecules possessing longitudinal electric modes. In the Fröhlich model several modes of polar vibrations are excited by a continuous supply of metabolic energy, with these polar modes interacting with a bath of acousticlike vibrations through nonlinear dynamics, which is the source for what we call the

*Fröhlich effect*, namely, that under appropriate nonlinear conditions the modes with the lowest frequencies increase enormously their population in a way reminiscent of a Bose-Einstein condensation. It has been stated that these polar modes, thus largely excited, may exhibit long-range phase correlations of the electret type [8–10], that may produce observable effects in biosystems [7].

Some microscopic approaches using modeled Hamiltonians have been proposed to describe Fröhlich system [11,12]. In these treatments the nonlinear kinetic terms arise out of nonlinear anharmonic interactions resulting in the creation (decay) of a longitudinal polar excitation from (into) a single excitation of the bath system and a polar excitation.

More recently, Davydov has proposed a model for a one-dimensional  $\alpha$ -helical protein molecular chain with oscillating peptide bonds, embedded in an elastic continuum. A theory of the transfer of metabolic energy and of electrons along the chain describe excitations accompanied by a local deformation of the chain that move uniformly and undamped in what is called a solitary exciton [13–15]. These ideas concerning the transfer of energy in biological systems have been extended mainly by Scott [16]. It should be stressed that the nonlinearity of the equations of evolution, arising out of the interaction with the elastic continuum, are responsible for the Fröhlich effect and the propagation of solitary excitons. In fact, Tuszynski *et al.* [9] have shown the equivalence of the Hamiltonians used to describe Fröhlich and Davydov models when both are placed in a representation in terms of normal coordinates.

Along this line, we consider the case of a chain of biomolecules, taken as a quasi-unidimensional system, and study the macroscopic nonequilibrium evolution of the polar vibrational modes they possess, whose kinetic equations—derived in an appropriate mechanostatistical scheme—are numerically solved. They are assumed to be excited by the pumping of biochemical energy (usually

thought of to be the energy released by hydrolysis of adenosine triphosphate) on the polar oscillations (associated to double-bonded carbon-oxygen), which sustain an anharmonic interaction with an elastic continuum, the latter being modeled in terms of a Debye acoustic-oscillation system. The system is far from equilibrium and therefore its description requires nonequilibrium dissipative thermodynamics. For that purpose we resort to the powerful, and also elegant and concise, nonequilibrium statistical operator method (NSOM), reviewed and brought under a unifying variational principle based on the predictive statistical mechanics of Jaynes in Ref. [17]. NSOM allows for the construction of a nonlinear generalized transport theory—a far reaching generalization of the methods of Chapman-Enskog and also Mori—that describes the evolution of the system at the macroscopic level in arbitrary nonequilibrium situations, as shown in Ref. [18]. Among the different NSOM, we resort to the method of Zubarev [19] and the so-called [18] second-order approximation in the theory of relaxation (SOART). It is also known in the literature as the quasilinear theory of relaxation [20], a name we avoid because of the misleading term “linear” that refers to a certain order of dissipation as described by the nonequilibrium statistical operator, although the equations of evolution remain highly nonlinear.

We are thus allowed to write the equations of evolution for the populations of the polar modes, with a bath of acoustic vibrations that is assumed to remain in a state of constant temperature through the action of an efficient homeostatic mechanism. The polar vibration’s frequency dispersion relation is modeled by a parabolic law around the zone center in reciprocal space. We use typical values for the different parameters that enter into the equations of evolution, which results in the fact that the polar modes are coupled in groups having a small number of modes, which greatly facilitates the computational solution of the coupled system of equations.

We solve the time-dependent equations of evolution to describe the transient period before the attainment of a stationary state. In that way, it is possible to define a transient time which is expressed in units of the relaxation time of the polar modes to the thermal bath. Furthermore, the solutions for the values of the populations in the steady state are obtained in terms of the intensity of the energy pumping source.

In the next section we specify the system and write the relevant Hamiltonian and the equations of evolution for the population of the modes derived in NSOM-SOART. We deal with an exactly soluble model for a chain of biomolecules where, we anticipate, Fröhlich effect follows: with increasing values of the pumping intensity, after a threshold is achieved, there follows a large amplification of a set of modes with the lowest frequencies. It is shown that the phenomenon can be realized even under conditions of weak contribution of the nonlinear terms in the equations of evolution that are relevant for the effect to appear, and under accessible levels of excitation. Also, it follows after a very short transient time after switching on the exciting external source, and, furthermore, as shown elsewhere [10], at the critical

point for the onset of the Fröhlich effect the lifetime of the oscillatory excitations largely increases, becoming near dissipationless waves, much in the way of Davydov’s solitary waves. Hence, both effects seem to have the same and simultaneous origin.

## II. POLAR MODES IN BIOPOLYMERS

Let us consider a quasilinear polymeric chain of biomolecules consisting of an arrangement of periodically repeated groups of molecules. Let  $a$  be the extension of the crystallographic unit cell. An example could be the  $\alpha$ -helix protein depicted in Fig. 1, considered by Davydov [15], more precisely three chains (channels) with peptide bonds, in a near one-dimensional array (the radius of the helix is 2.8 Å). The pitch of the spiral is 4.5 Å, and the crystallographic unit cell contains 18 peptide groups ( $a \approx 80$  Å). The energy is pumped in the system by metabolic processes, typically the energy released in the hydrolysis of adenosine 5-triphosphate (ATP) molecules, and it is assumed that the chain can sustain longitudinal polar vibrations. This vibrational energy is associated to the CO stretching (or amide I) oscillators. The latter have a frequency dispersion relation  $\omega_{\mathbf{q}}$ , where  $\mathbf{q}$  is a wave vector running over the reciprocal-space (Brillouin) zone of length  $2\pi/a$ . The chain is assumed to be embedded in an elastic continuum represented by a Debye model, i.e., with a frequency dispersion relation  $sq$ , where  $s$  is the sound velocity in such a medium and having a Debye cutoff frequency  $\omega_D$ . On the right-hand side of Fig. 1 we

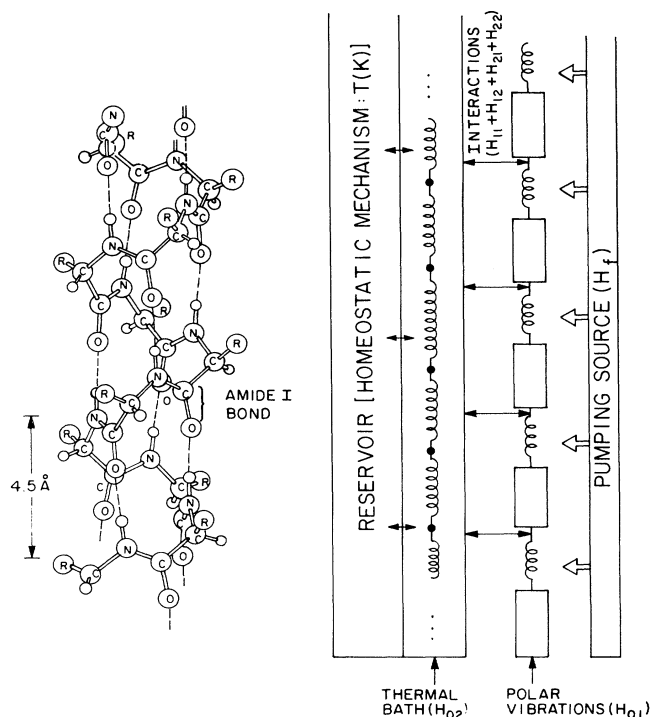


FIG. 1. An atomic model of the  $\alpha$ -helix structure in a protein (Refs. [15] and [16]), and on the right a rough description of the mechanical model considered in the text.

proceed to analyze a rough description of the mechanical model of the chain. Such a mechanical system is completely characterized at the dynamical level by the Hamiltonian

$$H = H_{01} + H_{02} + H_{11} + H_{12} + H_{21} + H_{22} + H_f, \quad (1)$$

where

$$H_{01} = \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} (a_{\mathbf{q}}^\dagger a_{\mathbf{q}} + \frac{1}{2}) \quad (2a)$$

is the Hamiltonian of the free polar vibrations;  $a$  ( $a^\dagger$ ), as usual, are the annihilation (creation) operators in mode  $\mathbf{q}$ ;

$$H_{02} = \sum_{\mathbf{q}} s_{\mathbf{q}} (b_{\mathbf{q}}^\dagger b_{\mathbf{q}} + \frac{1}{2}) \quad (2b)$$

is the Hamiltonian of the bath of free acousticlike vibrations; and  $b$  ( $b^\dagger$ ) are the corresponding annihilation (creation) operators. The next four terms arise out of anharmonic interactions involving three-quasiparticle collisions, given by the expressions

$$H_{11} = \sum_{\mathbf{q}, \mathbf{q}'} V_{\mathbf{q}\mathbf{q}'}^{(1)} a_{\mathbf{q}} b_{\mathbf{q}} b_{\mathbf{q}+\mathbf{q}'}^\dagger + \text{H.c.}, \quad (2c)$$

$$H_{12} = \sum_{\mathbf{q}, \mathbf{q}'} V_{\mathbf{q}\mathbf{q}'}^{(1)} a_{\mathbf{q}} b_{\mathbf{q}} b_{\mathbf{q}-\mathbf{q}'}^\dagger + \text{H.c.}, \quad (2d)$$

$$H_{21} = \sum_{\mathbf{q}, \mathbf{q}'} V_{\mathbf{q}\mathbf{q}'}^{(2)} a_{\mathbf{q}} a_{\mathbf{q}'} b_{\mathbf{q}+\mathbf{q}'}^\dagger + \text{H.c.}, \quad (2e)$$

and

$$H_{22} = \sum_{\mathbf{q}, \mathbf{q}'} V_{\mathbf{q}\mathbf{q}'}^{(2)} a_{\mathbf{q}}^\dagger a_{\mathbf{q}'} b_{\mathbf{q}-\mathbf{q}'} + \text{H.c.}, \quad (2f)$$

where  $V^{(1)}$  and  $V^{(2)}$  are the corresponding matrix elements of the interaction potential. Finally,

$$H_f = \sum_{\mathbf{q}} \varphi_{\mathbf{q}} a_{\mathbf{q}}^\dagger + \text{H.c.} \quad (2g)$$

represents the energy of interaction between the pumping source and the polar modes:  $\varphi$  ( $\varphi^\dagger$ ) are annihilation (creation) operators of excitations in the source, also containing the coupling strength. Furthermore, we introduce—as required by NSOM—the partial Hamiltonians

$$H_0 = H_{01} + H_{02}$$

and

$$H' = H_{11} + H_{12} + H_{21} + H_{22} + H_f.$$

To deal with this system in NSOM the first step is to define the basic set of variables deemed appropriate for the description of its macroscopic state. We choose the populations of the polar vibrations

$$\nu_{\mathbf{q}}(t) = \text{Tr} \{ a_{\mathbf{q}}^\dagger a_{\mathbf{q}} \rho(t) \} \equiv \text{Tr} \{ \hat{\nu}_{\mathbf{q}} \rho(t) \}, \quad (3)$$

and the energy of the free subsystem of acoustic vibrations (bath)

$$E_b(t) = \text{Tr} \left\{ \sum_{\mathbf{q}} \hbar s_{\mathbf{q}} (b_{\mathbf{q}}^\dagger b_{\mathbf{q}} + \frac{1}{2}) \rho(t) \right\}, \quad (4)$$

where  $\rho(t)$  is the nonequilibrium statistical operator (NSO) in Zubarev's approach [19]. We recall that the acoustic modes act as a thermal bath for the polar modes, remaining in an equilibrium state at constant temperature  $T$ , while in contact with a thermal reservoir providing an efficient homeostatic mechanism. Hence, the NSOM auxiliary operator [17,19] is, in this case,

$$\bar{\rho}(t, 0) = \exp \left\{ -\phi(t) - \sum_{\mathbf{q}} F_{\mathbf{q}}(t) \hat{\nu}_{\mathbf{q}} - \beta H_{02} \right\}, \quad (5)$$

where  $\beta = 1/kT$  and  $F_{\mathbf{q}}(t)$  are nonequilibrium thermodynamic parameters conjugated to the dynamical variable occupation number of polar vibrations,  $\phi(t)$  is a Massieu-Planck functional that ensures its normalization, and  $\beta$  is time independent because of the assumption that  $T$  is kept constant. Therefore, we are simply left with equations of evolution for the population of the polar modes, then characterizing the nonequilibrium dissipative thermodynamic state of the system.

As noted in the Introduction, these equations are derived by resorting to the nonlinear quantum generalized transport theory that NSOM provides [18]. But the collision operator they define, which contains highly nonlinear, nonlocal, and memory effects, is extremely difficult to handle in practical calculations; however, through an appropriate mathematical manipulation it can be rewritten in terms of an infinite series of partial collision operators which are instantaneous in time [given as averages over the auxiliary NSO—that of Eq. (5) in our case—at the time of measurement] and organized in increasing powers  $n$  of the interaction strengths [18]. The form of the collision operator thus obtained permits us to introduce approximations by means of a truncation of the series of partial collision operators in a given order of interaction. The lowest order that introduces relaxation effects is a truncation in second order in the interaction strengths, the SOART referred to in the Introduction: it renders the equations Markovian in character [17,18,20]. We resort here to this approximation; it produces the nonlinear contributions relevant to the question in hand, with the higher-order terms given small modifications. The NSOM-SOART equation of evolution for the mode populations are

$$\frac{d}{dt} \nu_{\mathbf{q}}(t) = J_{\mathbf{q}}^{(0)}(t) + J_{\mathbf{q}}^{(1)}(t) + J_{\mathbf{q}}^{(2)}(t), \quad (6)$$

where

$$J_{\mathbf{q}}^{(0)}(t) = \text{Tr} \left\{ \frac{1}{i\hbar} [a_{\mathbf{q}}^\dagger a_{\mathbf{q}}, H_0] \bar{\rho}(t, 0) \right\}, \quad (7a)$$

$$J_{\mathbf{q}}^{(1)}(t) = \text{Tr} \left\{ \frac{1}{i\hbar} [a_{\mathbf{q}}^\dagger a_{\mathbf{q}}, H'] \bar{\rho}(t, 0) \right\}, \quad (7b)$$

$$J_q^{(2)}(t) = \left[ \frac{1}{i\hbar} \right]^2 \int_{-\infty}^0 dt' e^{\varepsilon t'} \text{Tr} \{ [H'(t'), [H', a_q^\dagger a_q]] \bar{\rho}(t, 0) \} + \frac{1}{i\hbar} \int_{-\infty}^0 dt' e^{\varepsilon t'} \frac{\delta J_q^{(1)}(t)}{\delta v_q(t)} \text{Tr} \{ [a_q^\dagger a_q, H'] \bar{\rho}(t, 0) \}, \quad (7c)$$

where  $\delta$  stands for functional derivative,  $\bar{\rho}$  is given by Eq. (5), and Zubarev's approach was used.

In the NSOM-SOART calculation for the equations of evolution for the polar mode populations, it results that because of the symmetry properties of the system and the selected choice of the basic variables—and thus the form of the auxiliary NSO of Eq. (5)—several contributions are null, namely,  $J^{(0)}$  and  $J^{(1)}$ . There remains only the first contribution to  $J^{(2)}$ , which produces a result that correspond to the golden rule of quantum mechanics averaged with the auxiliary nonequilibrium statistical operator of Eq. (5); performing the required calculations we finally obtain

$$\begin{aligned} \frac{d}{dt} v_q(t) = & I_q(\omega_q) - \frac{2\pi}{\hbar^2} \sum_{q'} |V_{qq'}^{(1)}|^2 \{ v_q^b (1 + v_{q+q'}^b) v_q(t) - (1 + v_q^b) v_{q+q'}^b [1 + v_q(t)] \} \delta(s|\mathbf{q} + \mathbf{q}' - s|\mathbf{q}'| - \omega_q) \\ & - \frac{2\pi}{\hbar^2} \sum_{q'} |V_{qq'}^{(1)}|^2 \{ (v_q^b + 1)(v_{q-q'}^b + 1) v_q(t) - v_q^b v_{q-q'}^b [1 + v_q(t)] \} \delta(s|\mathbf{q} - \mathbf{q}'| + s|\mathbf{q}'| - \omega_q) \\ & - \frac{2\pi}{\hbar^2} \sum_{q'} |V_{qq'}^{(2)}|^2 \{ (1 + v_{q+q'}^b) v_q(t) v_q(t) - v_{q+q'}^b [1 + v_q(t)] [1 + v_q(t)] \} \delta(s|\mathbf{q}' + \mathbf{q}| - \omega_{q'} - \omega_q) \\ & - \frac{2\pi}{\hbar^2} \sum_{q'} |V_{qq'}^{(2)}|^2 \{ (1 + v_{q-q'}^b) [1 + v_q(t)] v_q(t) - v_{q-q'}^b v_q(t) [1 + v_q(t)] \} \delta(s|\mathbf{q} - \mathbf{q}'| + \omega_{q'} - \omega_q) \\ & - \frac{2\pi}{\hbar^2} \sum_{q'} |V_{qq'}^{(2)}|^2 \{ v_{q-q'}^b [1 + v_q(t)] v_q(t) - (1 + v_{q-q'}^b) v_q(t) [1 + v_q(t)] \} \delta(s|\mathbf{q}' - \mathbf{q}| - \omega_{q'} + \omega_q). \end{aligned} \quad (8)$$

We recall that  $\mathbf{q}$  when referred to the polar modes runs over the Brillouin zone ( $-\pi/a \leq q \leq \pi/a$ ), and that the Hamiltonian of Eq. (1) already contains information on the conservation of the linear momentum; in the equation above the  $\delta$  functions take care of the conservation of energy in the collision events. Furthermore, we expressed the time-dependent correlations involving the operators associated to the external source in terms of a spectral density, namely,

$$\frac{2\pi}{\hbar^2} \langle \varphi_q(t) \varphi_q^\dagger \rangle = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} I_q(\omega) e^{i\omega t}, \quad (9)$$

where  $I(\omega)$  represents the intensity of the source over the spectrum of frequencies. Finally,  $v^b$  is the population of the acoustic vibrational modes, namely,

$$v_q^b = [\exp(\beta s q) - 1]^{-1}. \quad (10)$$

Taking into account Eq. (10) and using the energy-conserving  $\delta$  functions, Eqs. (8) can be rewritten as

$$\begin{aligned} \frac{d}{dt} v_q(t) = & I_q(\omega_q) - \frac{2\pi}{\hbar^2} \sum_{q'} |V_{qq'}^{(1)}|^2 v_q^b v_{q+q'}^b e^{\beta \hbar \omega_{q'}} \left[ \frac{v_q(t)}{v_q^0} - 1 \right] \delta(s|\mathbf{q} + \mathbf{q}'| - s|\mathbf{q}'| - \omega_q) \\ & - \frac{2\pi}{\hbar^2} \sum_{q'} |V_{qq'}^{(1)}|^2 v_q^b v_{q-q'}^b \left[ \frac{v_q(t)}{v_q^0} - 1 \right] \delta(s|\mathbf{q} - \mathbf{q}'| + s|\mathbf{q}'| - \omega_q) \\ & + \frac{2\pi}{\hbar^2} \sum_{q'} |V_{qq'}^{(2)}|^2 v_{q+q'}^b \{ [1 + v_{q'}(t)] [1 + v_q(t)] - v_{q'}(t) v_q(t) e^{\beta \hbar \Omega_{qq'}} \} \delta(s|\mathbf{q} + \mathbf{q}'| - \omega_{q'} - \omega_q) \\ & + \frac{2\pi}{\hbar^2} \sum_{q'} |V_{qq'}^{(2)}|^2 v_{q-q'}^b \{ v_{q'}(t) [1 + v_q(t)] - [1 + v_{q'}(t)] v_q(t) e^{\beta \hbar \Delta_{qq'}} \} \delta(s|\mathbf{q} - \mathbf{q}'| + \omega_{q'} - \omega_q) \\ & + \frac{2\pi}{\hbar^2} \sum_{q'} |V_{qq'}^{(2)}|^2 v_{q-q'}^b \{ v_{q'}(t) [1 + v_q(t)] e^{-\beta \hbar \Delta_{qq'}} - [1 + v_{q'}(t)] v_q(t) \} \delta(s|\mathbf{q}' - \mathbf{q}| - \omega_{q'} + \omega_q), \end{aligned} \quad (11)$$

where

$$\Omega_{qq'} = \omega_q + \omega_{q'}, \quad (12a)$$

$$\Delta_{qq'} = \omega_q - \omega_{q'}, \quad (12b)$$

and  $v^0$  is the population in equilibrium (at temperature  $T$ ) of the polar vibrational mode.

Equation (11) is the type of equation proposed by Fröhlich. On the right-hand side of Eq. (11), besides the

pump term, which is the first one, the next two terms are associated to relaxation (decay) of the polar excitations to the thermal bath (related to  $H_{11}$  and  $H_{12}$ ); the fourth, arising out of  $H_{21}$ , is also a relaxation term of the vibrational mode; the last two terms are contributions arising from  $H_{22}$  that we call Fröhlich terms, because those are responsible for the transfer of excitations to the low-frequency polar modes. In fact, given mode  $\mathbf{q}$ , if  $\omega_q < \omega_{q'}$ , the bilinear terms containing  $v_q v_{q'}$  lead to an increase in

population for it, at the expense of the other  $\mathbf{q}'$  modes. It has been argued [21] that contributions coming from the fourth term wash away the effect of contributions arising out of  $H_{22}$ , but Fröhlich has countered [22] that it has a small contribution as a result of the different form of energy conservation in both processes as, in fact, characterized by the  $\delta$  functions in Eq. (8); we anticipate that for the parameters we use in our numerical calculations contributions arising from  $H_{21}$  are identically null.

To proceed further, we model the dispersion relation of the polar modes by a parabolic law, namely

$$\omega_{\mathbf{q}} = \omega_0 - \alpha q^2, \quad (13)$$

where  $\omega_0$  and  $\alpha$  are constant parameters. It should be noticed that this form for the dispersion law implies a maximum value  $\omega_0$  at the zone center and a minimum value at the zone boundaries. Also, the second and third terms on the right-hand side of Eq. (11) are written as

$$-\frac{1}{\tau_{\mathbf{q}}} (v_{\mathbf{q}} - v_{\mathbf{q}}^0), \quad (14)$$

which introduces the relaxation time

$$\begin{aligned} \tau_{\mathbf{q}}^{-1} = & \frac{2\pi}{\hbar^2} \frac{1}{v_{\mathbf{q}}^0} \sum_{\mathbf{q}'} |V_{\mathbf{q}\mathbf{q}'}^{(1)}|^2 \\ & \times [v_{\mathbf{q}}^b v_{\mathbf{q}+\mathbf{q}'}^b e^{\beta\hbar s|\mathbf{q}'|} \delta(s|\mathbf{q}+\mathbf{q}'|-s|\mathbf{q}'|-\omega_{\mathbf{q}}) \\ & + v_{\mathbf{q}}^b v_{\mathbf{q}-\mathbf{q}'}^b \delta(s|\mathbf{q}-\mathbf{q}'|+s|\mathbf{q}'|-\omega_{\mathbf{q}})]. \end{aligned} \quad (15)$$

Because of the choice given by Eq. (13) we are now in condition to evaluate the energy-conserving  $\delta$  functions, i.e., to determine the values of  $\mathbf{q}'$  that they fix. This requires one to look for the roots of the equations,

$$f_{11} \equiv \omega_0 - \alpha q^2 + s|\mathbf{q}'| - s|\mathbf{q} + \mathbf{q}'|, \quad (16a)$$

$$f_{12} \equiv \omega_0 - \alpha q^2 - s|\mathbf{q}'| - s|\mathbf{q} - \mathbf{q}'|, \quad (16b)$$

$$f_2 \equiv 2\omega_0 - \alpha(q^2 + q'^2) - s|\mathbf{q} + \mathbf{q}'|, \quad (16c)$$

$$f_3 \equiv \alpha(q'^2 - q^2) - s|\mathbf{q} - \mathbf{q}'|, \quad (16d)$$

$$f_4 \equiv \alpha(q'^2 - q^2) + s|\mathbf{q} - \mathbf{q}'|. \quad (16e)$$

In one dimension the vectors  $\mathbf{q}$  and  $\mathbf{q}'$  take the values  $q$  and  $q'$ , positive or negative. Taking this into account we have the following:

(1) The roots of  $f_{11}$  are

$$q'_{11} = \begin{cases} -(\omega_0 - \alpha q^2 + sq)/2s, \\ \quad \text{if } q' > 0 \text{ and } q + q' < 0 \\ (\omega_0 - \alpha q^2 - sq)/2s, \\ \quad \text{if } q' < 0 \text{ and } q + q' > 0; \end{cases} \quad (17a)$$

$$q'_{12} = \begin{cases} (\omega_0 - \alpha q^2 + sq)/2s, \\ \quad \text{if } q' > 0 \text{ and } q - q' < 0 \\ -(\omega_0 - \alpha q^2 - sq)/2s, \\ \quad \text{if } q' < 0 \text{ and } q - q' > 0; \end{cases} \quad (17c)$$

what implies that  $\omega_0 - \alpha q^2 \pm sq > 0$ .

(3) The roots of  $f_2$  are

$$q'_{2\pm} = \frac{s}{2\alpha} \pm \left[ \left[ \frac{s}{2\alpha} \right]^2 - q^2 + 4\frac{s}{\alpha}q + \frac{2\omega_0}{\alpha} \right]^{1/2}, \quad (17e)$$

for  $q + q' > 0$ ,

$$q'_{2\pm} = -\frac{s}{2\alpha} \pm \left[ \left[ \frac{s}{2\alpha} \right]^2 - q^2 - 4\frac{s}{\alpha}q + \frac{2\omega_0}{\alpha} \right]^{1/2}, \quad (17f)$$

for  $q + q' < 0$ .

(4) The roots of  $f_3$  are  $q'_2 = q$ , and

$$q'_2 = \begin{cases} -q - s/\alpha, & \text{if } q - q' > 0 \text{ and } q > -s/2\alpha \\ -q + s/\alpha, & \text{if } q - q' < 0 \text{ and } q < s/2\alpha; \end{cases} \quad (17g)$$

(5) The roots of  $f_4$  are  $q'_3 = q$ , and

$$q'_3 = \begin{cases} -q - s/\alpha, & \text{if } q - q' < 0 \text{ and } q < -s/2\alpha \\ -q + s/\alpha, & \text{if } q - q' > 0 \text{ and } q > s/2\alpha; \end{cases} \quad (17i)$$

It should be noted that the  $\delta$  functions in Eqs. (11) produce  $\delta$  functions in the variable of the integration  $q'$  through the known relation

$$\delta(f_j(q')) = \sum_n \left| \frac{df_j}{dq'} \right|^{-1} \delta(q' - q'_{jn}), \quad (18)$$

where  $n$  runs over all the roots of  $f_j$ .

To further simplify matters, but without losing the fundamental characteristics of the model, we take the matrix elements  $V_{\mathbf{q}\mathbf{q}'}^{(1)}$  and  $V_{\mathbf{q}\mathbf{q}'}^{(2)}$  as constants,  $V_1$  and  $V_2$ , respectively. We go over the quasicontinuum (large system) in the reciprocal space, i.e., in one dimension,

$$\sum_{\mathbf{q}} \rightarrow \frac{L}{2\pi} \int dq, \quad (19)$$

where  $L$  is the length of the chain, the limits of integration are for the values  $q$  of the polar vibrations  $Q_0 = \pi/a$  and  $-Q_0 = -\pi/a$ , i.e., the end values of the Brillouin zone, and those for the values of  $q'$  of the mode of vibrations in the continuum are in the interval  $Q_D$  and  $-Q_D$ , i.e., the Debye wave number fixed by the Debye cutoff frequency; we assume that  $Q_D \gg Q_0$ . Introducing the time scale  $\bar{\tau} = \hbar^2 s / L |V_1|^2$  and the reduced time  $\tau = t / \bar{\tau}$ , the coefficient  $\lambda = |V_1|^2 / |V_2|^2$ , and taking into account the expressions for the energy conserving  $\delta$  functions as given by Eqs. (18) and (17), we find that

$$\frac{d}{d\tau} v_{\mathbf{q}} = S_{\mathbf{q}} - \frac{\gamma(\mathbf{q})}{v_{\mathbf{q}}^0} [v_{\mathbf{q}} - v_{\mathbf{q}}^0] + R_1(\mathbf{q}) + R_2(\mathbf{q}), \quad (20)$$

where

note that this implies  $\omega_0 - \alpha q^2 \pm sq < 0$ .

(2) The roots of  $f_{12}$  are

$$S_q = I_q \bar{\tau}, \quad (21a)$$

$$\begin{aligned} \gamma(\mathbf{q}) = s \int_{-\mathcal{Q}_D}^{\mathcal{Q}_D} dq' v_q^b v_{q+q}^b e^{\beta \hbar s |q|} & \left\{ \frac{1}{2s} [1 - \Theta(q + q')] \Theta(q') \delta(q' + (\omega_0 - \alpha q^2 + sq)/2s) \right. \\ & + \frac{1}{2s} \Theta(q + q') [1 - \Theta(q')] \delta(q' - (\omega_0 - \alpha q^2 - sq)/2s) \left. \right\} \\ & + s \int_{-\mathcal{Q}_D}^{\mathcal{Q}_D} dq' v_q^b v_{q'-q}^b \left\{ \frac{1}{2s} [1 - \Theta(q - q')] \Theta(q') \delta(q' - (\omega_0 - \alpha q^2 + sq)/2s) \right. \\ & \left. + \frac{1}{2s} \Theta(q - q') [1 - \Theta(q')] \delta(q' + (\omega_0 - \alpha q^2 - sq)/2s) \right\}, \quad (21b) \end{aligned}$$

$$\begin{aligned} R_1(q) = \lambda s \int_{-\mathcal{Q}_0}^{\mathcal{Q}_0} dq' v_{q+q}^b & [(1 + v_{q'}) (1 + v_q) - v_{q'} v_q e^{\beta \hbar \Omega_{qq'}}] \\ & \times ([s^2 - 4\alpha^2 q^2 - 16\alpha s q + 8\alpha \omega_0]^{-1/2} \Theta(q + q') \{ \delta(q' - q_{2+}^{(1)}) + \delta(q' - q_{2-}^{(1)}) \} \\ & + [s^2 - 4\alpha^2 q^2 + 16\alpha s q + 8\alpha \omega_0]^{-1/2} [1 - \Theta(q + q')] \{ \delta(q' - q_{2+}^{(2)}) + \delta(q' - q_{2-}^{(2)}) \}), \quad (21c) \end{aligned}$$

$$\begin{aligned} R_2(q) = \lambda s \int_{-\mathcal{Q}_0}^{\mathcal{Q}_0} dq' v_{q-q}^b & [v_{q'} (1 + v_q) - (1 + v_{q'}) v_q e^{\beta \hbar \Delta_{qq'}}] \\ & \times \left\{ \frac{1}{|2\alpha q + s|} \Theta(q - q') \Theta(q + s/2\alpha) \delta(q' + q + s/\alpha) \right. \\ & + \frac{1}{|2\alpha q - s|} [1 - \Theta(q - q')] [1 - \Theta(q - s/2\alpha)] \delta(q' + q - s/\alpha) \left. \right\} \\ & + \lambda s \int_{-\mathcal{Q}_0}^{\mathcal{Q}_0} dq' v_{q'-q}^b [v_{q'} (1 + v_q) e^{-\beta \hbar \Delta_{qq'}} - (1 + v_{q'}) v_q] \\ & \times \left\{ \frac{1}{|2\alpha q + s|} [1 - \Theta(q - q')] [1 - \Theta(q + s/2\alpha)] \delta(q' + q + s/\alpha) \right. \\ & \left. + \frac{1}{|2\alpha q - s|} \Theta(q - q') \Theta(q - s/2\alpha) \delta(q' + q - s/\alpha) \right\}, \quad (21d) \end{aligned}$$

where  $\Theta(x)$  is Heaviside's step function accounting for the step limitations imposed on  $q'$  by Eqs. (17). It should be noted that in  $R_2$  the contributions from the roots  $q' = q$  in  $f_3$  and  $f_4$  are null. Furthermore, we recall that  $-\mathcal{Q}_0 \leq q \leq \mathcal{Q}_0$ , and it should be noted that Eq. (20) is invariant under the inversion operation in which  $\mathbf{q}$  and  $\mathbf{q}'$  change in  $-\mathbf{q}$  and  $-\mathbf{q}'$ .

For the sake of simplicity, we already take into account that for the values to be used later on for numerical calculations the first term in  $\gamma$  is null as well as the term  $R_1$ . Hence, leaving aside these contributions, performing the integrations in Eqs. (21) we find that ( $q$ , next, is the vector in one dimension)

$$\begin{aligned} \frac{d}{d\tau} v_q = S_q - \frac{\gamma(q)}{v_q^0} & [v_q - v_q^0] + \Theta(q + s/2\alpha) \lambda \varphi(q) [v_{q+s/\alpha} (1 + v_q) - e^{\beta \hbar s (2q + s/\alpha)} (1 + v_{q+s/\alpha}) v_q] \\ & + [1 - \Theta(q - s/\alpha)] \lambda \psi(q) [v_{q-s/\alpha} (1 + v_q) - e^{-\beta \hbar s (2q - s/\alpha)} (1 + v_{q-s/\alpha}) v_q] \\ & + [1 - \Theta(q + s/2\alpha)] \lambda \varphi(q) [v_{q+s/\alpha} (1 + v_q) e^{-\beta \hbar s (2q + s/\alpha)} - (1 + v_{q+s/\alpha}) v_q] \\ & + \Theta(q - s/2\alpha) \lambda \psi(q) [v_{q-s/\alpha} (1 + v_q) e^{\beta \hbar s (2q - s/\alpha)} - (1 + v_{q-s/\alpha}) v_q], \quad (22) \end{aligned}$$

where now

$$\begin{aligned} \gamma(q) = \frac{1}{2} [e^{\beta \hbar (1/2) |\omega_0 - \alpha q^2 - sq|} - 1]^{-1} \\ \times [e^{\beta \hbar (1/2) |\omega_0 - \alpha q^2 + sq|} - 1]^{-1}, \quad (23a) \end{aligned}$$

$$\varphi(q) = s / |2\alpha q + s| (e^{\beta \hbar s |q + s/\alpha|} - 1), \quad (23b)$$

$$\psi(q) = s / |2\alpha q - s| (e^{\beta \hbar s |2q - s/\alpha|} - 1). \quad (23c)$$

We can see that in the all important term  $R_2(q)$  (the one containing the nonlinear contributions) not all the polar modes are coupled, but those that differ between them in a spacing given by  $\pm s/\alpha$ , and are contained in the Brillouin zone. Hence, the modes contained in each segment of the extension  $s/\alpha$  are, each mode independently, coupled to a finite number  $2\bar{n}$  of modes outside it, such that  $\bar{n}$  equals the integer part of  $[\pi\alpha/sq]$ . For example, if the set contains the mode at the

zone center,  $q=0$ , then the coupled modes are  $\{\pm 0, \pm s/\alpha; \pm 2s/\alpha; \dots; \pm \bar{n}s/\alpha\}$  and the set that contains the end zone vector  $Q_0 = \pi/a$  is  $\{Q_0; Q_0 - s/\alpha; Q_0 - 2s/\alpha; \dots, Q_0 - (\bar{n}-1)s/\alpha\}$ . The bilinear terms connect the mode  $q$  to the modes  $q - s/\alpha$  and  $q + s/\alpha$ , in a process of transmission of energy from each mode  $q$  for the next lower in energy. Furthermore, we recall that because of symmetry considerations modes with negative wave vectors are equivalent to those with a positive value.

Having set the equations of evolution for the populations of the coupled modes let us first consider the stationary states that should follow after a certain transient, to be determined later on in this section, have elapsed. The steady state is the solution of Eqs. (22) when setting  $d\nu/d\tau=0$ . It is worth noting that in NSOM, because of the form of the auxiliary operator of Eq. (5), one finds that

$$\nu_q = 1/[e^{F_q} - 1], \quad (24)$$

i.e., the populations can be expressed in terms of the unknown nonequilibrium thermodynamic parameter  $F_q$ . In particular, we may choose the alternative form

$$F_q = \beta[\hbar\omega_q - \mu_q], \quad (25)$$

and then Eq. (24) resembles a Bose-Einstein distribution but with a quasichemical potential for each mode  $\mu_q$ , thus being of the form proposed by Fröhlich [7]. Clearly, replacing Eq. (25) in Eq. (24), and the latter for  $\nu_q$  in the steady-state equation of evolution, one gets an equation for the quasichemical potential in terms of the populations of different modes. This quasichemical potential increases with growing external pumping energy and then may signal a kind of Bose-Einstein condensation if at some critical intensity  $\mu_q$  coincides with  $\hbar\omega_q$ . This implies the possibility of emergence of the Fröhlich effect as described in the Introduction. The formal character of the quasichemical potential per mode,  $\mu_q$ , should be stressed, while  $F_q$  is the nonequilibrium intensive thermodynamic parameter that NSOM introduces, that is, Eq. (25) is an arbitrary choice deemed appropriate for the physical discussion of the problem. A quasichemical potential for the characterization of the population of nonequilibrium photons in the case of a nonequilibrium state of radiation and carriers in semiconductors was also used by Landsberg [23].

Returning to Eqs. (22) in the steady state, we proceed to obtain their numerical solution using an adaptation of a known computational algorithm [24]. For that purpose we need to introduce numerical values for the parameters involved; we take for them values that are typical of the biopolymers involved [7,15,16], namely,

$$\omega_0 = 10^{13} \text{ sec}^{-1}; \quad a = 100 \text{ \AA}$$

$$s = 10^5 \text{ cm/sec}; \quad \alpha = 0.19 \text{ cm}^2/\text{sec}$$

that is we simply take values within the order of magnitude to be expected in such types of systems, e.g., the  $\alpha$ -helix protein of Fig. 1. We stress that the characteristic behavior to be derived, as shown in Figs. 2–7, is indepen-

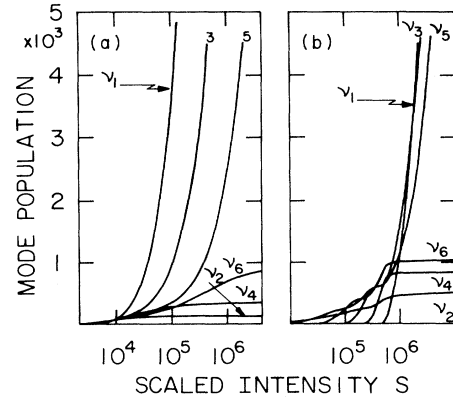


FIG. 2. The population of the different coupled modes, in a set that contains  $q=0$ , as a function of the scaled intensity  $S$  for (a)  $\lambda=1$  and (b)  $\lambda=0.01$ . Mode  $q=0$  is the only one pumped. Index 6 stands for  $q=0$ ; 5 for  $q-s/\alpha$ , . . . , 1 for  $q-5s/\alpha$  (mode 1 is the one with the lowest frequency).

dent of the numerical parameters, that is, the qualitative aspects remain but, of course, with changing numerical results. With these values it results that the end Brillouin-zone wave number is  $Q_0 = 3.14 \times 10^6 \text{ cm}^{-1}$ ; the width of the frequency spectrum of the polar modes is  $\Gamma = 1.87 \times 10^{12} \text{ sec}^{-1}$ ; the ratio  $s/\alpha = 5.27 \times 10^5 \text{ cm}^{-1}$ , and then the number  $\bar{n}$  of coupled modes is 12. The bath temperature is taken as 300 K. There is an open parameter, viz.  $\lambda$ , that measures—as its definition indicates—the ratio of the coupling strengths involved in the non-linear and linear (in the polar mode populations) anharmonic interactions; we will obtain solutions for several values of this parameter.

We consider the set that contains the mode at the zone center ( $q=0$ ), which is assumed to be the only one pumped by the external source, and we solve the equations of evolution for the populations  $\nu_q$  for the values  $\lambda=1$  and 0.01; the results are shown in Figs. 2(a) and

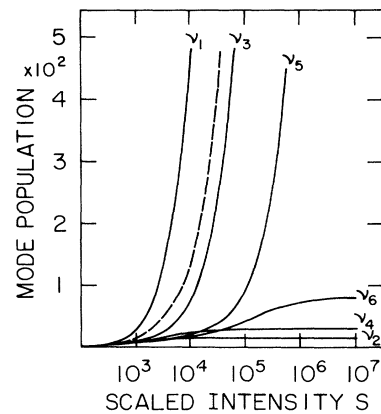


FIG. 3. As in the case of Fig. 1 but now with all modes equally pumped and  $\lambda=1$ . The dashed curve is the result for  $\lambda=0$  (uncoupled modes), when the population of the different twelve modes is roughly the same.

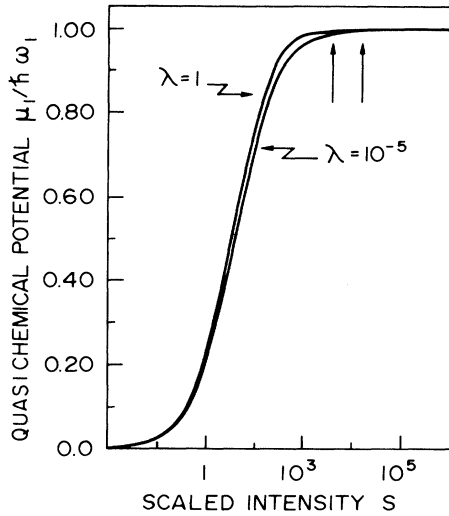


FIG. 4. The dependence on the scaled intensity of the quasichemical potential of the lowest-frequency mode (arrows indicate the approximate onset of condensation).

2(b). Next, we consider the more realistic case of all modes being pumped, and such that  $S_q = S$ , and  $\lambda = 1$  with the corresponding curves shown in Fig. 3.

Inspection of these curves clearly shows a complex behavior of the system: at a given threshold of the intensity  $S$  of the pumping source [we recall that  $S$  is a scaled quantity for the amplitude of the intensity in the spectral representation of Eq. (9); cf. Eq. (21a)] the mode with the lowest frequency begins to grow enormously, in a very steep fashion with increasing intensity  $S$ . The quasichemical potential associated with this mode tends asymptotically from below to the value of the frequency of the mode, but does not coincide with it; see Fig. 4. At and beyond the threshold intensity (indicated in an estimative

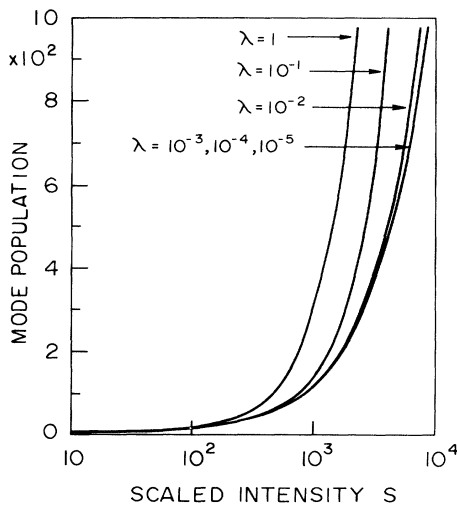


FIG. 5. Behavior of population of the lowest-frequency mode  $\nu_1$  for different values of the coupling strength.

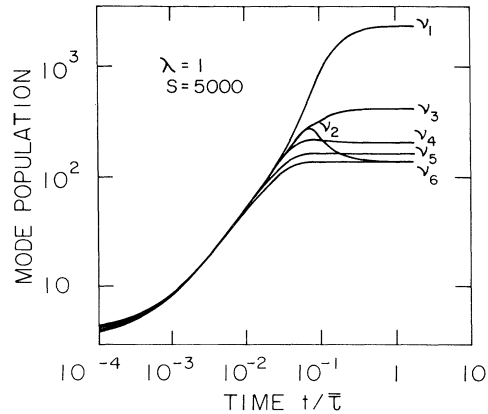


FIG. 6. Evolution in time of the populations of the modes for  $\lambda = 1$  and  $S = 5000$ .

way by the arrows) this very close approach of the quasichemical potential to the frequency of this lowest-frequency mode leads to a near Bose-Einstein condensation, in the sense that the distribution in the modes corresponds to a very large accumulation in the lowest-energy state. The comparison in Fig. 3 of the populations in the presence of the nonlinear coupling with those in the absence of coupling, allows us to better visualize the Fröhlich effect: the mode with the lowest energy has increased its population by almost an order of magnitude above the value expected for  $\lambda = 0$ , at the expenses of the other modes whose populations rest below the dashed line; some of them tend to a constant saturated value. After the critical intensity threshold has been achieved  $\nu_1$  grows quite steeply.

The first threshold intensity (at which there follows the steep increase in population of the lowest-frequency mode) is not strongly dependent on  $\lambda$ , which, we recall, measures the strength of the anharmonic interaction responsible for the nonlinear terms in the equations of evolution. This is shown in Fig. 5. Hence, the effect follows an intense form even at weak nonlinear contributions in the relevant (nonlinear) term that needs to be present for

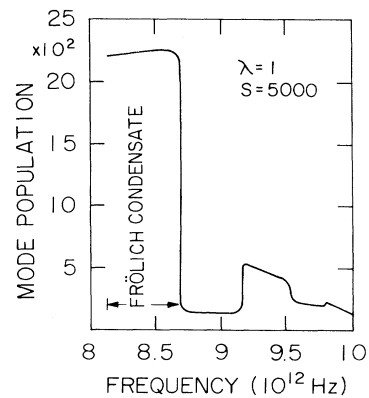


FIG. 7. The population of the modes in the band containing their frequencies of vibration, namely,  $\omega_0 - \alpha(\pi/a)^2 \leq \omega \leq \omega_0$ .



the phenomenon to arise.

Also, as previously mentioned, it has been argued that the anharmonic contribution contained in the fourth term in the Hamiltonian of Eq. (1) opposes and may eventually cancel the Fröhlich effect [21]. Fröhlich has replied that this is not so because the term should involve less important contributions to the kinetic equations [22]. Our calculations show this clearly; furthermore, for the particular numerical values of the parameters we use, the contribution from that term vanishes, because in the scattering events it produces it cannot be simultaneously satisfied by the conservation of energy and momentum.

Our results then show that protein polymers of the type considered by Davydov [13–15] display complex behavior manifested in the emergence of the Fröhlich effect.

As already noted, the Fröhlich effect seems to be accompanied by the formation of an electret state [8,9] and the propagation of undamped waves [10,13–15]. Therefore, it is of relevance to determine the transient time. For that purpose, we solve the equations of evolution (22), using as an initial condition the values for the populations in equilibrium, resorting to an adaptation of a known computer program [25]. Figure 6 shows the evolution of the population of the six modes for case  $\lambda=1$  and  $S=5000$  (slightly above the critical value for the condensation to follow). We are then in a condition to evaluate the transient time before the steady state is reached. Comparing Eqs. (12) and (19b) we find that

$$\tau_q^{-1} = L |V_1|^2 \gamma(q) / \hbar^2 s v_q^0 = \gamma(q) / v_q^0 \bar{\tau}. \quad (26)$$

Assuming these relaxation times to the bath being of the order of tens of picoseconds [7,16], we estimate the scale factor  $\bar{\tau}$  to be roughly 20 psec, and so the transient times are of this order or smaller (see Fig. 4).

Finally, after solving the set of 12 coupled equations for several different sets of 12 coupled modes, we are able to show in Fig. 7 the dependence of the mode populations along the interval of frequencies in the polar branch of vibrations. The region of low frequencies privileged by the onset of the Fröhlich effect is evident. We have already noted that the results described in the series of figures retain their qualitative characteristics when the numerical values of the parameters of the system are changed. Consider, for example, the case when the cell parameter is reduced by a factor of 4 (i.e.,  $a \approx 25 \text{ \AA}$ ). To maintain the width of the frequency dispersion spectrum of the vibrations, parameter  $\alpha$  needs to be reduced by a factor of 16. But now the number of coupled modes is 48. Numerical results are similar, but the main change is that the length of the region in frequency space (cf. Fig. 7) that includes the modes in the condensate is stretched by a factor of 4.

Furthermore, using the given value of  $\bar{\tau}$ , we find that for the critical intensity (for the onset of Fröhlich effect)  $S^* = I^* \bar{\tau}$  being roughly 5000 (cf. Figs. 3 and 4), the value of the critical intensity  $I^*$  is roughly  $5 \times 10^{13} \text{ sec}^{-1}$ , which implies for  $\omega_0 = 10^{13} \text{ sec}^{-1}$  a pumping power of  $5 \times 10^{-8} \text{ W}$  per mode. Since the number of modes is  $LQ_0/\pi$  (where  $L$  is the length of the chain), for the numbers used this is  $10^6 L$ , and then the total pumped power is  $5 \times 10^{-2} L \text{ W}$ . Assuming that this power is provided

through the hydrolysis of adenosine 5'-triphosphate (ATP), which produces 7.3 kcal/mol, in the event of absorption of a fraction  $f$  of this metabolic energy, to maintain the power intensity required would imply a rate of  $\sim (L/f)(1.6 \times 10^{-6}) \text{ mol/sec}$  or  $(Lf) \text{ mg/sec}$  of ATP. To obtain the stationary Fröhlich condensate, as seen, a time interval of the order of 10 psec is required, and then an expense of  $\sim (L/f)(10^{-14}) \text{ g}$  of ATP, which seems to be very accessible values for the phenomenon to occur. Moreover, we have considered here that the source creates single excitations in the vibrational modes [cf. Eq. (2g)] but multiple excitations are also energetically possible, which, furthermore, are enhanced by the same effect of condensation when the modes lowest in frequency are externally pumped.

In the next section we summarize and comment on the relevance of the phenomenon evidenced in this section.

### III. CONCLUDING REMARKS

We have studied a model of a biological polymer, namely a chain of biomolecules such as the  $\alpha$ -helix considered by Davydov [15], which is expected to possess polar modes of vibration. The latter are assumed to receive energy from an external pumping source, say, a metabolic feeding of these modes. At the same time, the polar modes interact with an elastic continuum via a nonlinear anharmonic-type potential. Equation (1) presents the Hamiltonian of this system. We studied the dissipative nonequilibrium state of the polar modes which is characterized by the populations of these modes of vibration. We derived for them the corresponding equations of evolution resorting to the nonequilibrium statistical operator method [17], but in the approximation SOART for the nonlinear transport equations that can be built within the framework of NSOM [18]. Even though the equations couple, in principle, all the modes characterized by the wave vector  $\mathbf{q}$  running over the whole Brillouin zone, conservation of energy and momentum in the scattering events allows for the separation of the whole set of coupled equations in reduced independent sets of equations composed of a certain number of modes. The equations of evolution for the populations of the polar modes of vibration are solved under the assumption of a constant pumping of energy by the external source, and that the thermal bath of acousticlike vibrations is constantly kept in equilibrium with a reservoir at a constant temperature  $T$  (i.e., it is regulated by an efficient homeostatic mechanism).

We have been able to demonstrate that such a system displays a complex behavior, namely, that at a certain distance from equilibrium, i.e., for a threshold value of the pump intensity, there occurs a steep increase in the population of the modes with the lowest frequencies, in a way reminiscent of a Bose-Einstein condensation that we term *Fröhlich effect*. There is a kind of self-organization in the system, governed by the nonlinear effects in the equations of evolution and, thus, this phenomenon may be considered as the emergence of a dissipative structure in Prigogine's sense [26].

Clearly, a very large population in certain modes im-

plies large amplitudes of vibrations, which may lead to a coherent effect among the vibrating units and to formation of some kind of space ordering; it has been suggested that this is an electretlike state, however, of a metastable character [8,9].

Furthermore, as is also shown elsewhere [10], a restudy of the propagation of the excitations in this media, not at the quantum-mechanical level but at the nonequilibrium statistical mechanical level that may describe, within NSOM, the far-from-equilibrium thermodynamic state of the open system, seems to indicate that beyond the point of emergence of Fröhlich's effect, polar waves propagate with a very weak damping. This appears to be of large interest for an eventual explanation of the effective energy transfer at the biomolecular level. At normal lifetimes, estimated in the picosecond range, vibrations cannot propagate further than a few micrometers, but beyond the critical point, as noted, the vibration lifetime is markedly increased and can propagate energy at long distances. Therefore, it is of relevance to determine the time interval (transient time) between the onset of excitation of the modes and the establishment of the steady state after the threshold for the Fröhlich effect: as shown in the last section it is estimated to be of the order of the relaxation time to the bath; if the latter is, as expected, in the tens of picosecond time scale, then the time of the transient is of the order of a few tens of picoseconds. Also, the threshold for Fröhlich effect, as our estimative presented in last section shows, may be attained with the use of the expending of low levels of power, i.e., a exceedingly small fraction of a mol of ATP molecules participating in energy-providing hydrolysis reactions.

The Fröhlich effect is then demonstrated to be present in biopolymers, like a large chain of protein molecules, that can sustain polar vibrations—like those originating in peptide groups. Its occurrence implies that the leading term for the phenomenon to arise—namely the nonlinear terms in Eq. (22)—whose origin was the anharmonic contribution contained in the term  $H_{22}$  of Eq. (2f)—overcomes the opposing effects of relaxation to the thermal bath, arising out of  $H_{11}$  and  $H_{12}$  of Eqs. (2c) and (2d), and the contribution from the anharmonic interaction in  $H_{21}$  of Eq. (2e), which, we recall, has a null contribution in the particular case we used for numerical calculations. We stress that the Fröhlich effect is of purely quantum-mechanical origin, i.e., the Planckian form of the mean populations of the vibrations of the bath and

the zero-point energy of their states: Taking the classical limit in Eq. (6) results in the cancellation of the nonlinear Fröhlich term. Finally, as shown, the phenomenon is dependent on the value of the coupling intensity, i.e., parameter  $\lambda$ , but it may follow even for very small values of it, and then it is possible under very broad circumstances.

It has been suggested as experimental evidence of the phenomenon [7] the investigation of the buildup of the reaction rate of enzyme molecules as a function of the enzyme density. In principle, it can be evidenced by direct observation of the excited vibrations, for example, with the use of scattering effects, since the intensity of the Raman line is proportional to the population of the mode. It should be noticed that Raman scattering allows us to probe only long-wavelength modes, because of the small value of photon wave number in the visible, IR, and UV regions of the spectrum. The nonthermal amplification of polar modes has been determined in several experiments in materials displaying biological activity [27]. Additional possible experimental evidences have been discussed in Refs. [6], [7], [12], [16], and [28].

In conclusion, we can summarize the result by saying that, the Fröhlich effect, which can be related to important biophysical aspects in biopolymers (i) may be of easy realization (it suffices to have even a very weak nonlinear anharmonic coupling strength of the type described, and a weak threshold of pumping power), (ii) is produced very rapidly after the initial release of the pumping (metabolic) energy, and (iii) also, as preliminary calculations seem to indicate [10], once in its domain, signals can be propagated in the medium with almost no decay, and, then, at very long distances (the lifetime of the excitation is very large). Furthermore, it can be shown [10] that the vibrations propagate in a coherent way, and then all the characteristics for the propagation of biochemical energy in this kind of biosystem formally resemble the situation one finds for the case of electromagnetic waves in laser devices.

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