

Influence of the fluctuations of polarization in molecular chains

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We analyze the influence of the fluctuations of polarization on the soliton transfer in one-dimensional biexciton molecular chains. Important modifications appear on the model Hamiltonian with different exciton-phonon coupling constants. The parameters of the solitary excitations (length and energy) are calculated. We show that the fluctuations of dipoles will increase the soliton width and its rest energy. Finally, a brief study of the statistical properties (partition function and specific heat) is done. [S1063-651X(97)00710-1]

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I. INTRODUCTION

Theoretical investigations carried out by many authors in the fields of nonlinear physics have shown that localized excitations that are self-consistent combinations of intramolecular excitations and longitudinal deformation may exist in molecular structures. Studies have been made in both one and two dimensions [1–6]. Such excitations are assumed to exist in α -helical protein molecules and other quasi-one-dimensional polymeric structures [3–5,7]. They play a major role in the transfer of energy and/or information and other vital processes [4,5,7]. The above studies did not take into account the interaction between the natural dipole of each molecule and the exciton-induced dipole moment that emerges due to the propagation of the excitation along the chain.

In this paper we analyze the influence of the fluctuations of the polarization on the different components of the Hamiltonian describing the dynamics of the system. We also present changes that these fluctuations might introduce in the parameters of the solitary wave. We consider one-dimensional molecular chains where longitudinal displacements of the molecules from their equilibrium positions are nonlinearly coupled with the intramolecular vibrations (excitons). In real nonlinear molecular chains there exist, in fact, many different types of excitons. Thus it is not appropriate to consider only one type as in the previous works [1,2,6]. We investigate in this paper the case of two exciton evolutions leading to equations of motion that we can solve exactly. In Sec. II we show that fluctuations do not affect the phonon's Hamiltonian, whereas important modifications occur in the exciton and exciton-phonon Hamiltonians. In Sec. III we show that the system admits a soliton solution and we propose a qualitative analysis of the parameters of the soliton. In Sec. IV we calculate the energies, the partition function, and the specific heat of the system under consideration.

II. INFLUENCE OF THE FLUCTUATIONS OF POLARIZATION ON THE MODEL HAMILTONIAN

The model's Hamiltonian of nonlinearly coupled excitons and phonons, investigated by various authors [1,8–10], is composed of three distinct contributions

$$H = H_{\text{ex}} + H_{\text{ph}} + H_{\text{int}}. \quad (2.1)$$

Here the exciton energy is

$$H_{\text{ex}} = \sum_n (J_0 A_n^\dagger A_n + \tilde{J}_0 B_n^\dagger B_n) + \sum_n M_0 (A_n^\dagger A_{n+1} + \text{H.c.}) + \sum_n \tilde{M}_0 (B_n^\dagger B_{n+1} + \text{H.c.}) - 4IA_n^\dagger A_n B_n^\dagger B_n. \quad (2.2)$$

A_n^\dagger (B_n^\dagger) and A_n (B_n) are boson creation and annihilation operators, respectively, for quanta of excitons of the A type (B type) with energy J_0 (\tilde{J}_0) at site n . These operators satisfy the Bose commutation relation. M_0 (\tilde{M}_0) is the energy of the resonant dipole-dipole interaction between the nearest-neighbor intramolecular excitations of the A type (B type) and $I > 0$ is the anharmonicity constant of the intramolecular vibrations. The phonon energy operator is

$$H_{\text{ph}} = \sum_n \left[\frac{P_n^2}{2M} + \frac{M\omega_0^2}{2} (Q_{n+1} - Q_n)^2 \right], \quad (2.3)$$

where ω_0 is the characteristic frequency and Q_n is the displacement operator, with the conjugate momentum operator P_n . Finally, the exciton-phonon interaction energy is given as

$$H_{\text{int}} = -J_1 \sum_n (Q_{n+1} - Q_{n-1}) A_n^\dagger A_n - \tilde{J}_1 (Q_{n+1} - Q_{n-1}) \times B_n^\dagger B_n - M_1 \sum_n (Q_{n+1} - Q_n) (A_n^\dagger A_{n+1} + \text{H.c.}) - \tilde{M}_1 \sum_n (Q_{n+1} - Q_n) (B_n^\dagger B_{n+1} + \text{H.c.}). \quad (2.4)$$

The nonlinear coupling constants $J_1, \tilde{J}_1, M_1, \tilde{M}_1$ arise from modulation of the on-site energy by the molecular displacements.

We are now interested in the energy of the polarization fluctuations of dipoles. When it travels along the chain, the solitary wave generates an electric dipole due to an intramolecular excitation. Then we might introduce an extra contribution to the Hamiltonian (2.1) to describe the coupling between this dipole moment and the intrinsic moment p of each molecule. Let us represent by d (\vec{d}) the dipole that emerges

resulting from the intramolecular excitation of the A type (B type). We assume that the two excitons have their dipole moments approximately directed along the one-dimensional molecular system. The interaction energy between the exciton-induced dipoles d and \tilde{d} at the site n and the dipole p of the molecule at site 1 can take the form

$$H_i = \sum_{n,l} \frac{pdK}{|r_{nl}|^3} A_n^\dagger A_n + \sum_{n,l} \frac{p\tilde{d}\tilde{K}}{|r_{nl}|^3} B_n^\dagger B_n, \quad (2.5)$$

where r_{nl} is the distance between the l th and n th sites and \tilde{K} (\tilde{K}) is the average value of $\cos \theta$ ($\cos \tilde{\theta}$), in which θ ($\tilde{\theta}$) is the angle between the direction of p and d (\tilde{d}).

In the case of only nearest-neighbor interactions the expression of the Hamiltonian H_i is simplified to

$$\begin{aligned} H_i = & 2 \frac{pdK}{a^3} \sum_n A_n^\dagger A_n + 2 \frac{p\tilde{d}\tilde{K}}{a^3} \sum_n B_n^\dagger B_n \\ & - 6 \frac{pdK}{a^4} \sum_n (Q_{n+1} - Q_n) A_n^\dagger A_n - 6 \frac{p\tilde{d}\tilde{K}}{a^4} \\ & \times \sum_n (Q_{n+1} - Q_n) B_n^\dagger B_n, \end{aligned} \quad (2.5')$$

a being the lattice constant. To account for this new interaction Hamiltonian H_i the basic Hamiltonian (2.1) must be replaced by

$$H^{(n)} = H_{\text{ex}}^{(n)} + H_{\text{ph}}^{(n)} + H_{\text{int}}^{(n)}. \quad (2.6)$$

The form of the phonon's Hamiltonian remains the same ($H_{\text{ph}}^{(n)} = H_{\text{ph}}$). But important modifications appear in the expression of the excitons' Hamiltonian and the exciton-phonon Hamiltonian. Indeed, to obtain $H_{\text{ex}}^{(n)}$, the parameters J_0 and \tilde{J}_0 of Eq. (2.2) have been replaced by

$$J_0^{(n)} = J_0 + 2 \frac{pdK}{a^3} \quad (2.7a)$$

and

$$\tilde{J}_0^{(n)} = \tilde{J}_0 + 2 \frac{p\tilde{d}\tilde{K}}{a^3}. \quad (2.7b)$$

As one can see, the energy of an isolated vibrational quantum of the A type (B type) is increased by $2(pdK/a^3)[2(p\tilde{d}\tilde{K}/a^3)]$ by the fluctuation of the dipoles. On the other hand, $H_{\text{int}}^{(n)}$ is obtained by adding to H_{int} the term

$$\begin{aligned} H_{\text{int}}^{\text{add}} = & -6 \frac{pdK}{a^4} \sum_n (Q_{n+1} - Q_n) A_n^\dagger A_n - 6 \frac{p\tilde{d}\tilde{K}}{a^4} \\ & \times \sum_n (Q_{n+1} - Q_n) B_n^\dagger B_n, \end{aligned} \quad (2.8)$$

such that

$$H_{\text{int}}^{(n)} = H_{\text{int}} + H_{\text{int}}^{\text{add}}. \quad (2.9)$$

Let us note in passing that H_{int} contains four terms. The first two terms describe a mixing of exciton and phonon vibrations, the last two terms are higher-order terms that have the effect of changing the propagation of intramolecular excitations as the Q_n amplitudes change. The additional terms are also mixing terms. The Hamiltonian $H_{\text{int}}^{(n)}$ now exhibits two forms of interactions. The first form ($Q_{n+1} - Q_{n-1})A_n^\dagger A_n$ is the one used by Davydov, Eremko, and Sergienko [11] to investigate solitons in α -helical protein molecules. The second form ($Q_{n+1} - Q_n)A_n^\dagger A_n$, which appears due to the fluctuations of the dipoles, has been presented by Scott [12] as more appropriate to describe phonon coupling of the amide-I mode in the α helix because this mode interacts primarily with the adjacent hydrogen bond. Thus new constants of mixing appear for the two types of excitons, i.e., $6(pdK/a^4)$ and $6(p\tilde{d}\tilde{K}/a^4)$, respectively. Therefore, it is clear from the above analysis that the fluctuations of polarization modify the mixing of exciton and phonon vibrations.

The second part of H_{int} preserves its form. We can then conclude that the fluctuations do not affect the direction of the propagation of excitons along the chain as the Q_n amplitudes change.

III. INFLUENCE ON THE PARAMETERS OF THE SOLITARY WAVE

To determine the basic equations governing the system, we introduce the coherent state ansatz

$$|D(t)\rangle = |\Psi(t)\rangle \exp[-S(t)] |0\rangle_{\text{ph}}, \quad (3.1)$$

where

$$|\Psi(t)\rangle = \sum_n [\psi_n(t) A_n^\dagger + \beta_n(t) B_n^\dagger] |0\rangle_{\text{ex}}, \quad (3.2)$$

$$S(t) = \frac{i}{\hbar} \sum_n [u_n(t) P_n - \pi_n(t) Q_n], \quad (3.3)$$

and $|0\rangle_{\text{ex}}$ and $|0\rangle_{\text{ph}}$ are the exciton and phonon vacuums, respectively.

Minimizing the expectation value of the total Hamiltonian within the coherent state yields a set of coupled ordinary differential equations for the classical excitons and phonon wave functions $\psi_n(t)$, $\beta_n(t)$, and $u_n(t)$,

$$\begin{aligned} i\hbar \frac{\partial \psi_n(t)}{\partial t} = & J_0^{(n)} \psi_n + M_0 (\psi_{n+1} + \psi_{n-1}) - J_1 \\ & \times (u_{n+1} - u_{n-1}) \psi_n - M_1 [(u_{n+1} - u_n) \psi_{n+1} \\ & + (u_n - u_{n-1}) \psi_{n-1}] - 4I \beta_n \beta_n^* \psi_n - 6 \frac{pdK}{a^4} \\ & \times (u_{n+1} - u_n) \psi_n, \end{aligned} \quad (3.4)$$

$$\begin{aligned}
i\hbar \frac{\partial \beta_n(t)}{\partial t} &= \tilde{J}_0 \beta_n + \tilde{M}_0 (\beta_{n+1} + \beta_{n-1}) - \tilde{J}_1 (u_{n+1} - u_{n-1}) \beta_n \\
&\quad - \tilde{M}_1 [(u_{n+1} - u_n) \beta_{n+1} + (u_n - u_{n-1}) \beta_{n-1}] \\
&\quad - 4I \psi_n \psi_n^* \beta_n - 6 \frac{p \tilde{d} \tilde{K}}{a^4} (u_{n+1} - u_n) \beta_n, \quad (3.5)
\end{aligned}$$

$$\begin{aligned}
M \frac{\partial^2 u_n(t)}{\partial t^2} &= M \omega_0^2 (u_{n+1} + u_{n-1} - 2u_n) - M_1 [\psi_n^* (\psi_{n+1} \\
&\quad - \psi_{n-1}) + \psi_n (\psi_{n+1}^* - \psi_{n-1}^*)] - \tilde{M}_1 [\beta_n^* (\beta_{n+1} \\
&\quad - \beta_{n-1}) + \beta_n (\beta_{n+1}^* - \beta_{n-1}^*)] - J_1 [|\psi_{n+1}|^2 \\
&\quad - |\psi_{n-1}|^2] - \tilde{J}_1 [|\beta_{n+1}|^2 - |\beta_{n-1}|^2] \\
&\quad - 6 \frac{p d K}{a^4} [|\psi_n|^2 - |\psi_{n-1}|^2] - 6 \frac{p \tilde{d} \tilde{K}}{a^4} \\
&\quad \times [|\beta_n|^2 - |\beta_{n-1}|^2]. \quad (3.6)
\end{aligned}$$

In the continuum approximation, the system of equations (3.4)–(3.6) becomes

$$\begin{aligned}
i\hbar \psi_t &= (J_0^{(n)} + 2M_0) \psi + M_0 a^2 \psi_{xx} \\
&\quad - 2 \left[(M_1 + J_1) a + 3 \frac{p d K}{a^3} \right] u_x \psi - 4I |\beta|^2 \psi, \quad (3.7)
\end{aligned}$$

$$\begin{aligned}
i\hbar \beta_t &= (\tilde{J}_0^{(n)} + 2\tilde{M}_0) \beta + \tilde{M}_0 a^2 \beta_{xx} \\
&\quad - 2 \left[(\tilde{M}_1 + \tilde{J}_1) a + 3 \frac{p \tilde{d} \tilde{K}}{a^3} \right] u_x \beta - 4I |\psi|^2 \beta, \quad (3.8)
\end{aligned}$$

$$\begin{aligned}
M u_{tt} &= M \omega_0^2 u_{xx} - 2 \left[(M_1 + J_1) a + 3 \frac{p d K}{a^3} \right] (|\psi|^2)_x \\
&\quad - 2 \left[(\tilde{M}_1 + \tilde{J}_1) a + 3 \frac{p \tilde{d} \tilde{K}}{a^3} \right] (|\beta|^2)_x. \quad (3.9)
\end{aligned}$$

In Eqs. (3.7)–(3.9), higher nonlinear terms have been neglected.

We are seeking the solution of Eqs. (3.7)–(3.9), which corresponds to propagating waves of constant form,

$$u(x, t) = u(x - vt), \quad |\psi(x, t)|^2 = \mu(x - vt), \quad s = x - vt. \quad (3.10)$$

v is the soliton velocity. In addition, the set of equations (3.7) and (3.8) can be reduced to a system of coupled nonlinear Schrödinger equations

$$\begin{aligned}
i\hbar \psi_t &= (J_0^{(n)} + 2M_0) \psi + M_0 a^2 \psi_{xx} - \frac{4\kappa^2}{M v_0^2 (1-s^2)} \left[|\psi|^2 \right. \\
&\quad \left. + \frac{\alpha}{\kappa^2} |\beta|^2 \right] \psi, \quad (3.11)
\end{aligned}$$

$$\begin{aligned}
i\hbar \beta_t &= (\tilde{J}_0^{(n)} + 2\tilde{M}_0) \beta + \tilde{M}_0 a^2 \beta_{xx} - \frac{4\tilde{\kappa}^2}{M v_0^2 (1-s^2)} \left[|\beta|^2 \right. \\
&\quad \left. + \frac{\alpha}{\tilde{\kappa}^2} |\psi|^2 \right] \beta. \quad (3.12)
\end{aligned}$$

Here

$$\kappa = (M_1 + J_1) a + 3 \frac{p d K}{a^3}, \quad \tilde{\kappa} = (\tilde{M}_1 + \tilde{J}_1) a + 3 \frac{p \tilde{d} \tilde{K}}{a^3} \quad (3.13a)$$

and

$$\alpha = \kappa \tilde{\kappa} + I M v_0^2 (1-s^2), \quad s = \frac{v}{v_0}. \quad (3.13b)$$

The basic equations (3.11) and (3.12) can be derived from Hamilton's canonical equations for Hamiltonian density

$$\begin{aligned}
H_d &= (J_0^{(n)} + 2M_0) |\psi|^2 + (\tilde{J}_0^{(n)} + 2\tilde{M}_0) |\beta|^2 - M_0 a^2 |\psi_x|^2 \\
&\quad - \tilde{M}_0 a^2 |\beta_x|^2 - 4I |\psi|^2 |\beta|^2 - \frac{2}{M v_0^2 (1-s^2)} \\
&\quad \times (\kappa |\psi|^2 + \tilde{\kappa} |\beta|^2)^2. \quad (3.14)
\end{aligned}$$

The above nonlinear cubic equations (3.11) and (3.12) have the soliton solution [13]

$$\psi(x, t) = \psi_0 \operatorname{sech} \left[\frac{x - vt}{\Delta} \right] \exp[i(kx - \omega t)], \quad (3.15)$$

$$\beta(x, t) = \beta_0 \operatorname{sech} \left[\frac{x - vt}{\Delta} \right] \exp[i(\tilde{k}x - \tilde{\omega} t)], \quad (3.16)$$

with

$$k = \frac{\hbar v}{2|M_0|a^2}, \quad \tilde{k} = \frac{\hbar v}{2|\tilde{M}_0|a^2}, \quad (3.17a)$$

$$\hbar \omega = J_0^{(n)} + 2M_0 - \frac{\hbar^2 v^2}{4|M_0|a^2} + \frac{M_0 a^2}{\Delta^2}, \quad (3.17b)$$

$$\hbar \tilde{\omega} = \tilde{J}_0^{(n)} + 2\tilde{M}_0 - \frac{\hbar^2 v^2}{4|\tilde{M}_0|a^2} + \frac{\tilde{M}_0 a^2}{\Delta^2}, \quad (3.17c)$$

$$\Delta = \frac{[M_0 \tilde{\kappa}^2 + \tilde{M}_0 \kappa^2 - (M_0 + \tilde{M}_0) \alpha] a}{I(\alpha + \kappa \tilde{\kappa})}, \quad (3.18a)$$

$$\psi_0^2 = \frac{a}{2\Delta} \frac{\tilde{M}_0 \alpha - M_0 \tilde{\kappa}^2}{(M_0 + \tilde{M}_0) \alpha - M_0 \tilde{\kappa}^2 - \tilde{M}_0 \kappa^2}, \quad (3.18b)$$

$$\beta_0^2 = \frac{a}{2\Delta} \frac{M_0 \alpha - \tilde{M}_0 \kappa^2}{(M_0 + \tilde{M}_0) \alpha - M_0 \tilde{\kappa}^2 - \tilde{M}_0 \kappa^2}. \quad (3.18c)$$

The analysis of Eq. (3.18) shows that the amplitudes and the soliton width are positive provided that

$$IMv_0^2(1-s^2) > (M_0\tilde{\kappa} - \tilde{M}_0\kappa)\tilde{\kappa}/\tilde{M}_0 \quad \text{for } M_0/\kappa > \tilde{M}_0/\tilde{\kappa} \quad (3.19)$$

and

$$IMv_0^2(1-s^2) > (\tilde{M}_0\kappa - M_0\tilde{\kappa})\kappa/M_0 \quad \text{for } M_0/\kappa > \tilde{M}_0/\tilde{\kappa} \quad (3.20)$$

are satisfied.

If we consider α -helix proteins, which are examples of one-dimensional molecular systems, the numerical values usually used in the case of only one type of exciton are [14–16]

$$\begin{aligned} J_0 &= 0.205 \text{ eV}, \quad M_0 = -7.8 \text{ cm}^{-1}, \quad d = 0.3 \text{ D}, \\ p &= 5 \text{ D}, \\ M_1 &= -10^{-12} \text{ N}, \quad J_1 = (-3.4) \times 10^{-11} \text{ N}, \\ a &= 4.5 \text{ \AA}, \\ M &= 114m_p, \quad v_0 = (4.6) \times 10^3 \text{ m/s}, \\ v &= (4.5) \times 10^3 \text{ m/s}. \end{aligned} \quad (3.21)$$

For the matter of calculations, we assume that the parameters concerning the second coordinate B_n differ from those of the first, as indicated in Ref. [10], such that we can set

$$\tilde{\kappa} = \kappa(1 + \varepsilon), \quad (3.22)$$

with $\varepsilon \ll 1$. This latter constraint avoids the hypothesis of important fluctuations between both types of excitons and allows a better cohesion of the system. In this context the expression of Δ takes the form

$$\Delta \cong \frac{a}{I} f(\kappa), \quad (3.23)$$

where

$$f(\kappa) = \frac{(M_0 + \tilde{M}_0)IMv_0^2(1-s^2) - \varepsilon\kappa^2}{2\kappa^2(1 + \varepsilon) + IMv_0^2(1-s^2)}. \quad (3.24)$$

In the absence of fluctuational terms, κ is reduced to

$$\kappa_r = (M_1 + J_1)a. \quad (3.25)$$

From the above numerical values, we obtain $\kappa_r = (-15.75) \times 10^{-21} \text{ N m}$ and $\kappa = (-2.25) \times 10^{-21} \text{ N m}$. Then it is clear that $\kappa_r^2 > \kappa^2$ and $f(\kappa_r) < f(\kappa)$. Consequently, we have $\Delta > \Delta_r$. It follows from Eqs. (3.23) and (3.24) that the fluctuations of polarization lead to an increase of the solitary width Δ . It appears that the expression presented in previous works, without account for these effects, was underestimated.

From Eqs. (3.18b) and (3.18c), one can notice that the amplitudes ψ_0 and β_0 of the soliton are inversely proportional to its width Δ . In the same vein, we can demonstrate that these amplitudes will decrease if the above influences are included in the model of the system. Let us mention in passing that the products $\Delta\psi_0^2$ and $\Delta\beta_0^2$ also increase.

IV. ENERGY CALCULATIONS: PARTITION FUNCTION

The exact expression of the energy per pulse is obtained through the formula [17]

$$E_p = \int_{-(1/2)\lambda}^{(1/2)\lambda} H_d(s) ds. \quad (4.1)$$

The parameter λ is the dimensionless pulse period. For the sech-soliton solution, $\lambda = \infty$. Then we find by substituting H_d by its expression (3.14)

$$\begin{aligned} E_p &= 2[(J_0^{(n)} + 2M_0)\psi_0^2 + (\tilde{J}_0^{(n)} + 2\tilde{M}_0)\beta_0^2] \frac{\Delta}{a} \\ &\quad - \left[M_0\psi_0^2 \left(k^2 + \frac{1}{\Delta^2} \right) a + \tilde{M}_0\beta_0^2 \left(\tilde{k}^2 + \frac{1}{\Delta^2} \right) a \right] \Delta \\ &\quad + \frac{4}{3} \left[\frac{M_0\psi_0^2 a}{\Delta} + \frac{\tilde{M}_0\beta_0^2 a}{\Delta} - \frac{2}{Mv_0^2(1-s^2)} \frac{\Delta}{a} \right. \\ &\quad \left. \times (\kappa\psi_0^2 + \tilde{\kappa}\beta_0^2)^2 - 4I \frac{\Delta}{a} \psi_0^2 \beta_0^2 \right]. \end{aligned} \quad (4.2)$$

There is an increase of each term of Eq. (4.2). According to α -helix parameters, in the second set of square brackets with a minus sign are less important than all the positive contributions. Finally, these fluctuations increase the energy per pulse.

On the other hand, the continuum limit of the Hamiltonian (2.6) leads to the determination of the total energy of the system

$$E = E_0 + \frac{1}{2} m_{\text{sol}} v^2, \quad (4.3)$$

with

$$\begin{aligned} E_0 &= [(J_0^{(n)} + 2M_0)\psi_0^2 + (\tilde{J}_0^{(n)} + 2\tilde{M}_0)\beta_0^2] \frac{\Delta}{a} \\ &\quad + \frac{8(1-3s^2)a^2}{3Mv_0^2(1-s^2)^2} [M_1 + J_1 + \alpha(\tilde{M}_1 + \tilde{J}_1)]^2 \Delta \psi_0^4 \end{aligned} \quad (4.4)$$

and

$$\begin{aligned} m_{\text{sol}} &= \left[\frac{16\psi_0^2 a^2}{3Mv_0^4(1-s^2)^2} [M_1 + J_1 + \alpha(\tilde{M}_1 + \tilde{J}_1)]^2 \right. \\ &\quad \left. - \frac{\hbar^2}{a^2} \left(\frac{\psi_0^2}{M_0} - \frac{\beta_0^2}{\tilde{M}_0} \right) \right] \Delta, \end{aligned} \quad (4.5)$$

where

$$\alpha = \frac{\beta_0^2}{\psi_0^2}. \quad (4.6)$$

Here E_0 is the rest energy of the soliton and m_{sol} is its effective mass. Accounting for the above analysis of Δ , ψ_0^2 , β_0^2 , $\Delta\psi_0^2$, and $\Delta\beta_0^2$, it is straightforward to demonstrate that E_0 and m_{sol} increase in such a situation.

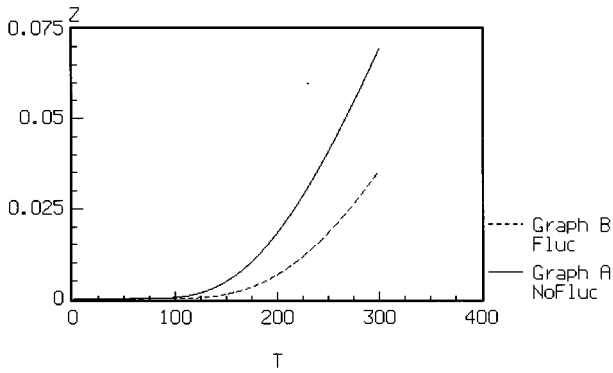


FIG. 1. Plot of the partition function Z versus temperature T (K): the dotted line corresponds to the case where the fluctuations are taken into account and the solid line is obtained in the absence of fluctuations. We have used $K=0.1$, $I=0.01$ eV, and $\varepsilon=0.001$.

We are now interested in the statistical properties of the system. It is worth noting that the solution (3.15) and (3.16) is obtained on the assumption that the length of the molecular chain is infinitely long. On the other hand, it is well known that the thermodynamic influence of solitary waves depends critically on the length of the system [17]. In large systems, such solitons play a relevant role in the evaluation of the partition function. In this case, the partition function Z and the specific heat C are expressed, respectively, as

$$Z = \exp\left(\frac{-E_p}{k_B T}\right), \quad (4.7)$$

and

$$C = k_B T \left(2 \frac{\partial \ln(Z)}{\partial T} + T \frac{\partial^2 \ln(Z)}{\partial T^2} \right). \quad (4.8)$$

E_p is defined in relation (4.2) and k_B is the Boltzmann constant. The calculations yield $C=0$, whatever the case. Therefore, the fluctuations do not modify the specific heat of the system under consideration.

We have plotted the partition function Z as a function of the temperature (Fig. 1). Both pictures have been considered: when the fluctuations of polarization are absent and when they are taken into account. The following results have been obtained: In all the cases the partition function grows as the temperature increases, but it grows very rapidly in the absence of the fluctuations.

V. CONCLUDING REMARKS

Our intention in this paper was to seek evidence for contributions to fluctuations of polarization of the dipoles in a

model of one-dimensional molecular chains. We have introduced two excitonic coordinates and have analyzed the influence of these fluctuations on the model's Hamiltonian and on the parameters of the solitary wave. In order to gain a better understanding of the changes that appear due to these effects, we have calculated the energies, the partition function, and the specific heat. The above investigations show that the results obtained in previous works relevant to molecular chains needed some improvements. Indeed, the soliton width was underestimated, its amplitude was overestimated, the rest energy of the soliton was underestimated, etc., because these fluctuations were ignored.

We conclude with a few remarks concerning the application of our two-excitonic model theory to the transfer of energy and/or information in biomolecular systems. We note that this application should be viewed very cautiously until more complete theoretical studies are available. The possibility of exciton self-trapping phenomenon to biophysics that give rise to the standard Davydov soliton, where only one mode of the exciton has been considered, tends to be very idealized. The inclusion of effects that are present in more realistic biophysical systems, especially various forms of dissipation, fluctuations, lattice discreteness, or several modes of intramolecular vibrations, leads to exciton-phonon problems that differ from the standard Davydov problems.

A very serious open question for the transfer of energy in biomolecular systems is to propose realistic models with lower energy. In the present work, solitons created by the coupling between the exciton of the chain corresponding to simultaneous excitations of two modes of intramolecular vibrations and the longitudinal phonon have higher energy than the standard Davydov's soliton. However, there are several lines of investigation to decrease this energy. (i) The generalized Fulton-Gouterman (FG) transcription and the topological property of the FG equation can be used to establish improved forms of the vibrational wave functions [18]. These solutions are shown to yield lower ground-state energies than the previous Davydov soliton theories [19]. (ii) For the particlelike properties of solitary waves, the stability appears to be a necessary condition. This stability is related to the complete integrability of the corresponding wave equation. The integrability permits an analytical study of the multisoliton interactions. Thus the integrability of the system of two coupled nonlinear Schrödinger equations based on the concept of the degenerative dispersion laws has been established [20] and multisoliton solutions have been obtained by using Hirota's method [21]. Thus one should pay particular attention to the solitonic ground-state energy when such models are applied to biomolecular systems. This question must be left to further investigation.

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