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Classical statistical mechanics of the nonlinearly polarizable shell-model chain for ferroelectric materials

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We study the classical statistical mechanics of a shell-model chain with a quartic electron-ion interaction in one ionic species. In order to avoid long-range interactions generated by the adiabatic treatment of the shells, we assign them a finite mass. Under integration of the harmonic degrees of freedom, the partition function is shown to correspond to an effective ϕ^4 model. This allows us to apply the transfer-integral technique for calculation of the free energy in the displacive limit. For the continuum we obtain exact kinktype solutions of the equations of motion. These excitations, together with phonons which represent oscillations about kink configurations, are considered as interacting quasiparticles for the construction of the free energy, thus reobtaining the exact results in the low-temperature limit. This approach allows the extension of our results to the adiabatic case.

I. INTRODUCTION

Nonperturbative studies of nonlinear interactions in solids, aimed at understanding phenomena near structural phase transitions, have been the subject of a considerable amount of work in the last decade.[1] The purpose is to describe observable effects in a neighborhood of the transition where the phonon basis is no longer valid. A typical feature is the appearance of a peak at zero-frequency transfer, the so-called central peak, in the dynamic response to an external probe such as neutrons or light.

A conventional model studied analytically in this respect consists of a monatomic,[2,3] or diatomic,[4] chain of atoms with nearest-neighbor interactions and an on-site double-well potential of ϕ^4 type acting on one atomic species. This can be considered as a crude representation of a ferroelectric material. Although such a model cannot really display a phase transition at finite temperature, the challenge for these one-dimensional treatments is that essentially exact calculations of the equilibrium statistical mechanics can be interpreted in terms of dynamical excitations of the system.[3–6] The partition function can be evaluated rigorously in one dimension with the aid of transfer-operator techniques.[7] The thermodynamic properties at sufficiently low temperature are exactly reproduced by considering a phenomenological gas of phonons interacting with kinks as elementary excitations. A kink represents a moving wall between domains where the atoms perform collective intrawell oscillations on opposite sides of the local potential barrier. These domains can be thought of as analogs of the fluctuating clusters of the low-temperature phase which appear increasingly larger when approaching T_c in molecular-dynamics simulations of two-dimensional[8] and three-dimensional[9] versions of the same model.

A drawback of this model is that the single-site nature of the double-well potential destroys the lattice translation invariance and implies neglect of the dynamics of some underlying sublattice. This imposes severe restrictions on its predictions about the dynamics of real systems.

On the other hand, the dynamics of oxides and chalcogenides with different structures showing ferroelectric soft modes has been described in the self-consistent phonon approximation by means of a shell model with a quartic core-shell interaction at the anion.[10–16] This corresponds to a nonlinear polarizability of the anion. Such anharmonic coupling treated in the self-consistent phonon approximation accounts for the temperature dependence of the ferroelectric soft mode and related branches of the phonon spectrum. The behavior of these modes has been reproduced by a one-dimensional diatomic version of the model.[16–18] For this version, exact solutions of the nonlinear equations of motion have been found.[19] Also, a monatomic chain of nonlinearly polarizable atoms has been investigated.[20] In this case, the coupling of the self-consistent phonons with exact periodic solutions leads to the softening of an incommensurate mode, as observed in K_2SeO_4.

The purpose of the present work is to develop the classical statistical mechanics of the nonlinearly polarizable chain and to analyze the contributions to the free energy from its dynamical excitations. In Sec. II the free energy is obtained by the transfer-operator method. After introducing the model and discussing the difficulty of treating the potential due to the adiabatic motion of the electronic shells, we consider a finite shell mass. With the purpose of carrying out an analytical treatment, we also discuss the conditions necessary for the application of the continuum approximation. It is further shown that similar results are obtained for the diatomic chain with one nonlinearly polarizable ion.

In Sec. III, phonons and kinks are obtained as small and large amplitude solutions of the equations of motion, respectively, and the kink-phonon interaction is studied. In Sec. IV, we consider the phenomenological approach for the calculation of the free energy based on the role of the kinks, phonons, and their interaction. Finally, in Sec. V, conclusions and a discussion are presented.

II. MODEL AND FREE-ENERGY CALCULATION

We consider the monatomic chain of nonlinearly polarizable atoms with nearest-neighbor interactions (Fig. 1). The potential for the motion of the cores with displacements u_i is given by

$$\Phi[u,v(u)]=\sum_i [\tfrac{1}{2}f'(u_i-u_{i-1})^2 + \tfrac{1}{2}f(v_i-v_{i-1})^2+V(v_i-u_i)] , \tag{2.1}$$

where

$$V(w)=-\tfrac{1}{2}g_2w^2+\tfrac{1}{4}g_4w^4 , \tag{2.2}$$

with positive g_2 and g_4. This represents a double-well interaction potential between cores and shells. v_i, the shell displacement, is determined implicitly by the adiabatic condition

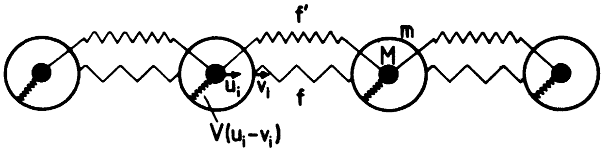

FIG. 1. Monatomic chain of nonlinearly polarizable units with harmonic nearest-neighbor interactions shell-shell f and core-core f', and double-well local core-shell interactions $V(u_i-v_i)$.

$$\frac{\partial\Phi}{\partial v_i}=0=-g_2(v_i-u_i)+g_4(v_i-u_i) +f(2v_i-v_{i+1}-v_{i-1}) . \tag{2.3}$$

This condition determines an effective potential with nonlinear long-range interactions among the u_i. This can be seen by writing the effective potential in terms of the relative displacements $w_i=v_i-u_i$:

$$\Phi_{\text{eff}}(w)=\sum_i \left[-\left[\frac{1}{2}+\frac{f'}{f}\right]g_2w_i^2+\left[\frac{1}{4}+\frac{f'}{f}\right]g_4\right]+\sum_{i,j}\left[\tfrac{1}{2}f'a_{ij}w_iw_j+\tfrac{1}{2}(f+f')\left[\frac{g_2}{f}\right]^2 b_{ij}w_iw_j - \left[1+\frac{f'}{f}\right]\frac{g_2g_4}{f}b_{ij}w_iw_j^3+\tfrac{1}{2}(f+f')\left[\frac{g_4}{f}\right]^2 b_{ij}w_i^3w_j^3\right] , \tag{2.4}$$

where $a_{ij}=2\delta_{ij}-\delta_{ij-1}-\delta_{ij+1}$ is the nearest-neighbor-interaction matrix and b_{ij} is its inverse. As is well known, b_{ij} represents a long-range interaction. Thus, it is useless to undertake an analytic treatment of the partition function for the effective potential (2.4). This difficulty can be overcome by assigning a finite mass m to the shell. The Hamiltonian of the chain becomes

$$H=\sum_i [\tfrac{1}{2}M\dot{u}_i^2+\tfrac{1}{2}m\dot{v}_i^2+\tfrac{1}{2}(f+f')(u_{i+1}-u_i)^2 +f(u_{i+1}-u_i)(w_{i+1}-w_i) +\tfrac{1}{2}f(w_{i+1}-w_i)^2+V(w_i)] . \tag{2.5}$$

Note that v_i will now contribute to the partition function as an independent dynamical variable

$$Z=\frac{1}{\hbar^{2N}}\int d^N\dot{u}\, d^N\dot{v}\, d^Nu\, d^Nw\, e^{-\beta H} . \tag{2.6}$$

For $m\to 0$ this partition function does not tend to the corresponding one of the adiabatic problem. We shall discuss this question later.

The terms of H containing u_i are diagonalized, and their contributions to Z are Gaussian integrals leading to the result

$$Z=Z_{\text{KE}}Z_uZ_w , \tag{2.7}$$

with

$$Z_{\text{KE}}=\left[\frac{2\pi k_BT}{\hbar^2}\sqrt{mM}\right]^N , \tag{2.8}$$

$$Z_u=\left[\frac{2\pi k_BT}{f+f'}\right]^{N/2}\prod_{n=1}^{N-1}\left[4\sin^2\left[\frac{n\pi}{N}\right]\right]^{1/2} , \tag{2.9}$$

$$Z_w=\int_{-\infty}^{+\infty}d^Nw\exp\left[-\beta\sum_{i-1}^{N}\left[\frac{\tilde{f}}{2}(w_i-w_{i-1})^2 +V(w_i)\right]\right] . \tag{2.10}$$

The effective potential for Z_w is formally equivalent to that of the commonly studied ϕ^4-type chain[1] with nearest-neighbor interaction $\tilde{f}=ff'/(f+f')$. Z_w is calculated by the transfer-integral-operator technique.[7,2,3] We consider strong coupling between nearest neighbors relative to the energy barrier of the double well, $\tilde{f}w_0^2 \gg V(w_0)$, where $w_0=\pm(g_2/g_4)^{1/2}$ locates the potential minima. This is the displacive regime where the displacement pattern varies smoothly over a lattice spacing a. In this limit the eigenvalues of the transfer operator satisfy an effective Schrödinger equation. In the thermodynamic limit only the lowest eigenvalue E_0 is significant for the partition function which now becomes

$$Z_w=e^{-\beta E_0} . \tag{2.11}$$

E_0 is the ground state of a particle whose effective mass increases with $T\rightarrow 0$ in a double-well potential. At low temperatures the semiclassical WKB approximation can be used, and so two contributions are found for E_0. One corresponds to the oscillations in each well, and the other to tunneling between the two wells. The free-energy density, relative to the lowest energy where $w=w_0$, is then[3]

$$f=f_{\text{vib}}+f_{\text{tun}} \tag{2.12}$$

with

$$f_{\text{vib}}=\frac{k_B T}{a}\left\{\ln\left[\left[\frac{\hbar}{k_B T}\right]^2\left[\frac{ff'}{mM}\right]^{1/2}\right]+\left[\frac{g_2}{2\tilde{f}}\right]^{1/2}\right\} \tag{2.13}$$

and

$$f_{\text{tun}}=-\frac{1}{a}\frac{4g_4 w_0^4}{[\frac{3}{2}\pi\beta E_K(0)]^{1/2}}e^{-\beta E_K(0)} . \tag{2.14}$$

$E_K(0)$ will be interpreted later as the energy of a static kink

$$E_K(0)=\tfrac{2}{3}w_0^2(2\tilde{f}g_2)^{1/2} . \tag{2.15}$$

The diatomic chain, with an additional nonpolarizable ion between those shown in Fig. 1, coupled to them with the same spring f, can be treated in a similar fashion. Since the additional ion interacts harmonically with its neighbors, its coordinates can be readily integrated and the resulting configurational contribution to the partition function becomes of the same form obtained earlier for the monatomic chain, with an effective nearest neighbor shell-shell coupling $f/2$.

III. DYNAMICAL EXCITATIONS

The system admits small-amplitude motions (phonons) which are solutions of the equations of motion linearized about the relative shell-core displacement $w=w_0$. In addition, large-amplitude motions which involve relative shell-core displacements between $+w_0$ and $-w_0$ will be found to exist as stable traveling kinks in the continuum approximation.

A. Small-amplitude excitations

When the equations of motion corresponding to the Hamiltonian (2.5) are linearized about one of the bottoms of the double-well potential $V(w)$, the dispersion relations for the propagation of coherent motion in that bottom are

$$\omega_{\pm}^2(q)=\left[\frac{g_2}{\mu}+\Omega^2\sin^2\left[\frac{qa}{2}\right]\right]\left[1\pm\left[1-\frac{8\sin^2(qa/2)[2\sin^2(qa/2)+g_2/\tilde{f}]ff'/(Mm)}{[\Omega^2\sin^2(qa/2)+g_2/\mu]^2}\right]\right] , \tag{3.1}$$

where $\mu=mM/(m+M)$ and $\Omega^2=2(f/m+f'/M)$. We note the existence of an acoustic branch $\omega_-(q)$ due to the translation invariance of our chain, in contrast with previously treated ϕ^4 chains.

B. Large-amplitude nonlinear solutions

In the continuum limit the Hamiltonian (2.5) becomes

$$H=\int\frac{dx}{a}[\tfrac{1}{2}M\dot{u}^2+\tfrac{1}{2}m\dot{v}^2+\tfrac{1}{2}a^2f'u'^2+\tfrac{1}{2}a^2fv'^2+V(v-u)] . \tag{3.2}$$

The coupled equations of motion for cores and shells are

$$M\ddot{u}-a^2f'u''-\frac{dV}{dw}=0 , \tag{3.3}$$

$$m(\ddot{w}+\ddot{u})-a^2f(w''+u'')+\frac{dV}{dw}=0 . \tag{3.4}$$

The use of the relative coordinate w for the shells allows the decoupling of this system for propagating solutions of form $u(x,t)=u(x-ct)$ and $w(x,t)=w(x-ct)$. If, in addition, kink boundary conditions $w(\pm\infty)=\pm w_0$ and $dw/dx_{x=\pm\infty}=du/dx_{x=\pm\infty}=0$ are imposed, a first quadrature gives

$$\left[\frac{dw}{ds}\right]^2=\frac{2}{g_2\xi^2}V(w) \tag{3.5}$$

and

$$u=\gamma w , \tag{3.6}$$

where

$$\frac{1}{g_2\xi^2}=\frac{M^{-1}}{c_u^2-c^2}+\frac{m^{-1}}{c_v^2-c^2} \tag{3.7}$$

and

$$\gamma=-\left[1+\frac{M}{m}\frac{c_u^2-c^2}{c_v^2-c^2}\right]^{-1} . \tag{3.8}$$

Here we define the characteristic velocities $c_u^2=a^2f'/M$ and $c_v^2=a^2f/m$. The general solution of (3.5) can be formally expressed as an elliptic integral of the first kind.[2] However, for our purposes, we consider the particular solutions of kink form:

$$w_K(x,t)=\pm w_0 \tanh \left[\frac{x-ct}{\sqrt{2}\xi} \right] , \tag{3.9}$$

$$u_K(x,t)=\pm u_0 \tanh \left[\frac{x-ct}{\sqrt{2}\xi} \right] , \tag{3.10}$$

where the core displacement amplitude $u_0=\gamma w_0$ is a velocity-dependent quantity. This is due to the fact that the nonlinear interaction does not act on-site, but depends on the relative core-shell displacement. The kink width is approximately given by $2\sqrt{2}\xi$. The plus sign in the preceding equations corresponds to a kink and the minus sign to an antikink. The strong coupling condition which allowed the continuum limit implies through (3.7) that the static kink width be $\xi_0 \gg a$. Note that the kink velocity c is a parameter-independent arbitrary quantity, with the sole limitation that the second member of (3.7) must be positive.

The energy $E_K(c)$ associated with these kinks is relevant for the interpretation in Sec. IV of the free energy of the chain in terms of its dynamical excitations. In order to obtain $E_K(c)$, the relations (3.5), (3.6), and

$$\int_{-\infty}^{+\infty} \frac{dx}{a} V(w_K)=\frac{\xi}{a} \left[\frac{g_2}{2} \right]^{1/2} \int_{-w_0}^{+w_0} \frac{dw}{\sqrt{V(w)}} \tag{3.11}$$

are used in expression (3.2) of H, with the result

$$E_K(c)= \left[1+\frac{1}{g_2\xi^2}[M\gamma^2+m(1+\gamma)^2]c^2 \right] \frac{1}{2}\frac{\xi}{\xi_0} E_K(0). \tag{3.12}$$

Here we note that the quantity $E_K(0)$, Eq. (2.15), is the static kink energy. Equation (3.12) gives the transformation relation for the kink energy from a rest frame to a moving one with velocity c. For $c_u=c_v$, Eq. (3.12) takes the form of the Lorentz transformation, as also obtained for nonlinear Klein-Gordon models.[3] In the general case $c_u \neq c_v$ the transformations which leave the equations of motion invariant are of a more complicated nature. The existence of kinks with arbitrary velocity c and energy $E_K(c)$ allows the construction of the free energy as a phenomenological gas of these excitations in Sec. IV.

C. Kink-phonon interaction

In order to reproduce accurately the previously calculated free energy by means of a gas phenomenology of kinks and phonons, it is necessary to take into account the effects on the phonons produced by the presence of kinks, as has been thoroughly discussed.[3,6] At low temperatures, $k_B T \ll E_K(0)$, the low kink density enables the interaction of phonons with a single kink at a time to be treated. In addition, we shall work in the kink rest frame since the results are independent of the kink velocity due to the invariance of the equation of motion, as discussed elsewhere.[3]

The treatment is more apparent when we consider the equations of motion (3.3) and (3.4) in matrix notation:

$$\ddot{\boldsymbol{\phi}}-\underline{A}\boldsymbol{\phi}''+\nabla_\phi V(\boldsymbol{\phi})=0 , \tag{3.13}$$

with

$$\boldsymbol{\phi}=\begin{bmatrix} \sqrt{M}\, u \\ \sqrt{m}\, v \end{bmatrix}, \quad \underline{A}=\begin{bmatrix} c_u^2 & 0 \\ 0 & c_v^2 \end{bmatrix} , \tag{3.14}$$

and

$$V(\boldsymbol{\phi}) \equiv V(\phi_1/\sqrt{M}-\phi_2/\sqrt{m}) . \tag{3.15}$$

As a solution for (3.13), we propose a superposition of a phonon $\boldsymbol{\chi}(x,t)$ and a static kink $\boldsymbol{\phi}_K^{(0)}(x)$,

$$\boldsymbol{\phi}(x,t)=\boldsymbol{\phi}_K^{(0)}(x)+\boldsymbol{\chi}(x,t) . \tag{3.16}$$

By placing this in (3.13), linearizing in $\boldsymbol{\chi}(x,t)$, and considering that $\phi_K^{(0)}(x)$ is a static solution of (3.13), the following equation is obtained for $\boldsymbol{\chi}$:

$$\ddot{\boldsymbol{\chi}}-\underline{A}\boldsymbol{\chi}''+\{\nabla_\phi \cdot \nabla_\phi V[\boldsymbol{\phi}_K^{(0)}(x)]\}\boldsymbol{\chi}=0 . \tag{3.17}$$

The time dependence of $\boldsymbol{\chi}$ can be separated by writing

$$\boldsymbol{\chi}(x,t)=\mathbf{G}(x)e^{-i\omega t} , \tag{3.18}$$

which leads to

$$-\underline{A}\mathbf{G}''+\{\nabla_\phi-\nabla_\phi V[\boldsymbol{\phi}_K^{(0)}(x)]\}\mathbf{G}=\omega^2\mathbf{G} . \tag{3.19}$$

This equation represents a generalization for a two-component field of the one obtained in previous treatments of kink-phonon interactions.[3] The discrete spectrum of eigenvalues of (3.19) belongs to phonons trapped by kinks, and the continuum states are free phonons far from kinks with phase shifts originated by the scattering from them. For the eigenvalue $\omega^2=0$ there is a solution which is proportional to $d\phi_K^{(0)}(x)/dx$. This follows easily by differentiation of Eq. (3.13) in the static case. This solution is a Goldstone mode and must necessarily exist because it represents a kink translation which leaves the equations of motion invariant. This translation mode must be distinguished from the phonon $\omega_-(q=0)=0$ which corresponds to a rigid translation of the whole chain. In addition, there may be other bound states whose number N_b is relevant for the calculation of free energy.

The continuum states $\mathbf{G}_q(x)$ behave asymptotically like the continuum limit of the phonons found previously whose dispersion relations are given by (3.1) with $qa \ll 1$. This follows from the fact that, for $x \to \infty$, Eq. (3.19) becomes the equations of motion linearized about one of the bottoms of the double-well potential. The most general asymptotic form of $\mathbf{G}_q(x)$ is

$$\mathbf{G}_q(x \to \infty) \to \sum_\nu \Big(\mathbf{A}_q^\nu e^{i[qx+(1/2)\Delta_\nu(q)]} + \mathbf{B}_q^\nu e^{-i[qx+(1/2)\Delta_\nu(g)]} \Big) , \tag{3.20}$$

where $\Delta_\nu(q)$ is the phase shift of the phonons due to the scattering by the kink. We note that there are two phase shifts, which correspond to the optic and acoustic phonons. The contribution of the kink-phonon interaction to the free-energy density can only be calculated when $\Delta_\nu(q)$

is known. By imposing periodic boundary conditions on a long chain of length L, the change of the phonon density of states at each branch due to the trapping by kinks is as follows:

$$\Delta\rho_\nu(q)=\frac{1}{2\pi}\frac{d\Delta_\nu(q)}{dq} . \tag{3.21}$$

The decrease of the total number of phonons due to the trapping is

$$-N_b=\sum_{\nu=\pm} \mathrm{P}\int dq\,\Delta\rho_\nu(q) . \tag{3.22}$$

Thus, in order to determine $\Delta_\nu(q)$, it is necessary to obtain the exact continuum eigenstates of (3.19). By using the explicit form of $V[\phi_K^{(0)}(x)]$ this equation takes the form

$$-\underline{A}\mathbf{G}''+W(x)\underline{D}\mathbf{G}=\omega^2\mathbf{G} , \tag{3.23}$$

with

$$W(x)=2g_2\left[1-\tfrac{3}{2}\mathrm{sech}^2\frac{x}{\sqrt{2}\xi_0}\right] \tag{3.24}$$

and

$$\underline{D}=\begin{bmatrix} 1/M & -1/\sqrt{mM} \\ -1/\sqrt{mM} & 1/m \end{bmatrix} . \tag{3.25}$$

So as to decouple the system of ordinary differential equations (3.23), we consider the case $c_u=c_v=c_0$. Now, $\underline{A}=c_0^2\underline{I}$ and the diagonalization of $\underline{D}$ leads to

$$c_0^2H_1''=-\omega^2H_1 , \tag{3.26}$$

$$c_0^2H_2''-\frac{1}{\mu}W(x)H_2=\omega^2H_2 , \tag{3.27}$$

where

$$G_1=\sqrt{M}H_1-\sqrt{m}H_2 , \tag{3.28}$$

$$G_2=\sqrt{M}H_1+\sqrt{m}H_2 . \tag{3.29}$$

Equation (3.26) is satisfied by free acoustic phonons with the dispersion relation $\omega_-^2=c_0^2q^2$, which means that these do not interact with kinks.

On the other hand, H_2 behaves asymptotically as optic phonons with the dispersion relation

$$\omega_+^2(q)=\omega_0^2+c_0^2q^2 , \tag{3.30}$$

with $\omega_0^2=2g_2/\mu$. Equation (3.27) has the same form as the one obtained in the study of the kink-phonon interaction in the ϕ^4 chain.[3] It follows that the phase shift of an optic phonon scattered by a kink is

$$\Delta_+(q)=2\pi\,\mathrm{sgn}(q)-2\tan^{-1}\frac{q\xi_0}{\sqrt{2}}-2\tan^{-1}(\sqrt{2}q\xi_0). \tag{3.31}$$

Thus, only the density of states of the optic branch will be affected by the kink-phonon interaction in the case $c_u=c_v$.

IV. IDEAL-GAS PHENOMENOLOGY

As is common practice,[6] we shall construct the free energy of the chain on the basis of an ideal gas of quasiparticles, all of which are finite energy solutions of the equations of motion. This is justified by the fact that the dominant contribution to the classical partition function arise from the classical trajectories of the system. In the preceding picture, the phonons appear formally as Gaussian corrections to the contributions of the external trajectories (kinks, in our case).

The interactions between kinks are negligible at sufficiently low temperature $[k_BT\ll E_K(0)]$ where the kink density is very low. However, in order to obtain accurate agreement with the transfer integral evaluation of the free energy, it has been shown that it is necessary to take into account the change in the phonon free-energy density due to the presence of a kink. When this effect is considered as kink self-energy, the grand partition function can be approximated by

$$\Xi=\Xi_p\Xi_K , \tag{4.1}$$

where Ξ_p is the free-phonon grand partition function and Ξ_K is the one corresponding to a gas of kinks and antikinks.

For the phonons we have

$$\Xi_p=e^{-\beta Lf_p} , \tag{4.2}$$

where L is the length of the chain. The phonon free-energy density f_p in the continuum limit is obtained from the lattice result

$$\begin{aligned} f_p&=\frac{k_BT}{2\pi}\int_{-\pi/a}^{\pi/a}\ln\left[\frac{\hbar\omega_+}{k_BT}\frac{\hbar\omega_-}{k_BT}\right]dq \\ &=\frac{k_BT}{a}\left[\ln\left[\left[\frac{\hbar}{k_BT}\right]^2\left[\frac{ff'}{mM}\right]^{1/2}\right]\right. \\ &\qquad\left.+\tfrac{1}{2}\ln\left\{1+\frac{g_2}{\tilde f}+\left[\left[1+\frac{g_2}{\tilde f}\right]^2-1\right]^{1/2}\right\}\right] . \end{aligned} \tag{4.3}$$

In the strong-coupling regime $g_2/\tilde f\ll 1$, we obtain the result for the continuum which coincides with expression (2.13) for the contribution f_{vib} to the free-energy density calculated using the transfer-integral technique.

We now turn to the kink contribution to the free-energy density. At sufficiently low temperatures, when the kink velocity c is very small compared with the characteristic velocities c_u and c_v, the kink energy becomes

$$E_K(c)\approx\tfrac{1}{2}M_kc^2+E_K(0) , \tag{4.4}$$

where M_K is the kink effective mass:

$$M_K=(\tilde f/a^2)(M/f'^2+m/f^2)E_K(0) . \tag{4.5}$$

The kink free-energy density is $-k_BTn_K$, with the average total kink-number density n_K evaluated by the standard procedure[3] as

$$n_K=\frac{\partial}{\partial\mu}\left[\frac{k_BT}{L}\ln\Xi_K\right]_{\mu=0}$$
$$=\frac{1}{\hbar}(2\pi k_BTM_K)^{1/2}e^{-\beta[E_K(0)+\Sigma_K]}\,, \tag{4.6}$$

where Σ_K is the kink self-energy.

This has two contributions, the first being due to the change Δf in the phonon free-energy density, while the second contribution arises from the localized vibrations $\omega_{b,n}$ of a kink which corresponds to modes of the discrete spectrum other than the Goldstone mode. Thus,

$$\Sigma_K(T)=L\Delta f(T)+k_BT\sum_{n=2}^{N_b}\ln(\beta\hbar\omega_{b,n})\,. \tag{4.7}$$

With the purpose of comparing the kink contribution to the free energy with the previously found f_{tun}, we can write from (4.6)

$$-k_BTn_K=\frac{1}{2\sqrt{3}}\frac{k_BT}{\hbar\tilde{\omega}_0}e^{-\beta\Sigma_K}f_{\text{tun}}\,, \tag{4.8}$$

where

$$\tilde{\omega}_0=\left[\frac{2g_2}{\tilde{M}}\right]^{1/2} \text{ with } \tilde{M}=\frac{Mf^2+mf'^2}{(f+f')^2}\,. \tag{4.9}$$

In the case $c_u=c_v$, $\tilde{M}=\mu$ and $\tilde{\omega}_0$ becomes ω_0. Now there is only one nonvanishing bound state $\omega_{b,2}=(\sqrt{3}/2)\omega_0$, and with the expression of $\Delta f(T)$ corresponding to $\Delta_+(q)$ we obtain

$$\Sigma_K=-k_BT\ln(2\sqrt{3}\beta\hbar\omega_0)\,. \tag{4.10}$$

In this result exact agreement may be observed between the free energy of the phenomenological gas of phonons and kinks, and that determined via the transfer integral. Although the result deals with the specific case of $c_u=c_v$, the development we have used to reach (4.8) makes it highly feasible to believe that the above conclusion is also valid in general. Thus, the notion that phonons and kinks are the dominant excitations at low temperatures is fully confirmed.

V. Discussion and conclusions

We have studied the statistical mechanics of a nonlinearly polarizable shell-model chain that has been used as a simplified version of a lattice dynamical model for ferroelectric materials. By considering a finite shell mass we have shown that the configurational part of the partition function takes essentially the form corresponding to a ϕ^4 model. The system is treated in the displacive limit, where the equations of motion for the continuum admit kink-type solutions. These excitations propagate with arbitrary velocity, their energies being related to the rest energy by a transformation of a more general form than the Lorentz one. These excitations, as well as small-amplitude vibrations around the kink configurations, account exactly for the thermodynamical behavior of the system at low temperatures. The periodic nonlinear solutions which have been found for the discrete chain[19,20] do not survive in the continuum limit. When approaching $T=0$, the kink density falls off exponentially and the most significant excitations for the equilibrium thermodynamics are the phonons. However, it has been shown[2,21] that the kink dynamics which correspond to the precursor clusters are responsible for the appearance of a quasielastic peak in the dynamic response, as experimentally observed.

The dynamic excitations found in this paper show the same properties when the adiabatic condition is imposed over the shells. This is achieved by simply setting $m=0$ in expressions (3.7) and (3.8) of the kink parameters ξ and γ. When the same is performed on the phonons, the optic branch $\omega_+(q)$ in Eq. (3.1) rises to infinity and these phonons cease to contribute to the free energy, while the acoustic branch $\omega_-(q)$ takes the form corresponding to the adiabatic model. Thus, in principle, the phenomenological gas of kinks interacting with phonons allows the free energy of the adiabatic chain to be obtained. When, however, the adiabatic condition $m=0$ is considered for the free energy (2.12)–(2.14) calculated via the transfer integral, it is not clear how to distinguish the contribution which arises from the shells as dynamic variables.

Let us nevertheless remark that the shell mass m should not be neglected when the polarizable unit of the chain actually refers to an atomic cluster, as appears to be the case in the monatomic chain simulation of K_2SeO_4 (Ref. 20), or diatomic chain representation of ABO_3 perovskites.[16,17]

Numerical methods must be applied when extending these studies to discrete cases and higher temperatures. This would enable us to calculate dynamical correlation functions and to make comparisons with dispersion curves obtained experimentally or by self-consistent phonon calculations. It is also of interest to analyze properties in the neighborhood of a true transition, as for example in the crossover from a displacive to an order-disorder regime, which can be studied numerically in two or three dimensions. Molecular-dynamic calculations with this purpose in mind are under way.

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[1] A. D. Bruce, Adv. Phys. **29**, 111 (1980); A. D. Bruce and R. A. Cowley, *ibid.* **29**, 219 (1980).

[2] J. A. Krumhansl and J. R. Schrieffer, Phys. Rev. B **11**, 3535 (1975).

[3] J. F. Currie, J. A. Krumhansl, A. R. Bishop, and S. E. Trullinger, Phys. Rev. B **22**, 477 (1980).

[4] B. I. Henry and J. Oitmaa, Aust. J. Phys. **36**, 339 (1983); **38**, 171 (1985); Solid State Commun. **55**, 587 (1985).

[5] G. F. Mazenko and P. S. Sahni, Phys. Rev. B **18**, 6139 (1978).

[6] A. R. Bishop, J. A. Krumhansl, and S. E. Trullinger, Physica (Amsterdam), **D1**, 1 (1980).

[7] D. J. Scalapino, M. Sears, and R. A. Ferrell, Phys. Rev. B **6**, 3409 (1972).

[8] T. Schneider and E. Stoll, Phys. Rev. B **13**, 1216 (1976).

[9] T. Schneider and E. Stoll, Phys. Rev. B **17**, 1302 (1978).

[10] R Migoni, H. Bilz, and D. Bäuerle, Phys. Rev. Lett. **37**, 1155 (1976); in *Lattice Dynamics,* Proceedings of the International Conference, Paris, 1977, edited by M. Balkanski (Flammarion, Paris, 1978), p. 650.

[11] M. D. Fontana, G. E. Kugel, and C. Carabatos, J. Phys. (Paris) **42**, 66 (1981).

[12] R. Migoni, R. Currat, C. H. Perry, H. Buhay, W. G. Stirling, and J. D. Axe (unpublished).

[13] F. Gervais and W. Kress, Phys. Rev. B **28**, 2962 (1983).

[14] G. E. Kugel, M. D. Fontana, and W. Kress, Phys. Rev. B **35**, 813 (1987).

[15] R. Migoni, D. Khatib, G. E. Kugel, and L. Godefroy (unpublished).

[16] H. Bilz, G. Benedek, and A. Bussmann-Holder, Phys. Rev. B **35**, 4840 (1987).

[17] H. Bilz, A. Bussmann, G. Benedek, H. Büttner, and D. Strauch, Ferroelectrics **25**, 339 (1980).

[18] A. Bussmann-Holder, H. Bilz, and W. Kress, J. Phys. Soc. Jpn. Suppl. A, **49**, 737 (1980).

[19] H. Büttner and H. Bilz, in *Recent Developments in Condensed Matter Physics,* edited by J. T. Devreese (Plenum, New York, 1981), Vol. 1, p. 49.

[20] H. Bilz, H. Büttner, A. Bussmann-Holder, W. Kress, and U. Schröder, Phys. Rev. Lett. **48**, 264 (1982).

[21] P. S. Sahni and G. F. Mazenko, Phys. Rev. B **20**, 4674 (1979).