PHYSICAL REVIEW E VOLUME 58, NUMBER 6 DECEMBER 1998

Solitons in highly excited matter: Dissipative-thermodynamic and supersonic effects

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(Received 6 August 1998)

Solitary waves — arising out of nonlinearity-induced coherence of optical and acoustical vibrational modes in dissipative open systems (polymers and bulk matter) — are described in terms of a statistical thermodynamics based on a nonequilibrium ensemble formalism. The undistorted progressive wave is coupled to the normal vibrations, and three relevant phenomena follow in sufficiently away-from-equilibrium conditions: (i) A large increase in the populations of the normal modes lowest in frequency, (ii) accompanied by a large increase of the solitary-wave lifetime, and (iii) emergence of a Cherenkov-like effect, consisting in a large emission of phonons in privileged directions, when the velocity of propagation of the soliton is larger than the group velocity of the normal vibrations. Comparison with experiments is presented, which points out to the corroboration of the theory. [S1063-651X(98)00412-7]

PACS number(s): 63.70.+h, 05.70.Ln, 63.20.Pw, 87.22.−q

I. INTRODUCTION

Solitary waves are a particular kind of excitation in condensed matter, which nowadays are evidenced as ubiquitous and of large relevance in science and technology. Their role as a new concept in applied science was already emphasized by Scott *et al.* in 1973 [1], who discussed the case of several wave systems where the phenomenon may arise. Recently, solitons have been shown to play a very important role in three significant areas: conducting polymers [2,3], fiber optics in communication engineering [4,5], and as conveyors of energy in biological and organic polymers [6–8].

We consider here solitary waves arising out of vibronic modes, both optical and acoustical, when in the presence of external pumping sources driving the open system arbitrarily away from equilibrium. We evidence the possibility of the emergence of a particular complex behavior brought about by the nonlinearities present in the kinetic equations which govern the evolution of the nonequilibrium (dissipative) macroscopic state of the system. For that purpose we resort to the so-called informational statistical thermodynamics (IST for short [9], and see, for example, Refs. [10–14]). IST is based on a particular nonequilibrium ensemble formalism, namely, the nonequilibrium statistical operator method (NESOM; see, for example, Refs. [15–17]), and Zubarev's approach is by far the most concise, soundly based, and a quite practical one [16,17]. Besides providing microscopic foundations to IST, Zubarev's NESOM yields a nonlinear quantum kinetic theory of a large scope [16–22], the one we used to derive the results we report in what follows.

II. FRÖHLICH CONDENSATION AND SCHRÖDINGER-DAVYDOV SOLITON

Let us consider a system which can sustain longitudinal vibrations, optical and acoustical (e.g., polar semiconductors, polymers, and biopolymers, etc.), with, say, a frequency dispersion relation $\omega_{\vec{q}}$; $\vec{q}$ is a wave vector in reciprocal space running over the Brillouin zone. The vibronic system is taken to be in contact with a thermal bath, modeled as a continuum of acousticlike vibrations, with frequency dispersion relation $\Omega_{\vec{p}}=s_B|\vec{p}|$ and a cutoff Debye frequency Ω_D. System and bath interact via an anharmonic potential, and the whole Hamiltonian is taken as

$$H=H_0+H_I=H_{0S}+H_{0B}+H_I, \tag{1}$$

where

$$H_{0S}=\sum_{\vec{q}} \hbar\omega_{\vec{q}}(a^\dagger_{\vec{q}}a_{\vec{q}}+\tfrac{1}{2}), \tag{2a}$$

$$H_{0B}=\sum_{\vec{p}} \hbar\Omega_{\vec{p}}(b^\dagger_{\vec{p}}b_{\vec{p}}+\tfrac{1}{2}), \tag{2b}$$

$$\begin{aligned}H_I=&\sum_{\vec{q}} Z_{\vec{q}}\varphi_{\vec{q}}a^\dagger_{\vec{q}}+\sum_{\vec{q}_1\vec{p}} V^{(1)}_{\vec{q}_1\vec{p}}a_{\vec{q}_1}b_{\vec{p}}b^\dagger_{\vec{q}_1+\vec{p}}\\&+\sum_{\vec{q}_1\vec{p}} V^{(1)}_{\vec{q}_1\vec{p}}a_{\vec{q}_1}b^\dagger_{\vec{p}}b_{-\vec{q}_1+\vec{p}}+\sum_{\vec{q}_1\vec{p}} V^{(1)}_{\vec{q}_1\vec{p}}a_{\vec{q}_1}b_{\vec{p}}b_{-\vec{q}_1-\vec{p}}\\&+\sum_{\vec{q}_1\vec{p}} V^{(1)}_{\vec{q}_1\vec{p}}a_{\vec{q}_1}b^\dagger_{\vec{p}}b^\dagger_{\vec{q}_1-\vec{p}}+\sum_{\vec{q}_1\vec{q}_2} V^{(2)}_{\vec{q}_1\vec{q}_2}a_{\vec{q}_1}a_{\vec{q}_2}b^\dagger_{\vec{q}_1+\vec{q}_2}\\&+\sum_{\vec{q}_1\vec{q}_2} V^{(2)}_{\vec{q}_1\vec{q}_2}a_{\vec{q}_1}a_{\vec{q}_2}b_{-\vec{q}_1-\vec{q}_2}+\sum_{\vec{q}_1\vec{q}_2} V^{(2)}_{\vec{q}_1\vec{q}_2}a^\dagger_{\vec{q}_1}a_{\vec{q}_2}b_{\vec{q}_1-\vec{q}_2}\\&+\sum_{\vec{q}_1\vec{q}_2} V^{(2)}_{\vec{q}_1\vec{q}_2}a_{\vec{q}_1}a^\dagger_{\vec{q}_2}b^\dagger_{\vec{q}_1-\vec{q}_2}+\text{H.c.}\end{aligned} \tag{2c}$$

It consists of the energy of the free system and bath, H_{0S} and H_{0B}, respectively, and in H_I are present the interaction of the system with an external source (a mechanism for excitation which pumps energy on the system), which is the first term on the right, and the anharmonic interaction composed of several contributions, namely those associated with three-particle (phonons) collisions involving one of the sys-

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tem and two of the bath (we call $V^{(1)}_{\vec{q}\vec{q}'}$ the corresponding matrix element) and two of the system and one of the bath (we call $V^{(2)}_{\vec{q}\vec{q}'}$ the associated matrix element). Moreover, $a_{\vec{q}}$ ($a^\dagger_{\vec{q}}$) and $b_{\vec{p}}$ ($b^\dagger_{\vec{p}}$) are, as usual, annihilation (creation) operators of, respectively, normal-mode vibrations in the system and bath and $\varphi_{\vec{q}}$ ($\varphi^\dagger_{\vec{q}}$) of excitations in the source, with $Z_{\vec{q}}$ being the coupling strength (see also Ref. [23]). We recall that the wave vector runs over the system Brillouin zone in the case of the vibronic modes and between the zero and Debye cutoff wave vector in the bath.

Next, following NESOM-based IST, we need to define the thermodynamic space for the description of the nonequilibrium macroscopic state of the system, in other words the set of basic variables relevant to the problem at hand: They are as follows in the present case. First, we take the number of excitations in each mode, i.e., the operator $\hat{\nu}_{\vec{q}}=a^\dagger_{\vec{q}}a_{\vec{q}}$. Second, once the formation of a coherent state of vibronic modes (the solitary wave) is expected, we must introduce the amplitudes $a_{\vec{q}}$ and $a^\dagger_{\vec{q}}$ averaged over the nonequilibrium ensemble. Finally, we take the thermal bath as constantly remaining in equilibrium at a temperature T_0, and then we introduce its Hamiltonian H_{0B} as a basic dynamical variable. Therefore the basic set of chosen microdynamical variables consists of

$$\{\hat{\nu}_{\vec{q}},a_{\vec{q}},a^\dagger_{\vec{q}},H_{0B}\}. \tag{3a}$$

The nonequilibrium statistical operator in NESOM — we recall that we use Zubarev's approach and call it $\varrho_\varepsilon(t)$ — is a superoperator depending on the above-mentioned basic dynamical microvariables, and an associated set of Lagrange multipliers (which constitute the corresponding set of intensive variables in IST, which also completely describes the nonequilibrium macroscopic-thermodynamic state of the system) [10,13–17], which we designate as

$$\{F_{\vec{q}}(t),f_{\vec{q}}(t),f^*_{\vec{q}}(t),\beta_0\}, \tag{3b}$$

and in the first part of Appendix A we describe ϱ_ε.

The set of basic macrovariables is indicated by

$$\{\nu_{\vec{q}}(t),\langle a_{\vec{q}}|t\rangle,\langle a^\dagger_{\vec{q}}|t\rangle,E_B\}, \tag{4}$$

that is,

$$\nu_{\vec{q}}(t)=\mathrm{Tr}\{\hat{\nu}_{\vec{q}}\varrho_\varepsilon(t)\}, \tag{5}$$

$$\langle a_{\vec{q}}|t\rangle=\mathrm{Tr}\{a_{\vec{q}}\varrho_\varepsilon(t)\}, \tag{6}$$

$$E_B=\mathrm{Tr}\{H_{0B}\varrho_\varepsilon(t)\}. \tag{7}$$

Moreover, E_B (the energy of the thermal bath) is time independent as is $\beta_0=(k_BT_0)^{-1}$, because of the assumption that the bath is constantly kept in equilibrium at temperature T_0. Hence, the whole statistical operator is $\varrho_\varepsilon(t)=\tilde{\varrho}_\varepsilon(t)\times\varrho_B$, where now $\tilde{\varrho}_\varepsilon(t)$ is Zubarev's statistical operator of the vibronic system and ϱ_B is the canonical statistical distribution of the free thermal bath at temperature T_0 (which then plays the role of an ideal reservoir).

The equations of evolution for the three basic variables describing the evolution of the vibronic system are derived in the NESOM-based kinetic theory [15–22]. Taking into account that the anharmonic interaction is weak, we restrict the calculation to the Markovian limit, that is, we consider collision integrals only up to second order in the interaction strength [16,19–21]. We briefly describe in the second part of Appendix A the fundamentals of these kinetic equations, particularly the origin of the collision operators that are present on the right-hand side of Eq. (8).

After some lengthy calculation, we find that

$$\frac{d}{dt}\nu_{\vec{q}}(t)=I_{\vec{q}}+\sum_{j=1}^{5}J_{\vec{q}_{(j)}}(t)+\zeta_{\vec{q}}(t), \tag{8}$$

where $I_{\vec{q}}$ represents the rate of production of $\vec{q}$-mode phonons generated by the external pumping source,

$$J_{\vec{q}_{(1)}}(t)+J_{\vec{q}_{(2)}}(t)=-\tau^{-1}_{\vec{q}}[\nu_{\vec{q}}(t)-\nu^{(0)}_{\vec{q}}], \tag{9}$$

with $\nu^{(0)}_{\vec{q}}$ being the $\vec{q}$-mode population in equilibrium, i.e., Planck distribution at temperature T_0, and $\tau_{\vec{q}}$ is a relaxation time given by

$$\tau^{-1}_{\vec{q}}=\frac{4\pi}{\hbar^2}\frac{1}{\nu^{(0)}_{\vec{q}}}\sum_{\vec{p}}|V^{(1)}_{\vec{q}\vec{p}}|^2\nu^B_{\vec{p}}\nu^B_{\vec{q}-\vec{p}}[\delta(\Omega_{\vec{p}}+\Omega_{\vec{q}-\vec{p}}-\omega_{\vec{q}})+2e^{\beta\hbar\Omega_{\vec{p}}}\delta(\Omega_{\vec{p}}-\Omega_{\vec{q}-\vec{p}}+\omega_{\vec{q}})], \tag{10}$$

where $\nu^B_{\vec{p}}$ is the population (Planck distribution) of the phonons in the bath at temperature T_0, and the other terms are

$$J_{\vec{q}_{(3)}}(t)=\frac{8\pi}{\hbar^2}\sum_{\vec{q}'}|V^{(2)}_{\vec{q}\vec{q}'}|^2[\nu^B_{\vec{q}-\vec{q}'}(\nu_{\vec{q}'}-\nu_{\vec{q}})-\nu_{\vec{q}}(1+\nu_{\vec{q}'})]\delta(\Omega_{\vec{q}-\vec{q}'}+\omega_{\vec{q}'}-\omega_{\vec{q}}), \tag{11}$$

$$J_{\vec{q}_{(4)}}(t)=\frac{8\pi}{\hbar^2}\sum_{\vec{q}'}|V^{(2)}_{\vec{q}\vec{q}'}|^2[\nu^B_{\vec{q}-\vec{q}'}(\nu_{\vec{q}'}-\nu_{\vec{q}})+\nu_{\vec{q}'}(1+\nu_{\vec{q}})]\delta(\Omega_{\vec{q}-\vec{q}'}-\omega_{\vec{q}'}+\omega_{\vec{q}}), \tag{12}$$

$$J_{\vec{q}_{(5)}}(t)=\frac{8\pi}{\hbar^2}\sum_{\vec{q}'}|V^{(2)}_{\vec{q}\vec{q}'}|^2[\nu^B_{\vec{q}+\vec{q}'}(1+\nu_{\vec{q}'})-(\nu_{\vec{q}'}-\nu^B_{\vec{q}+\vec{q}'})\nu_{\vec{q}}]\delta(\Omega_{\vec{q}+\vec{q}'}-\omega_{\vec{q}'}-\omega_{\vec{q}}), \tag{13}$$

and, finally, the term $\zeta_{\vec{q}}$ is the one which couples the populations with the amplitudes, namely

$$\zeta_{\vec{q}}(t)=\frac{|\langle a_{\vec{q}}|t\rangle|^2}{\tau_{\vec{q}}}+\frac{8\pi}{\hbar^2}\sum_{\vec{q}'}|V^{(2)}_{\vec{q}\vec{q}'}|^2\{|\langle a_{\vec{q}}|t\rangle|^2(1+\nu_{\vec{q}'}+\nu^B_{\vec{q}-\vec{q}'})-|\langle a_{\vec{q}'}|t\rangle|^2(\nu_{\vec{q}}-\nu^B_{\vec{q}-\vec{q}'})\}\delta(\Omega_{\vec{q}-\vec{q}'}+\omega_{\vec{q}'}-\omega_{\vec{q}})$$
$$-\frac{8\pi}{\hbar^2}\sum_{\vec{q}'}|V^{(2)}_{\vec{q}\vec{q}'}|^2\{|\langle a_{\vec{q}}|t\rangle|^2(\nu_{\vec{q}'}-\nu^B_{\vec{q}-\vec{q}'})-|\langle a_{\vec{q}'}|t\rangle|^2(1+\nu_{\vec{q}}+\nu^B_{\vec{q}-\vec{q}'})\}\delta(\Omega_{\vec{q}-\vec{q}'}-\omega_{\vec{q}'}+\omega_{\vec{q}})$$
$$+\frac{8\pi}{\hbar^2}\sum_{\vec{q}'}|V^{(2)}_{\vec{q}\vec{q}'}|^2\{|\langle a_{\vec{q}}|t\rangle|^2(\nu_{\vec{q}'}-\nu^B_{\vec{q}+\vec{q}'})-|\langle a_{\vec{q}'}|t\rangle|^2(\nu_{\vec{q}}-\nu^B_{\vec{q}+\vec{q}'})\}\delta(\Omega_{\vec{q}+\vec{q}'}-\omega_{\vec{q}'}-\omega_{\vec{q}}). \quad (14)$$

In Eqs. (11)–(14), the presence of Dirac's δ function is evident accounting for energy conservation in the anharmonic-interaction-generated collisional processes; momentum conservation is taken care of in the energy operators of Eq. (2). In the case of acoustical vibrational excitations, the matrix elements of the anharmonic interaction are proportional to the square roots of the three wave numbers involved, typically $K^{(1),(2)}[|\vec{q}||\vec{q}\,'||\vec{q}-\vec{q}\,'|]^{1/2}$, with indexes 1 or 2 in K corresponding to the matrix elements $V^{(1)}$ and $V^{(2)}$, respectively; $K^{(1)}$ can be determined via measurements of bandwidths in scattering experiments and $K^{(2)}$ is left an open parameter.

The equations of evolution for the amplitudes are

$$\frac{\partial}{\partial t}\langle a_{\vec{q}}|t\rangle=-i\tilde{\omega}_{\vec{q}}\langle a_{\vec{q}}|t\rangle-\Gamma_{\vec{q}}\langle a_{\vec{q}}|t\rangle+\Gamma_{\vec{q}}\langle a^\dagger_{\vec{q}}|t\rangle^*-iW_{\vec{q}}\langle a^\dagger_{\vec{q}}|t\rangle^*+\sum_{\vec{q}_1\vec{q}_2}R_{\vec{q}_1\vec{q}_2}\langle a_{\vec{q}_1}|t\rangle\langle a^\dagger_{\vec{q}_2}|t\rangle(\langle a_{\vec{q}-\vec{q}_1+\vec{q}_2}|t\rangle+\langle a^\dagger_{-\vec{q}+\vec{q}_1-\vec{q}_2}|t\rangle), \quad (15)$$

$$\frac{\partial}{\partial t}\langle a^\dagger_{\vec{q}}|t\rangle=\text{the complex conjugate of the right-hand side of Eq. (15)}, \quad (16)$$

where $\tilde{\omega}_{\vec{q}}$ is the frequency renormalized by the anharmonic interaction, with $W_{\vec{q}}$ being a term of renormalization of frequency, and the lengthy expression for $R_{\vec{q}_1\vec{q}_2}$ is given elsewhere [24] (their detailed expressions are not necessary for our purposes here). Finally, $\Gamma_{\vec{q}}(t)$, which has a relevant role in what follows, is the reciprocal of a relaxation time, given by

$$\Gamma_{\vec{q}}(t)=\tau^{-1}_{\vec{q}}(t)+\frac{4\pi}{\hbar^2}\sum_{\vec{q}'}|V^{(2)}_{\vec{q}\vec{q}'}|^2[1+\nu_{\vec{q}'}+\nu^B_{\vec{q}-\vec{q}'}]\delta(\Omega_{\vec{q}-\vec{q}'}+\omega_{\vec{q}'}-\omega_{\vec{q}})-\frac{4\pi}{\hbar^2}\sum_{\vec{q}'}|V^{(2)}_{\vec{q}\vec{q}'}|^2[\nu_{\vec{q}'}-\nu^B_{\vec{q}-\vec{q}'}]\delta(\Omega_{\vec{q}-\vec{q}'}-\omega_{\vec{q}'}+\omega_{\vec{q}})$$
$$+\frac{4\pi}{\hbar^2}\sum_{\vec{q}'}|V^{(2)}_{\vec{q}\vec{q}'}|^2[\nu_{\vec{q}'}-\nu^B_{\vec{q}+\vec{q}'}]\delta(\Omega_{\vec{q}+\vec{q}'}-\omega_{\vec{q}'}-\omega_{\vec{q}}). \quad (17)$$

Equations (15) and (16) are coupled together, and contain linear and trilinear terms. They give rise to two types of solutions: one is a superposition of normal vibrations and the other is of Davydov's soliton type [6,25,26], as we proceed to show. First, we neglect the coupling of the amplitude $\langle a_{\vec{q}}|t\rangle$ and its conjugate, which can be shown to follow when the original Hamiltonian is truncated in the so-called rotating-wave approximation [27], which can be used in this case. Next, we introduce the averaged (over the nonequilibrium ensemble) field operator

$$\psi(x,t)=\sum_q \langle a_{\vec{q}}|t\rangle e^{iqx} \quad (18)$$

for one-dimensional propagation along the x direction (the only one in the case of quasi-one-dimensional polymers or semiconductor quantum wires). At this point we need to define the dispersion relation $\omega_{\vec{q}}$: we may consider two cases, namely, optical and acoustical vibrations. The first case has already been considered [28] in the particular case of acetanilide (in which the CO-stretching polar modes are of the same type as those in biopolymers, e.g., the α-helix protein). It is shown that *Davydov's soliton-type excitation* in the form of an undeformed wave packet consisting of a coherent state of CO stretching (or Amide-I) vibration is present. However, it is damped when propagating in the dissipative medium, a damping dependent on the thermodynamic state of the system, as evidenced in the NESOM-IST calculation. Moreover, a calculation in NESOM-based response function theory has allowed us to derive the infrared absorption spectra [28], characterizing the soliton and obtaining an excellent agreement with the experimental data of Careri *et al.* [29]. For illustration we present in Fig. 1 the infrared spectra in three different conditions, namely at temperatures of 20 K, 50 K, and 80 K.

Let us consider next the case of acoustic vibrations, with a frequency dispersion relation $\omega_{\vec{q}}=s|\vec{q}|$ (s being the velocity of sound in the system). Using this dispersion relation, and proceeding on the ansatz that a well localized and spatially undeformed solitary-wave-type solution is expected,

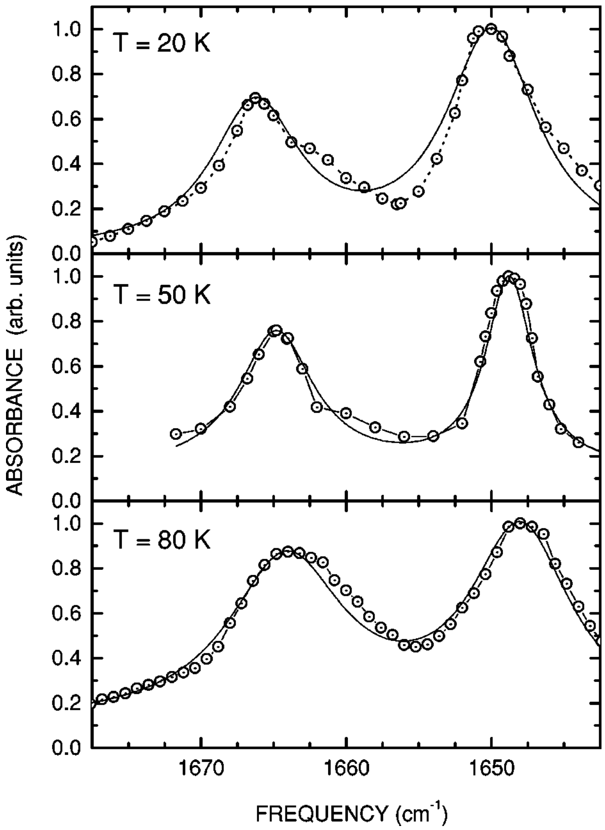

FIG. 1. The infrared absorption spectrum of acetanilide in the frequency range of the CO-stretching mode, showing the normal band and a redshifted one adjudicated to the soliton. After Ref. [28]: the full line is the calculation in NESOM and the dots are experimental points taken from Ref. [29].

using Eqs. (15) and (18), we find (see Appendix B) that the field amplitude satisfies the local (space correlations neglected, as noticed) equation

$$i\hbar \frac{\partial}{\partial t}\psi(x,t)+\frac{\hbar^2}{2M_S}\frac{\partial^2}{\partial x^2}\psi(x,t)+i\hbar\gamma_s\psi(x,t)$$
$$=\hbar G|\psi(x,t)|^2\psi(x,t), \tag{19}$$

which is formally identical to the one for the optical vibrations [28], where $\hbar^2/2M_S=\hbar s w$, with w being the width of the wave packet (see below) and M_S is a pseudomass. This is a nonlinear Schrödinger-type equation with damping [1,30], and where γ_s and G are the values in the local approximation of the transforms of $\Gamma_{\vec{q}}$ of Eq. (17) and $R_{\vec{q}_1\vec{q}_2}$ in Eq. (15) to direct space (see Ref. [28]). Equation (19) for the average field amplitude admits two types of solutions. One is a simple plane wave composed of the superposition of the normal-mode vibrations (corresponding to *first-sound-like waves* associated with the motion of density). The other is a *Schrödinger-Davydov soliton-type excitation*: Let us consider as an initial and boundary condition an impinged signal with a hyperbolic secant shape, which satisfactorily approaches a Gaussian profile. It has an amplitude, say, $\mathcal{A}$, which defines its energy content, and a momentum characterized by a velocity of propagation v. Resorting to the inverse scattering method [31] we obtain that the solution of Eq. (19) is

$$\psi(x,t)=\mathcal{A}\exp\left\{i\left[\frac{M_S v}{\hbar}x-(\omega_s-i\,\gamma_s)t-\frac{\theta}{2}\right]\right\}$$
$$\times\,\mathrm{sech}\left(\mathcal{A}\left[\frac{|G|M_S}{\hbar}\right]^{1/2}(x-vt)\right), \tag{20}$$

where γ_s is the reciprocal lifetime of the excitation. We used $G=|G|e^{i\theta}$ and

$$\omega_s=\frac{|G|\mathcal{A}^2}{2}-\frac{M_S v^2}{4\hbar}, \tag{21}$$

which is an amplitude- and velocity-dependent frequency.

We recall that the amplitude $\mathcal{A}$ and the velocity v are determined by the initial and boundary conditions of excitation determined by the perturbing source (the ''exciting antenna array''). Davydov's soliton of Eq. (20) can be interpreted as being that the vibrational acoustic modes are localized by means of the nonlinear coupling with the external bath; the distortion then reacts — also through anharmonic coupling — to trap the oscillations while keeping the packet undistorted, in a process also referred to as self-trapping [1,7]. Moreover, as noticed, in conditions of excitation in near equilibrium with the bath, the solitary wave is damped, relaxing with a lifetime γ_s^{-1}. However, the situation is substantially modified in sufficiently far-from-equilibrium conditions, i.e., for high values of the pumping intensity $I_{\vec{q}}$ in Eq. (8). In this equation it can be noticed that $J_{\vec{q}(4)}$ and $J_{\vec{q}(5)}$ contain nonlinear contributions in the populations of the modes. These nonlinear contributions have the remarkable characteristic that when $\omega_{\vec{q}}<\omega_{\vec{q}'}$ there follows a net transmission of the energy, received from the external source, from the modes higher in frequency to those lower in frequency, in a cascade-down process: This a consequence of the presence of the nonlinear terms (containing the product $\nu_{\vec{q}}\nu_{\vec{q}'}$) in the collision integrals of Eqs. (11)–(13), which are present in the equation of evolution for the population in mode $\vec{q}$, viz., Eq. (8). For $\omega_{\vec{q}}<\omega_{\vec{q}'}$, the collision integrals of Eqs. (11) and (13) do not contribute, as a consequence of the fact that energy conservation in the collisional events (accounted for the δ functions) cannot be satisfied. Hence, the collision integral of Eq. (12) survives, giving rise to the already mentioned increase of population in mode $\vec{q}$, at the expense of all the other modes $\vec{q}'$ having higher frequencies than $\omega_{\vec{q}}$. For $\omega_{\vec{q}}>\omega_{\vec{q}'}$, only the collisional integral of Eq. (15) survives, implying a transmission of energy from mode q to those with lower frequencies, that is, these nonlinear terms redistribute energy among the modes.

As a consequence, the populations of the modes lowest in frequency (i.e., those around the zone center) are largely increased. Such a phenomenon was predicted by Fröhlich almost 30 years ago [32]. This so-called *Fröhlich effect*, in sufficiently far-from-equilibrium conditions, has a dramatic effect on the propagation of the Davydov soliton described above. With increasing population $\nu_{\vec{q}}$ in the modes lowest in frequency, the lifetime of these modes of vibration, as given

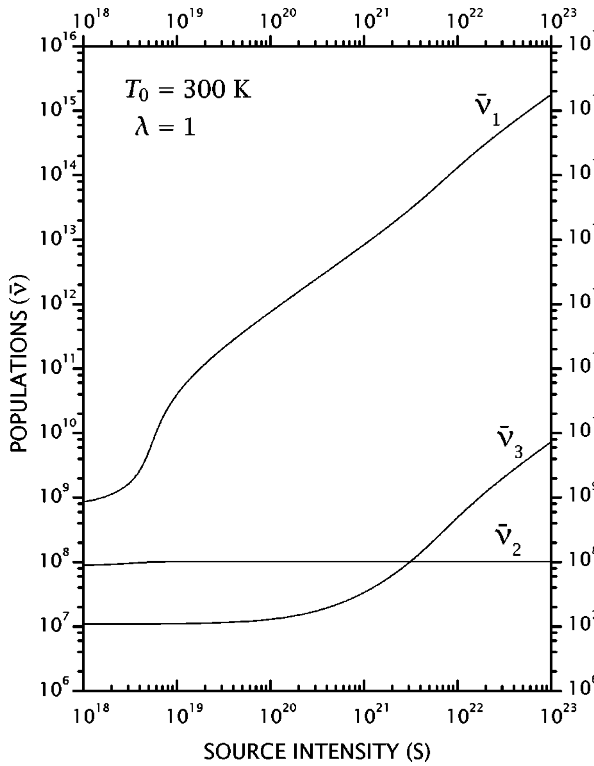

FIG. 2. Populations of the three relevant modes in the set—as described in the main text—with increasing values of the intensity of the external source pumping modes labeled 2 and 3 in the ultrasonic region.

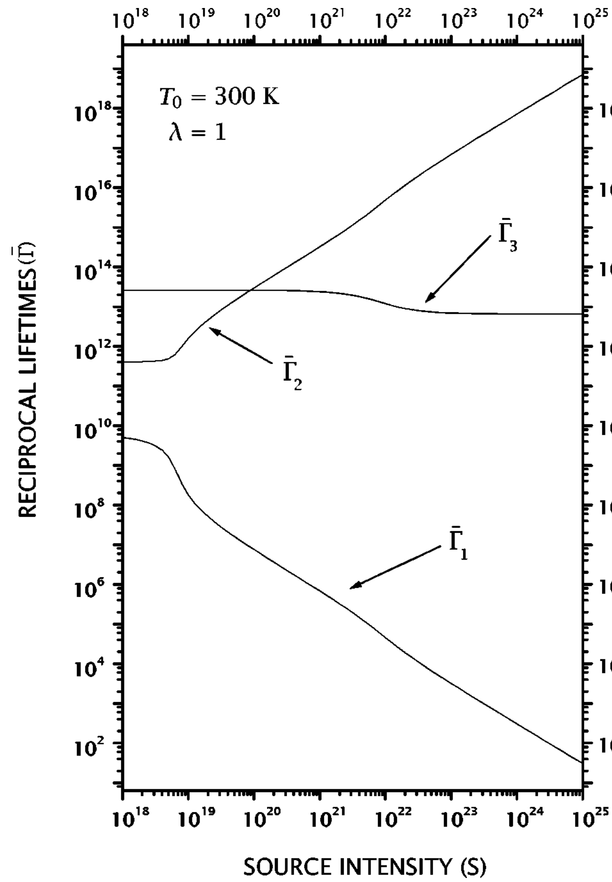

FIG. 3. The reciprocal of the lifetime of the modes whose population is shown in Fig. 2.

by the reciprocal of the $\Gamma_{\vec{q}}$ of Eq. (17), is largely increased. Therefore, in the field amplitude $\psi(x,t)$, as given by Eq. (18), after typically a fraction of a picosecond has elapsed after switch-on of the excitation, the amplitudes $\langle a_{\vec{q}}|t\rangle$ for modes at intermediate to high frequencies in the dispersion relation band die down, but those for the modes lowest in frequency (in the neighborhood of the zone center) survive for long times (their lifetime being larger and larger for increasing values of the pump intensity). We illustrate this point in Figs. 2 and 3: Consider a sample with the soliton traveling in a given direction along the extension L of the sample. Then the permitted vibrational modes are those in the interval of wave numbers $\pi/L \leqslant q \leqslant q_B$, where q_B is the Brillouin zone-end wave number. We take $L=10$ cm and the values for the parameters involved in an order of magnitude for typical polymers and thermal bath, namely $q_B = 3.14\times 10^7$ cm^{-1} (hence the lattice parameter has been taken as $a=10$ Å), $s\simeq 1.8\times 10^5$ cm/s, $s_B\simeq 1.4\times 10^5$ cm/s, $\tau_{\vec{q}}\simeq 10$ ps for all $\vec{q}$, and from the latter we can estimate $K^{(1)}$ in the matrix elements, while we keep as an open parameter the ratio $\lambda=|K^{(2)}|^2/|K^{(1)}|^2$. For these characteristic values it follows that, because of energy and momentum conservation in the scattering events, the set of equations of evolution, Eqs. (8), which in principle couple all modes among themselves, can be grouped into independent sets, each one having nine modes. For example, taking the mode with the lowest wave number π/L, the set to which it belongs contains the modes $\kappa^{n-1}\pi/L$, where $\kappa=(s+s_B)/(s-s_B)=8$ in this case, and $n=2,3,\ldots,9$. Let us call $\nu_1,\ldots,\nu_9$ the corresponding populations, their frequencies being $\omega_1=5.6\times 10^4$ Hz, $\omega_2=4.5\times 10^5$ Hz, $\omega_3=3.6\times 10^6$ Hz, $\omega_4=2.9\times 10^7$ Hz, $\omega_5=2.3\times 10^8$ Hz, $\omega_6=1.8\times 10^9$ Hz, $\omega_7=1.5\times 10^{10}$ Hz, $\omega_8=1.2\times 10^{11}$ Hz, and $\omega_9=9.5\times 10^{11}$ Hz. Moreover, for illustration, the open parameter λ is taken equal to 1, and we consider that only the modes 2 and 3 (in the ultrasonic region) are pumped with the same constant intensity $S=I\bar{\tau}$, where $I_2=I_3=I$, I_1 and I_n with $n=4,\ldots,9$ are null, and $\bar{\tau}$ is a characteristic time used for scaling purposes (as in [22]), here equal to 0.17 s. The large enhancement of the population is evident in the mode lowest in frequency (ν_1), for $S_0\simeq 10^{19}$, at the expense of the two pumped modes ν_2 and ν_3, while the modes ν_4 through ν_9 have minor modifications acquiring populations which are very near that in equilibrium with the thermal bath at temperature T_0; that is, they are practically unaltered. The emergence of the Fröhlich effect is clearly evidenced for this case of acoustical vibrations: In fact, pumping of the modes in a restricted ultrasonic band (in the present case in the interval 4.5×10^5 Hz$\leqslant\omega\leqslant 2.8\times 10^7$ Hz) leads, at sufficiently high intensity of excitation, to the transmission of the pumped energy in these modes to those with lower frequencies ($\omega<\omega_2$), while those with larger frequencies ($\omega>2.8\times 10^7$ Hz) remain at near equilibrium. It may be noticed that for the given value of $\bar{\tau}$, $S=10^{19}$ corresponds to a flux power, provided by the external source in the given interval of ultrasound frequencies being excited, of the order of milliwatts.

The dependence of the lifetime with the level of excitation is illustrated in Fig. 3: A large increase of the lifetime is

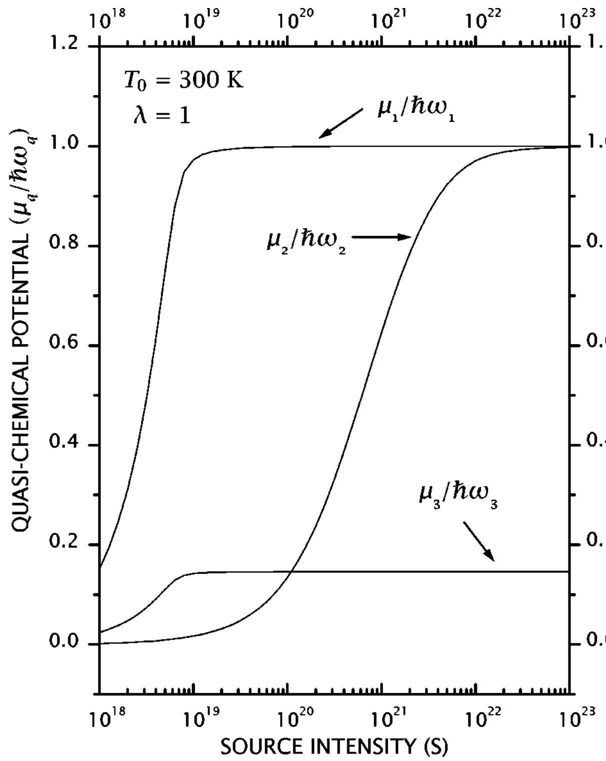

FIG. 4. The quasichemical potential of the modes labeled 1–3 in Fig. 2, with mode 1 corresponding to the one with the lowest frequency in the given set: The emergence of a ''Bose-Einstein-like condensation'' for S approaching a critical value of the order of 10^{19} is evident.

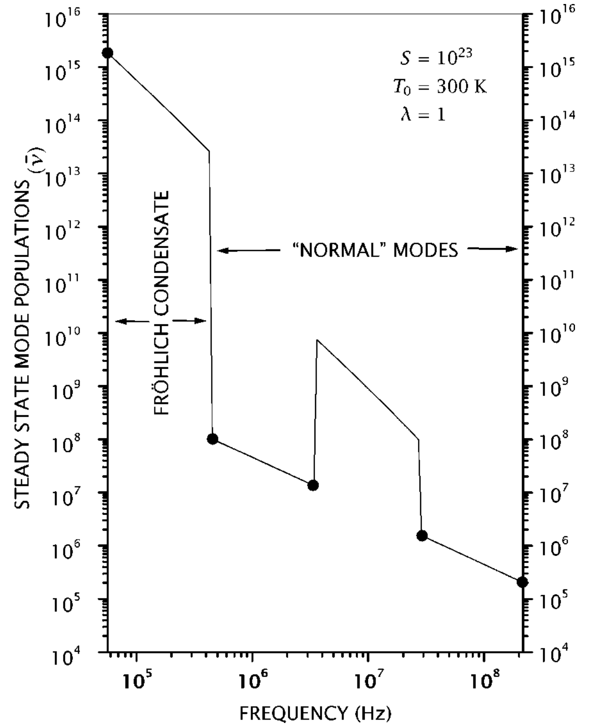

FIG. 5. The population in the steady state for a pumping intensity $S=10^{23}$ of the modes along the spectrum of frequencies of the acoustic modes. Dots indicate the modes in the first set (the remaining part of the spectrum up to the highest Brillouin frequency $\omega_B = 9.5\times 10^{11}$ Hz has been omitted).

shown for the mode lowest in frequency, that is, the reciprocal of the lifetime, Γ_1, largely decreases.

The Fröhlich effect can be evidenced in an alternative way. A straightforward calculation in NESOM leads to the result that, in terms of the intensive nonequilibrium thermodynamic variables of Eq. (3b), the population and the amplitude are given by

$$\nu_{\vec{q}}(t)=[e^{F_{\vec{q}}(t)}-1]^{-1}+|\langle a_{\vec{q}}|t\rangle|^2, \quad (22)$$

$$\langle a_{\vec{q}}|t\rangle=-f_{\vec{q}}(t)^*/F_{\vec{q}}(t). \quad (23)$$

Moreover, the intensive thermodynamic variable $F_{\vec{q}}$ can alternatively be written in either of two forms: One is

$$F_{\vec{q}}(t)=\beta_0(\hbar\omega_{\vec{q}}-\mu_{\vec{q}}(t)), \quad (24)$$

introducing a pseudochemical potential per mode $\mu_{\vec{q}}$, usually referred to as a quasichemical potential, as done by Fröhlich [32] and Landsberg [33] [we recall that $\beta_0 = (k_B T_0)^{-1}$]. The steady-state values of the quasichemical potential of mode populations $\bar{\nu}_j$, with $j=1$, 2, and 3, in Fig. 2 versus the intensity of the external source are shown in Fig. 4, where it is evident that μ_1 approaches ω_1 for $\underline{S}$ of the order of 10^{19}, which results in a near singularity in $\bar{\nu}_1$. (This phenomenon is sometimes referred to as a kind of nonequilibrium ''Bose-Einstein-like condensation'' because of the characteristic of ''piling up''of excitations in the lowest levels of vibronic energy. Also a ''two-fluid-like'' model may be considered in a descriptive way, as, in a sense, shown in Fig. 5.)

Otherwise, it can be written

$$F_{\vec{q}}(t)=\hbar\omega_{\vec{q}}/k_B T^*_{\vec{q}}(t), \quad (25)$$

introducing a nonequilibrium pseudotemperature (or quasitemperature) per mode, as used in the physics of the photoinjected plasma in semiconductors (e.g., [34–36]); its dependence on the intensity of the external source is displayed in Fig. 6.

III. FRÖHLICH-CHERENKOV EFFECT OR *X* WAVES

Moreover, another novel phenomenon may be expected in the out-of-equilibrium nonlinear system we are considering. In both cases of ''optical'' or ''acoustical'' Schrödinger-Davydov solitons that we have described, the amplitude and the velocity of propagation are determined by the initial condition of excitation. Hence, the velocity v can be either smaller or larger than the group velocity of the normal waves. For the polymer acetanilide in the conditions of the experiment of Careri *et al.* [29], v is larger than the group velocity of the phonons of the CO-stretching vibrations [28]. In the case of acoustic vibrations in bulk, we may have $v > s$, leading to the emergence of a kind of Cherenkov-like effect (a so-called superluminal effect in the case of charges moving in a dielectric with a velocity larger than the velocity of light in the medium [37,38]) as we proceed to show. This could be the case in the experiments of Lu and Greenleaf

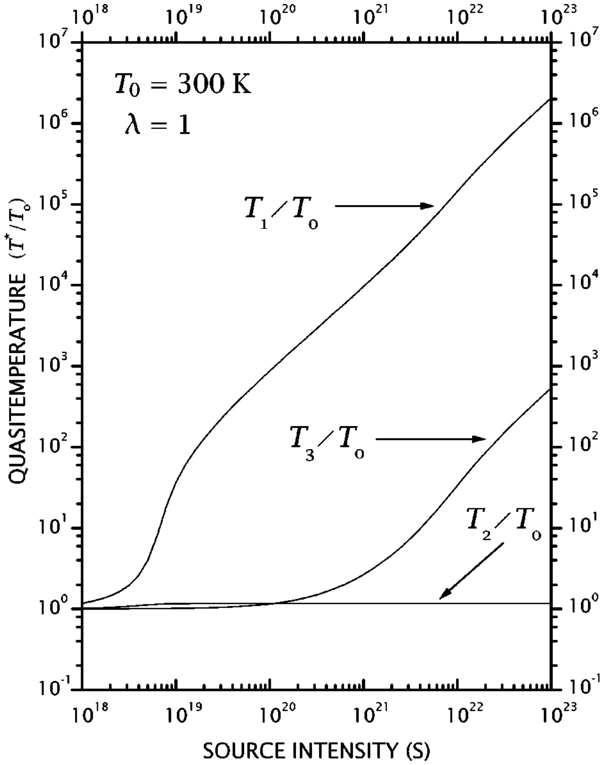

FIG. 6. The quasitemperature, defined in Eq. (25), for the modes in Fig. 2.

[39]; in Fig. 7 we reproduce a related figure [40] showing on the one side the excitation of a normal sound wave, and the other an apparent (in our interpretation) ''superluminal'' solitary wave, more aptly called a *supersonic solitary wave*, accompanied by a Cherenkov-like large emission of phonons, as described next. Such excitation has been dubbed an X wave, and interpreted in terms of an undeformed progressive wave [40,41], created by the particular excitation provided by the pumping transducer.

Consider propagation of a soliton with velocity v $(>s)$ in, say, the x direction in bulk, which introduces a privileged direction in the system. It can be noticed that according to Eq. (8) [cf. also Eq. (22)], the populations of the vibronic modes increase as a result of the direct excitation provided by the source with intensity $I_{\vec q}$ in Eq. (8), with, as previously shown, such pumped energy being concentrated in the modes lowest in frequency (see Figs. 2 and 3), and as a consequence of such a so-called Fröhlich effect, the lifetime of the soliton is largely increased. Moreover, we notice that for the modes in the Fröhlich condensate it can be estimated that $|\langle a_{\vec q}|t\rangle|^2 \simeq w^2\mathcal{A}^2/L^2$, where we recall $\mathcal{A}$ is the amplitude and we have written w for the width of the solitary wave packet. On the other hand, for the preferentially populated modes with small $\vec q$, using Eqs. (22) and (24) it follows that

$$\mu_{\vec q}=\hbar sq\left[1-\frac{k_BT_0}{\hbar sq}\ln\left(1+\frac{1}{\nu_{\vec q}-|\langle a_{\vec q}\rangle|^2}\right)\right]$$

$$=\hbar sq\left[1-\frac{k_BT_0}{\hbar sq}F_{\vec q}\right]=\hbar vq\cos\theta_{\vec q}, \qquad (26)$$

where we have introduced the angle $\theta_{\vec q}$ whose cosinus is

$$\cos\theta_{\vec q}=\frac{s}{v}\left[1-\frac{k_BT_0}{\hbar sq}\ln\left(1+\frac{1}{\nu_{\vec q}-|\langle a_{\vec q}\rangle|^2}\right)\right]$$

$$=\frac{s}{v}\left[1-\frac{T_0}{T^*_{\vec q}}\right]\equiv\frac{s}{vn_{\vec q}}, \qquad (27)$$

after Eq. (25) is used, and $n_{\vec q}$ defines a ''pseudorefraction index'' introduced simply for giving an expression resem-

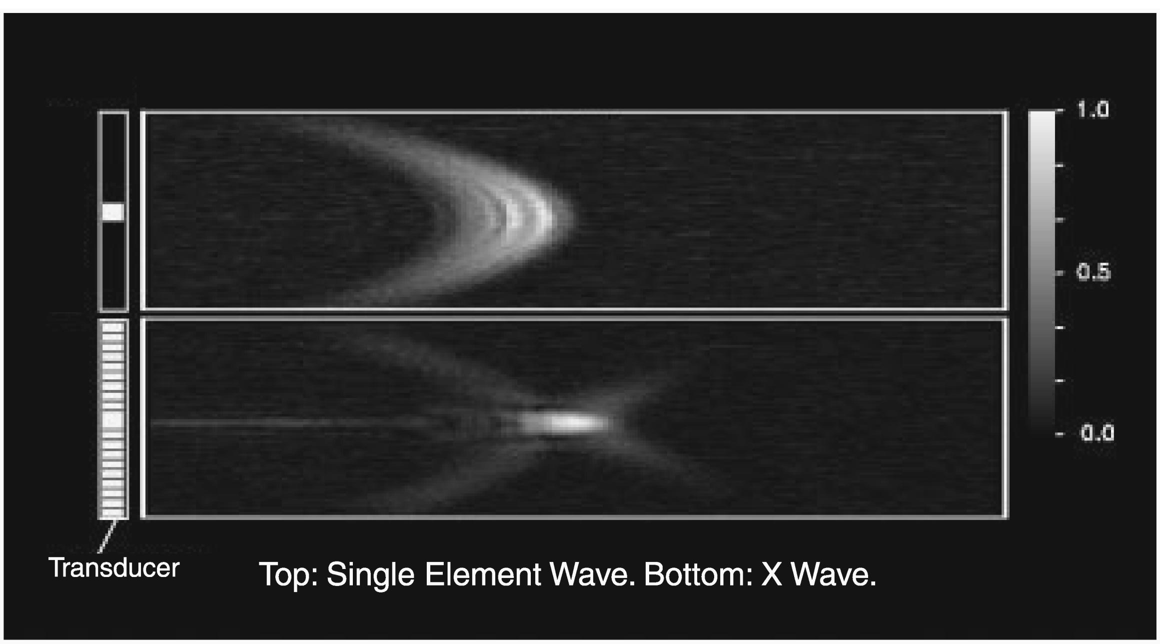

FIG. 7. Excited normal sound wave (upper figure) and the undistorted progressive X wave (lower figure) [40].

bling the case of the Cherenkov effect in radiation theory (when $\nu_{\vec{q}}$ is the Planck distribution of photons) [37,38]. Hence, since

$$\nu_{\vec{q}}=(\exp\{\beta_0\hbar sq[1-(v/s)\cos\theta_{\vec{q}}]\}-1)^{-1}+|\langle a_{\vec{q}}\rangle|^2 \tag{28}$$

(where $|\langle a_{\vec{q}}\rangle|^2\simeq w^2\mathcal{A}/L^2$), then it follows that a large emission of phonons follows when $\cos\theta_{\vec{q}}$ approaches the value s/v, that is, for $T^*_{\vec{q}}$ much larger than T_0 (cf. Fig. 6) and which are emitted in the direction $\vec{q}$ forming an angle $\theta_{\vec{q}}$ with the direction of propagation of the supersonic soliton $(v>s)$. Forward and backward symmetrical propagations are present because modes $\pm\vec{q}$ are equivalent ($\mu_{\vec{q}}$ depends on the modulus of $\vec{q}$). This is a particular characteristic here of what in radiation theory are the normal and anomalous Cherenkov effects in a spatially dispersive medium [38]. As already noticed, the phenomenon, which we call the *Fröhlich-Cherenkov effect*, may provide a microscopic interpretation of the X waves in experiments of ultrasonography [39], shown in the lower part of Fig. 7 [40]. From this figure we roughly estimate that $\theta\simeq 13°$, and then $v/s\simeq 1.02$, that is, the velocity of propagation of the ultrasonic soliton is 2% larger than the velocity of sound in the medium, once we admit an excitation strong enough to imply that $T^*_{\vec{q}}\gg T_0$.

These X waves have been described in terms of a mathematical approach pertaining to the theory of undeformed progressive waves [41,40]. This appears to be a particularly interesting applied mathematical treatment for a practical handling of the phenomenon, for example in engineering for medical imaging [39,41], as another applied mathematical method does for engineering in Refs. [42,43]. The interesting case of medical imaging is treated in detail elsewhere [44], where we use the results presented in this paper.

Summarizing, we have described, resorting to a statistical thermodynamics based on a nonequilibrium ensemble formalism, the solitary waves which arise out of nonlinearity-induced coherence of optical and acoustical vibrations in open systems driven away from equilibrium. The resulting Schrödinger-Davydov soliton is coupled to the normal vibrations, and complex behavior is evidenced in the form of three relevant phenomena, namely (i) a large increase in the populations of the normal modes lowest in frequency (the so-called Fröhlich condensation), (ii) an accompanying large extension of the solitary-wave lifetime (producing a near undamped soliton), and (iii) large emission of phonons in privileged directions when the velocity of propagation of the soliton is larger than the group velocity of the normal vibrations (or Fröhlich-Cherenkov effect).

Finally, we call attention to the fact that, in any material system, mass and thermal motions are coupled together through thermostriction effects (in the case of charged particles is the thermoelectric effect). Thermal motion consists of the so-called second sound propagation, for which we apply all the considerations we have presented here. Also, the case of the zero-sound-like excitation in the double photoinjected plasma in semiconductors (the so-called acoustic plasmons, with the corresponding first-sound-like excitation being the optical plasmons) may be added [45,46]. Similarly, one may consider as candidates for these kinds of phenomena a large variety of normal-mode vibrations in matter, such as, e.g., polaritons, plasmaritons, phonoritons, and all kind of excitonic waves propagating in nonlinear media. A particular case that may eventually prove relevant is the case of the so-called ''excitoner,'' that is, the stimulated amplification of excitons low in energy (dubbed a kind of Bose condensation) and their propagation in the form of a weakly undamped packet [47,48]. It is analyzed on the basis of the statistical thermodynamics as described in [49].

ACKNOWLEDGMENTS

We acknowledge financial support provided to our group, in different forms, by the São Paulo State Research Foundation (FAPESP), the National Research Council (CNPq), the Ministry of Planning (Finep), Unicamp Foundation (FAEP), IBM Brazil, the National Science Foundation (U.S.–Latin American Cooperation, Washington), and the John Simon Guggenheim Memorial Foundation (N.Y.).

APPENDIX A: THE STATISTICAL OPERATOR AND THE EQUATIONS OF EVOLUTION

The nonequilibrium statistical operator in Zubarev's approach (e.g., [15–17]) is

$$\varrho_\varepsilon(t)=\exp\left\{\ln\bar{\varrho}(t,0)-\int_{-\infty}^{t}dt'\,e^{\varepsilon(t'-t)}\frac{d}{dt'}\ln\bar{\varrho}(t',t'-t)\right\}, \tag{A1}$$

where $\bar{\varrho}$ is the auxiliary (sometimes called ''coarse-grained'' or ''instantaneous'' quasiequilibrium) statistical operator, in the present case given by

$$\bar{\varrho}(t,0)=\exp\left\{-\phi(t)-\sum_{\vec{q}}\,[F_{\vec{q}}(t)\hat{\nu}_{\vec{q}}+f_{\vec{q}}(t)a_{\vec{q}}+f^*_{\vec{q}}(t)a^\dagger_{\vec{q}}-\beta_0H_{0B}]\right\}, \tag{A2}$$

where $\phi(t)$ ensures its normalization, and

$$\bar{\varrho}(t',t'-t)=\exp\left\{-\frac{1}{i\hbar}(t'-t)H_S\right\}\bar{\varrho}(t',0)\times\exp\left\{-\frac{1}{i\hbar}(t'-t)H_S\right\} \tag{A3}$$

with H_S being the Hamiltonian of Eq. (1) excluding the interaction with the external source (i.e., the free system Hamiltonian in an interaction representation).

We recall that ε is a positive infinitesimal which goes to zero after the trace operation in the calculation of averages has been performed. Its presence in the exponential introduces a so-called fading memory in the formalism, from which follows irreversible behavior from an initial condition of preparation of the nonequilibrated system [15–17].

The equations of evolution for the basic macrovariables, Eqs. (8), (15), and (16), consist in the averaging over the nonequilibrium ensemble of Heisenberg equations of motion, that is,

$$\frac{\partial}{\partial t}\nu_{\vec{q}}(t)=\mathrm{Tr}\left\{\frac{1}{i\hbar}[\hat{\nu}_{\vec{q}},H]\varrho_{\varepsilon}(t)\right\}, \tag{A4a}$$

$$\frac{\partial}{\partial t}\langle a_{\vec{q}}|t\rangle=\mathrm{Tr}\left\{\frac{1}{i\hbar}[a_{\vec{q}},H]\varrho_{\varepsilon}(t)\right\}, \tag{A4b}$$

$$\frac{\partial}{\partial t}\langle a^{\dagger}_{\vec{q}}|t\rangle=\mathrm{Tr}\left\{\frac{1}{i\hbar}[a^{\dagger}_{\vec{q}},H]\varrho_{\varepsilon}(t)\right\}, \tag{A4c}$$

and $dE_B/dt=0$ because of the assumption that the system of acoustical vibrations remains constantly in equilibrium with an ideal thermal reservoir at fixed temperature T_0.

The right sides of Eqs. (A4a) have a formidable structure of almost unmanageable proportions. But an appropriate way of handling them is provided by the NESOM-based kinetic theory [16–22]. Details are given in these references, where it is shown that in general we can write, for example for Eqs. (A4a) and (A4b),

$$\frac{d}{dt}\nu_{\vec{q}}(t)=\sum_{n=0}^{\infty}\Omega^{(n)}\{\nu_{\vec{q}}(t)|t\}, \tag{A5}$$

$$\frac{d}{dt}\langle a_{\vec{q}}|t\rangle=\sum_{n=0}^{\infty}\Omega^{(n)}\{\langle a_{\vec{q}}|t\rangle|t\}, \tag{A6}$$

where the Ω's for $n\geqslant 2$ are interpreted as collision operators corresponding to scattering by 2,3, . . . particles, n is the order of the interaction strength in H' present in $\Omega^{(n)}$, and memory effects are included.

On the other hand, each one of these collision operators can be rewritten in the form of a series of partial collision operators instantaneous in time, and expressed in the form of correlation functions over the auxiliary ensemble characterized by the coarse-grained operator $\overline{\varrho}(t)$, that is,

$$\Omega^{(n)}\{\nu_{\vec{q}}|t\}=\sum_{m=n}^{\infty}{}_{(n)}J^{(m)}\{\nu_{\vec{q}}|t\}, \tag{A7}$$

and similarly for the case of Eq. (A6) (for details, see [19]). Introducing Eq. (A7) in Eq. (A5), their right-hand sides consist of a double series of partial collision operators. This still involves extremely complicated calculations, which, however, are greatly simplified when the Markovian limit is taken [19,50]. We recall that the Markovian approach consists of retaining only memoryless-binary-like collisions, an approximation valid in the weak coupling limit [50–52], which is maintained in the present case of anharmonic interactions. The corresponding Markov equations retain only the three lowest-order contributions $\Omega^{(0)}$, $\Omega^{(1)}$, and ${}_{(2)}J^{(2)}$ in $\Omega^{(2)}$, which are the right-hand sides of Eqs. (8) and (15). We notice that in the present case, ${}_{(2)}J^{(2)}$ simply reduces to the golden rule of quantum mechanics averaged over the nonequilibrium ensemble.

APPENDIX B: SCHRÖDINGER-DAVYDOV EQUATION, EQ. (19)

In direct space, after the terms that couple the amplitude $\langle a_{\vec{q}}\rangle$ with its conjugate are neglected (which, as noticed in the main text, is accomplished using the rotating-wave approximation), Eq. (15) takes the form

$$i\hbar\frac{\partial}{\partial t}\psi(x,t)=-i\sum_{q}\hbar\omega_{\vec{q}}\int\frac{dx'}{L}e^{iq(x-x')}\psi(x',t)-i\hbar\sum_{\vec{q}}\Gamma_{\vec{q}}\int\frac{dx'}{L}e^{iq(x-x')}\psi(x',t)$$
$$+\sum_{q_1q_2}R_{\vec{q}_1\vec{q}_2}\int\frac{dx'}{L}\int\frac{dx''}{L}e^{iq_1(x-x')}e^{iq_2(x-x'')}\psi(x',t)\psi(x'',t)\psi^{*}(x,t), \tag{B1}$$

where we recall $\omega_{\vec{q}}=sq$. Considering the formation of a highly localized packet (the soliton) centered in point x and with a Gaussian-like profile with a width, say, w (fixed by the initial condition of excitation) extending along a certain large number of lattice parameter a (i.e., $w\gg a$), in Eq. (A1) we make the expansion

$$\psi(x',t)\approx\psi(x,t)-\xi\frac{\partial}{\partial x}\psi(x,t), \tag{B2}$$

where $\xi=x-x'$ is roughly restricted to be smaller or at most of the order of w. The first term on the right-hand side of Eq. (A1) is

$$-i\sum_{q}s|q|\int\frac{dx'}{L}e^{iq(x-x')}\psi(x',t)=-\frac{Ls}{2\pi}\frac{\partial}{\partial x}\int_0^{\pi/a}dq\int_0^{L}\frac{dx'}{L}[e^{iq(x-x')}-e^{-iq(x-x')}]\psi(x',t)$$
$$\approx-\frac{is}{\pi}\frac{\partial}{\partial x}\int_0^{\pi/a}dq\int_{x-w/2}^{x+w/2}d\xi\sin(q\xi)\left[\psi(x,t)-\xi\frac{\partial}{\partial x}\psi(x,t)\right]$$
$$=\frac{is}{\pi}\frac{\partial}{\partial x}\left[\int_{x-(1/2)w}^{x+(1/2)w}\left(1-\cos\frac{\pi}{a}\xi\right)\frac{d\xi}{\xi}\right]\psi(x,t)+\frac{is}{\pi}\left[\int_{x-(1/2)w}^{x+(1/2)w}\left(1-\cos\frac{\pi}{a}\xi\right)\frac{d\xi}{\xi}\right]\frac{\partial}{\partial x}\psi(x,t)$$
$$-\frac{is}{\pi}\left[\int_{x-(1/2)w}^{x+(1/2)w}\left(1-\cos\frac{\pi}{a}\xi\right)d\xi\right]\frac{\partial}{\partial x}\psi(x,t)-\frac{is}{\pi}\left[\int_{x-(1/2)w}^{x+(1/2)w}\left(1-\cos\frac{\pi}{a}\xi\right)d\xi\right]\frac{\partial^2}{\partial x^2}\psi(x,t). \tag{B3}$$

But, of the four terms after the last equal sign in Eq. (A3), the second and third are null, because of the ansatz that a soliton would follow, since the derivative at the center of the packet is null. Consider now the last term, which after the integrations are performed becomes

$$-\frac{isw}{\pi}\left(1-\frac{2a}{\pi w}\sin\frac{\pi}{a}\frac{w}{2}\cos\frac{\pi}{a}x\right)\frac{\partial^2}{\partial x^2}\psi(x,t). \tag{B4}$$

But, we notice that the width of the packet is $w \gg a$, and the cosine in Eq. (A4a) has a period $2a$, and then it oscillates many times in w, and with amplitude $(2a/\pi w) \ll 1$, and can be neglected. Similarly, the first term becomes proportional to

$$\frac{is}{\pi}\frac{\psi(x)}{x^2-(w/2)^2}\left\{w\left[1-\cos\left(\frac{\pi x}{a}\right)\cos\left(\frac{\pi w}{2a}\right)\right]-2x\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{\pi w}{2a}\right)\right\}, \tag{B5}$$

where, on the one hand, the oscillatory terms cancel on average, and, on the other hand, the term decays as x^{-2}. Consequently, using these results in Eq. (B1), after introducing the notation $(\hbar sw/\pi) \equiv \hbar^2/(2M_s)$, and the local approximation in the second and third term on the right-hand side of Eq. (B1), we find Eq. (19).

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