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Solitons and electroacoustic interactions in ferroelectric crystals. I. Single solitons and domain walls

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This paper is devoted to the study of single solitons and one-wall motion in elastic ferroelectrics in the presence of electromechanical couplings. To that purpose, a rather simple microscopic model is devised for ferroelectric crystals presenting a molecular group (e.g., $NaNO_2$). Continuum nonlinear coupled equations are deduced from this model and are given a Hamiltonian form, allowing for the analytical and numerical study of single ferroelectric solitons coupled to acoustic phenomena. For single solitons it is shown that the whole problem can be recast as a double sine-Gordon equation of which one solution is stable and can be interpreted as the motion of a ferroelectric wall with electromechanical couplings. The remaining mechanical equations then allow one to evaluate the stress field generated by ferroelectric solitons also as the corresponding elastic displacement, since strain compatibility conditions are satisfied in the present case. Numerical graphs illustrate the space-time evolution of a wall and the accompanying stress and displacement fields. Energies involved such as the wall energy, as well as the thickness of a moving wall, can be evaluated on account of electromechanical couplings. An interpretation of all results is finally given in terms of phase-transition phenomena including an incommensurate phase. To that purpose, a Landau-Ginzburg type of approach is formulated in which a Lifshitz invariant and electromechanical couplings are accounted for. The initiation of the ferroelectric phase takes place within the incommensurate phase, locally in the crystal, with the formation of domains and the motion of walls.

I. INTRODUCTION

A. Ferroelectricity, walls, and phase transitions

The purpose of this work is to treat the wave problem in elastic ferroelectrics in the neighborhood of the phase transition by directly introducing parameters which characterize the domain structure of those media. However, the essential property of ferroelectrics of exhibiting one or several phases is not overlooked. Ferroelectric domains are separated by (fictitious) walls which, in the neighborhood of the phase transition or under the action of an electric field, can start to move so as to yield eventually a globally nonvanishing mean polarization within each domain. This is the ferroelectric phase ($T < T_C$, where T_C is the transition or Curie temperature). In contradistinction, the mean polarization vanishes in the paraelectric phase ($T > T_C$), which implies that polarizations in different domains compensate both in magnitude and direction. Therefore, one easily understands that the motion of walls separating domains will obviously cause a change in the polarization of the ferroelectric specimen. This wall motion is related to the appearance of a spontaneous polarization P_s as a function of temperature. However, the relationship between wall motion and phase transition is not so simple and it becomes rapidly complex depending on the nature of the transition. The phase-transition problem is generally approached through statistical thermodynamics (free energy of Landau[1,2]), while the motion of walls and the evolution of domains are geometrical features of the "morphology" of crystals. It follows that the variation in electric polarization at the level of a wall is necessarily connected with a *nonlinear* phenomenon. Except for differing physical interpretations, the motion of domain walls in ferroelectrics can be compared to the motion of Bloch walls in ferromagnets for which the orientation of magnetic spins within the wall evolves by rotating parallel to the plane of the wall to yield an antiparallel arrangement of spins on the two sides of the wall.[3]

From the point of view of dynamics, the propagation of waves in ferroelectrics is strongly altered by phase-transition phenomena. Indeed, in a general manner, ferroelectric and paraelectric phases are associated with different crystal symmetries and, therefore, different speeds of propagation for both acoustic and optic modes. More precisely, in the ferroelectric state, a wave mode—here called *ferroelectric mode*—is associated with the order parameter (e.g., the polarization). Numerous experiments have shown that the cutoff frequency of this mode dramatically decreases as temperature approaches T_C from below.[4] Such a mode is therefore referred to as a *soft* ferroelectric mode; that is, the natural frequency of elementary oscillators associated with the order parameter goes to zero as $T \rightarrow T_C^-$, which, in turn, causes an increase in the amplitude of oscillations. As a consequence, we note that the *dynamical* electric susceptibility presents a discontinuity at T_C. A linear model is inadequate in the neighborhood of the phase transition where parameters should exhibit a marked dependence on temperature. We are thus led to introducing *anharmonicities.* On the other hand, thermodynamical arguments lead one to consider a thermodynamical potential which includes higher-order terms in the order parameter as well as its gradient in order to account for "exchange" between domains (Ginzburg's criterion[5]). Considered as a classical solid crystal, the ferroelectric crystal exhibits mechanical phenomena and provides a substratum for the propagation of acoustic waves. The latter will also depend in some way on the transition phenomenon through a structural change in the medium. In addition, an essential property of deformable ferroelectrics is to exhibit a *strong piezoelectricity* in their ferroelectric phase.[6] This will materialize in a coupling between acoustic and ferroelectric modes. If we are in the ferroelectric phase but far enough from (i.e., below) the phase transition, then a *linear* model is sufficient to place these couplings and the associated mode conversion in evidence.[7,8] However, when temperature T approaches T_C from below, the ferroelectric mode goes to zero and, via the indicated coupling, carries the acoustic mode with it, thus causing a drastic decrease in the velocity of the acoustic mode. Such a phenomenon is experimentally exhibited by means of infrared and Raman spectroscopies and inelastic neutron scattering experiments.[4] Once the transition is reached and overcome, the velocity of the acoustic mode takes a different value from what it was in the ferroelectric phase since the symmetry group is different. Obviously, crystals of interest may not present any piezoelectricity. In this case it is electrostriction or higher-order piezoelectricity which may provide the electromechanical coupling of interest.

For the study of critical phenomena, solid-state physics has placed in evidence an anomaly in the frequency spectrum of the response function $S(q,\omega)$, and this can be interpreted as the origin of the *central peak* in the frequency spectrum in the neighborhood of T_C,[9,12] which is certain-related to the notion of ferroelectric domains. At this level one cannot do without introducing statistical physics, especially in the neighborhood of the phase transition where large fluctuations in domain take place, as if the system hesitated between the "high-temperature" paraelectric phase and the "low-temperature" ferroelectric phase. In reality, we have only locally, within the paraelectric phase, the initiation of the ferroelectric phase with simultaneous creation and annihilation of domains. Similarly, we note that certain ferroelectric crystals present, between a paraelectric phase and a ferroelectric one, an intermediate phase in which there exists a structural distortion. More precisely, considering a one-dimensional monoatomic chain for the sake of illustration, whenever there exists a modulation of the crystal structure, we can write for the equilibrium position of the atom at site n

$$x_n = na + f(q)\exp(inqa) , \tag{1.1}$$

where n is an integer, a is the lattice spacing, and q is the wave-number modulation. It is said that the structure is *incommensurate* if $(qa/2\pi) = a/\lambda = \sigma$ is irrational so that, mathematically, the wavelength of the modulation and the crystal mesh have "no common measure." A phase in which the structure presents this property is called an *incommensurate phase.* This property can be extended to types of distortions other than the structural ones (e.g., helimagnetism in ferromagnets, Bloch electron in an external magnetic field). For instance, in the case of sodium nitrite $NaNO_2$ in which $NO_2{}^-$ is equipped with its own electric dipole and it rotates like a rigid body about crystallographic axes, we have a paraelectric phase I where dipoles are disordered and a ferroelectric phase III where they are ordered.[13,14] However, one does not go directly from I to III as temperature decreases since there is in between these two phases an incommensurate antiferroelectric phase II for which the orientation of dipoles is distributed periodically but with a period which is not commensurate to the crystal mesh. This phase lies in the temperature interval (T_C, T_I) where T_I is the transition temperature between the paraelectric phase and the incommensurate one [in $NaNO_2$, $T_\text{I} \simeq 164\,^\circ\text{C}$, $T_C \simeq 162.8\,^\circ\text{C}$ (Refs. 15 and 16)]. In other terms, regions where the order parameter is almost uniform are separated in the incommensurate phase by narrow transition regions that can be assimilated to solitons (see below). It is customary to introduce one or two components of the order parameter in the expansion of the thermodynamical potential (where anharmonic terms are retained) with intentions of describing an incommensurate phase.[17–19] The very periodic nature of the structural distortion of an incommensurate phase follows from such a description.[20] Furthermore, as one approaches the incommensurate-commensurate phase transition, the solution which describes the distortion degenerates to become a solitary wave for the order parameter (the orientation of dipoles in the case of $NaNO_2$). The term "phasons" is also coined for these solitary waves. In other terms, in approaching the incommensurate-commensurate phase transition, the initiation of the ferroelectric phase takes place within the incommensurate phase, locally in the crystal. Ferroelectric domains are created or annihilated locally. Therefore, motions of walls (solitons) take place which yield an alignment of all polarizations in a privileged direction resulting in the ferroelectric phase.

The above-given physical description corresponds to the microscopic description envisaged in this work; that is, essentially, the case of ferroelectrics in which molecular electric dipoles rotate rigidly and strong anharmonicities lead to the description of incommensurate-commensurate transitions in terms of solitons. The latter can be interpreted as the motion of walls separating ferroelectric domains. In addition, the deformation of the medium is taken into account so that we shall account for the interaction between acoustic modes (phonons) and solitons (phasons). This interaction plays a predominant role in the study.

B. Solitons

The nonlinearities introduced in the present model of ferroelectric crystals lead inevitably to *solitary waves or solitons,*[21] that is, exact propagative solutions of a certain class of nonlinear partial differential equations (e.g., Korteweg—de Vries equation, Schrödinger equation, etc.) in the general form

$$\phi(x,t)=\phi_T(\xi),\ \ \xi=x-ut\ , \tag{1.2}$$

where u is the propagation speed of this "wave" of infinite period. More precisely, a solitary wave is a *localized* wave which transits from an asymptotic value for $\xi\rightarrow-\infty$ to another asymptotic value for $\xi\rightarrow+\infty$ and is essentially localized at ξ.[22] In the present case, these waves can be interpreted as representing the motion of walls that separate ferroelectric domains. The study of these solitons in the present work will require the use of the whole analytical machinery devised in the treatment of such waves. The problem envisaged is more complex than the simple study of the the sine-Gordon equation, for the latter here is perturbed by electromechanical couplings with acoustic phenomena in the ferroelectric crystal. Hence the motion of a wall will, in general, be accompanied by a nonlinear elastic wave. Conversely, if we are close enough to the phase transition, an elastic wave will initiate the motion of a wall, an effect which may accelerate or slow down the transition process depending on the case considered, this being even more marked if the transition if of the incommensurate-commensurate type. Note that electromechanical couplings allow for the generation of a solitary wave in stresses while the medium remains elastically linear.

We concentrate here on the case of a *single soliton* or *one* wall in motion, the interaction between several walls and the interactions of one wall and an acoustic wave being examined in detail in a planned future work. In Sec. II below we give a description of a simple microscopic model of ferroelectric crystals with a molecular group for which $NaNO_2$ provides a prototype. This is simplified maximally by a schematization as a one-dimensional monoatomic chain equipped with microscopic electric dipoles associated with the molecular groups. Despite this overall simplicity, this provides a model which is rich enough to allow for a detailed analysis of nonlinear effects. The equations of motion for the chain are deduced from a Lagrangian density. Continuum nonlinear coupled equations are deduced from this set of discrete equations by considering perturbations whose characteristic length is large as compared to the lattice spacing. The continuum equations are also given a Hamiltonian form, which greatly facilitates the numerical analysis and the obtention of graphs on a computer. Single ferroelectric solitons coupled to acoustic phenomena provide the subject matter of Sec. III. The transverse acoustic mode is generally coupled with the ferroelectric one. It is shown that the problem can first be recast as a *double sine-Gordon equation.* This equation is solved by a now classical technique and two different solutions are obtained with the accompanying "dispersion relations," which involve pseudowave numbers and frequencies. Only one of these two solutions is stable and can be interpreted as the motion of a ferroelectric wall. The remaining mechanical equations then allow one to evaluate the stress field generated by the ferroelectric solitons through electromechanical coupling as also the corresponding elastic displacement, since strain-compatibility conditions are satisfied in the present case. Numerical graphs obtained by computer illustrate in space-time the motion of a wall and the accompanying stress and displacement fields. Finally, energies involved are evaluated, and this allows one (i) to show the influence of electromechanical couplings on the total energy, (ii) to evaluate the wall energy per unit area, and (iii) to evaluate the thickness of the moving wall, including the effect of electromechanical couplings. In the final section an interpretation of all results is given in terms of phase-transition phenomena. There, on the basis of a Landau-Ginzburg type of approach in which electromechanical couplings and a Lifshitz invariant are taken into account and the two components of the electric polarization provide primary order parameters, it is shown that a physical interpretation can be given to the phenomena of soliton-like solutions and of formation of domains in terms of a phase transition that involves an incommensurate phase. Only the case of one ferroelectric wall, hence a single-soliton solution, is considered in the present part. Multiple-soliton solutions which require the use of a more elaborated mathematical machinery are studied in a future work.

II. MODEL AND EQUATIONS

A. Model

The conception of the present model of ferroelectric crystals relies on the crystallographic description of $NaNO_2$. As already mentioned, this crystal possesses a molecular group (cf. Fig. 1). In its ferroelectric phase, its crystalline structure is centered orthorhombic of symmetry group C_{2v}^{20} or $Im2m$. The unit cell has dimensions $a=3.560$ Å, $b=5.563$ Å, and $c=5.384$ Å in the ferroelectric phase.[23] The NO_2^- molecule is considered as a rigid body and, therefore, is subjected to (i) a displacement of its center of mass and (ii) a rigid-body rotation about the center of rotation. These two centers are distinct and separated by a distance of 0.26 Å.[24] However, we should approximate this in making the two centers coincide. The NO_2 molecular group rotates about the $\vec{a}$ axis (small rotation in general) as well as about $\vec{c}$.[25] The electric polarization of the NO_2 group is directed along $\vec{b}$ in the ordered phase and it has a magnitude of the order of 7 μC.[26] The motion of the NO_2^- group relative to the Na^+ ions can be neglected in the first approximation since this relative motion would yield frequencies higher than 10^{13} Hz, while typical frequencies of the NO_2 group in rotation are of the order of 10^9–10^{10} Hz.[27] Therefore, we can reduce the crystal cell to a point equipped with the global mass of the cell at its center of mass of which the translational motion will give rise to acoustic branches. Insofar as the NO_2 molecular group and its motion are concerned, we consider the simple scheme of a "microscopic" electric dipole $\vec{P}_0$ placed at the center of mass of the crystalline cell, and a rotational *inertia I* is associated with the NO_2 group. The simplified monoatomic chain equipped with microscopic dipoles thus obtained is sketched out in Fig. 2. Such a model has already allowed us to study linear waves.[28] Note that if we account for the relative motion of the NO_2^- group and the Na^+ ions, then a *diatomic* chain equipped with dipoles is necessary.[29] Such models also apply to molecular crystals which are not ferroelec-

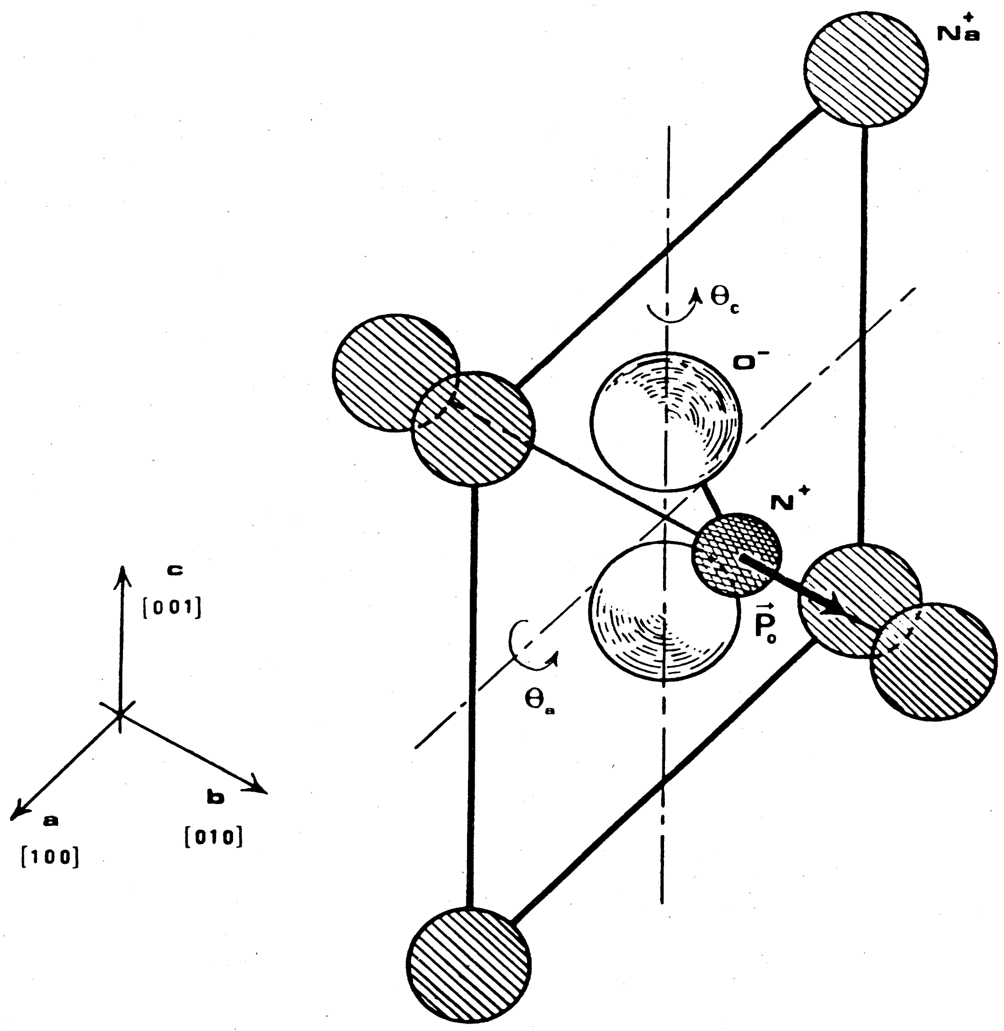

FIG. 1. Crystalline structure of $NaNO_2$. The NO_2^- group is considered as rigid in the case formed by Na^+ ions.

trics [e.g., KNO_3 (Ref. 30), KCN (Refs. 31 and 32), NaCN, NH_4Br, etc.] where, in addition to translational degrees of freedom, one has to account for the rotational degrees of freedom of the molecular group, thus resulting eventually in additional low optical branches (so-called "librons").

Three types of motion can be distinguished in the monoatomic chain of Fig. 2: (i) a longitudinal motion of the lattice points n, (ii) a transverse motion of the same points, and (iii) the rigid-body rotational motion of the electric dipole. The displacement of the lattice point in the plane of the chain is noted $\vec{U}_n=(u_n,v_n)$ or

$$\vec{U}_n=\vec{x}_n-\vec{X}_n=u_n\,\vec{i}+v_n\,\vec{j}\ , \tag{2.1}$$

where $\vec{X}_n$ denotes the equilibrium position, $\vec{x}_n$ being the position of the same point after deformation. In addition, the electric dipole at site n rotates by an angle θ_n from its equilibrium position. The forces acting on a lattice point n result from the interaction with neighboring points

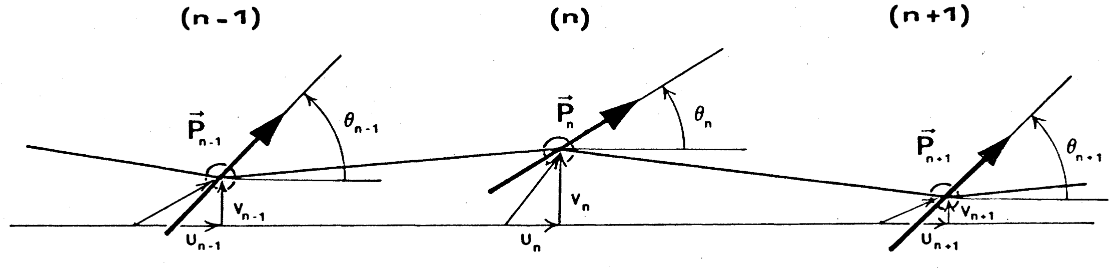

FIG. 2. Monoatomic chain with electric microscopic dipoles.

(short- and long-range interactions). These are modeled by means of a stretching coefficient $k_{\parallel}$ and a flexion coefficient $k_{\perp}$. These two coefficients, for the lack of a finer analysis, represent globally all forces of attraction and repulsion between particles. The energy of deformation of the chain thus reads

$$W_{\text{def}}=\tfrac{1}{2}\sum_n\{k_{\parallel}[(u_{n-1}-u_n)^2+(u_{n+1}-u_n)^2] + k_{\perp}[(v_{n-1}-v_n)^2+(v_{n+1}-v_n)^2]\}\ . \tag{2.2}$$

The existence of an electric dipole at each lattice site leads us to account for the mutual interaction between such dipoles. The interaction energy between two neighboring dipoles is written in the electrostatic form

$$w_{\text{elec}}=-\vec{P}\cdot\vec{E}\ , \tag{2.3}$$

where $\vec{E}$ is the electric field produced by a neighboring dipole at the site of the $\vec{P}$ dipole. The interaction between dipoles is altogether much more complex than the simple expression (2.3) states, since interactions between ions of NO_2 molecular groups is of the Coulombic type (long-range interactions). This yields the electrostatic energy W_{elec} between dipoles. In addition, we have a short-range interaction between molecular groups which is of the Born-Mayer type and account should also be taken of the interaction between Na^+ ions and each $NO_2{}^-$ group. But this could only be achieved correctly in the fully three-dimensional model. In the present simplified model, for two dipoles at sites n and $n-1$ in the chain, the electrostatic interaction energy reads

$$W_n^{n-1}=-\epsilon\left[1-3\left[\frac{u_n-u_{n-1}}{a}\right]+6\left[\frac{u_n-u_{n-1}}{a}\right]^2-\frac{3}{2}\left[\frac{v_n-v_{n-1}}{a}\right]^2\right] \times[3\cos(\theta_n-\theta_{n-1})+(1-\varphi_{n-1}^2)\cos(\theta_n+\theta_{n-1})+2\varphi_{n-1}\sin(\theta_n+\theta_{n-1})]+O(u_n^3,v_n^3)\ , \tag{2.4}$$

where we have set

$$\epsilon=P_0^2/8\pi\epsilon_0 a^3,\quad \varphi_{n-1}=(v_n-v_{n-1})/a\ , \tag{2.5}$$

where ϵ_0 is the vacuum dielectric constant. For the whole chain, accounting for interactions on the left and right of each atom site, by summing over n, we obtain the total electrostatic energy as

$$W_{\text{elec}}=\tfrac{1}{2}\sum_n(W_n^{n-1}+W_{n+1}^n)\ . \tag{2.6}$$

Finally, the kinetic energy of the chain, accounting for translational and rotational motions, is given by

$$T=\tfrac{1}{2}\sum_n[m(\dot{u}_n^2+\dot{v}_n^2)+I\dot{\theta}_n^2]\ , \tag{2.7}$$

where m is the total mass of the crystalline cell, and I is the inertia of the molecular group. The corresponding Lagrangian is

$$\mathcal{L}=T-(W_{\text{def}}+W_{\text{elec}})\ . \tag{2.8}$$

Note that no hypothesis has been made concerning the amplitude of the rotation of dipoles so that θ_n is arbitrary for the moment.

B. Equations of the discrete model

Owing to Eqs. (2.2)—(2.8) and for θ_n of any amplitude, we deduce the following equations of motion:

$$m\ddot{u}_n=\hat{k}_{\parallel}(u_{n+1}+u_{n-1}-2u_n)-\frac{24\epsilon}{a^2}(2u_n-u_{n-1}-u_{n+1})\left[3\sin^2\left[\frac{\theta_n-\theta_{n-1}}{2}\right]+\sin^l\left[\frac{\theta_n+\theta_{n+1}}{2}\right]\right] + \frac{6\epsilon}{a}\sin\left[\frac{\theta_{n+1}-\theta_{n-1}}{2}\right]\left[3\sin\left[\frac{\theta_{n+1}+\theta_{n-1}-2\theta_n}{2}\right]+\sin\left[\frac{\theta_{n+1}+\theta_{n-1}+2\theta_n}{2}\right]\right], \tag{2.9a}$$

$$m\ddot{v}_n=\hat{k}_{\perp}(v_{n+1}+v_{n-1}-2v_n)+\frac{2\epsilon}{a^2}(2v_n-v_{n+1}-v_{n-1})\left[5\sin^2\left[\frac{\theta_n+\theta_{n+1}}{2}\right]+9\sin^2\left[\frac{\theta_n-\theta_{n-1}}{2}\right]\right] -\frac{4\epsilon}{a}\sin\left[\frac{\theta_{n+1}-\theta_{n-1}}{2}\right]\cos\left[\frac{2\theta_n+\theta_{n+1}+\theta_{n-1}}{2}\right], \tag{2.9b}$$

$$
\begin{aligned}
I\ddot{\theta}_n = {} & 2\epsilon\cos\left[\frac{\theta_{n+1}-\theta_{n-1}}{2}\right]\left[3\sin\left[\frac{\theta_{n+1}+\theta_{n-1}-2\theta_n}{2}\right]-\sin\left[\frac{\theta_{n+1}+\theta_{n-1}+2\theta_n}{2}\right]\right] \\
& +\frac{2\epsilon}{a}(v_n-v_{n-1})\cos(\theta_n+\theta_{n-1})+\frac{2\epsilon}{a}(v_{n+1}-v_n)\cos(\theta_{n+1}+\theta_n) \\
& +\frac{3\epsilon}{a}(2u_n-u_{n+1}-u_{n-1})[3\sin(\theta_n-\theta_{n-1})+\sin(\theta_n+\theta_{n+1})]\ , \qquad (2.9c)
\end{aligned}
$$

where we have set

$$\hat{k}_{\parallel}=k_{\parallel}+\frac{48\epsilon}{a^2},\quad \hat{k}_{\perp}=k_{\perp}+\frac{14\epsilon}{a^2}\ . \qquad (2.10)$$

The latter two quantities are spring constants *stiffened* by the presence of electrostatic dipole interactions. The three equations (2.9) are coupled and are relatively involved. An appreciable simplification follows when one assumes that the orientation of dipoles varies slowly over a crystalline spacing. That is,

$$|\theta_n-\theta_{n-1}| \ll 1 \quad \text{for any } n\ ,$$

so that $|\theta_{n+1}+\theta_{n-1}-2\theta_n| \ll 1$ also. On expanding the trigonometric functions present in Eqs. (2.9) with respect to differences of the type $\theta_n-\theta_{n-1}$ and keeping terms of the first order, and then discarding contributions such as $(\epsilon/a^2)\sin\theta_n$ as compared to $\hat{k}_{\parallel}$ or $\hat{k}_{\perp}$, we obtain

$$
\begin{aligned}
m\ddot{u}_n = {} & \hat{k}_{\parallel}(u_{n+1}+u_{n-1}-2u_n) \\
& +\frac{3\epsilon}{a}(\theta_{n+1}-\theta_{n-1})\sin(2\theta_n)\ , \qquad (2.11a)
\end{aligned}
$$

$$
\begin{aligned}
m\ddot{v}_n = {} & \hat{k}_{\perp}(v_{n+1}+v_{n-1}-2v_n) \\
& -\frac{2\epsilon}{a}(\theta_{n+1}-\theta_{n-1})\cos(2\theta_n)\ , \qquad (2.11b)
\end{aligned}
$$

$$
\begin{aligned}
I\ddot{\theta}_n = {} & 2\epsilon(\theta_{n+1}+\theta_{n-1}-2\theta_n)-2\epsilon\sin(2\theta_n) \\
& +\frac{2\epsilon}{a}(v_{n+1}-v_{n-1})\cos(2\theta_n) \\
& -\frac{3\epsilon}{a}(u_{n+1}-u_{n-1})\sin(2\theta_n)\ . \qquad (2.11c)
\end{aligned}
$$

The solution of this discrete form of the equations of motion is much complicated by the presence of couplings (the linear case, however, was solved numerically in Ref. 29). Only the case of simple anharmonic chains is solvable and leads to soliton waves in certain cases (Toda's chains[33]). Here, Eqs. (2.11) are only used as a physical support for the continuum model used therein after.

C. Equations of the continuum model

If we suppose that the crystalline structure is subjected to dynamical processes of which the characteristic length L is large as compared to the lattice spacing, $L \gg a$, then the "point" quantities u_n, v_n, and θ_n can be expanded about n as functions of x. After some manipulations we obtain thus the following system of partial differential equations for the continuum variables (u,v,θ):

$$\rho\ddot{u}=\hat{C}_{\parallel}\frac{\partial^2 u}{\partial x^2}\ , \qquad (2.12a)$$

$$\rho\ddot{v}=\hat{C}_{\perp}\frac{\partial^2 v}{\partial x^2}-\frac{e}{2}\frac{\partial}{\partial x}(\sin 2\theta)\ , \qquad (2.12b)$$

$$J\ddot{\theta}=K\frac{\partial^2\theta}{\partial x^2}+\mathcal{X}\sin(2\theta)+e\frac{\partial v}{\partial x}\cos(2\theta)\ , \qquad (2.12c)$$

where we have set

$$
\begin{aligned}
& \hat{C}_{\parallel}=\hat{k}_{\parallel}/a,\quad \hat{C}_{\perp}=\hat{k}_{\perp}/a,\quad e=4\epsilon/a\ , \\
& K=2\epsilon/a,\quad \mathcal{X}=-2\epsilon/a^3,\quad \rho=m/a^3,\quad J=I/a^3\ . \qquad (2.13)
\end{aligned}
$$

In deducing Eqs. (2.12) we have chosen to neglect the coupling between the longitudinal displacement u and the rotation [in Eq. (2.12a)], primarily for the sake of simplification, but also because of the analogy with the linear case,[34] where only couplings between the transverse displacement v and the rotation θ were shown to be of interest. The various phenomenological densities and coefficients introduced bear the following physical significance. ρ is the mass density of the crystal considered as a continuum, J is an inertia per unit volume, $\hat{C}_{\parallel}$ and $\hat{C}_{\perp}$ are longitudinal and transverse elasticity coefficients, e is an electromechanical coupling coefficient (playing the same role as piezoelectricity in the linear case), and $\mathcal{X}$ is an electric susceptibility.[35] The *linearized* version of Eqs. (2.12) can be compared, on the one hand, to the *linear* equations obtained for the same model (cf. Ref. 28) when studying coupled harmonic waves and, on the other hand, to the one-dimensional version of the governing equations of the so-called elastic *micropolar* media.[36] These equations can also be compared to the equations deduced from a fully continuum approach (Refs. 7 and 8) to elastic ferroelectrics. This is readily achieved by introducing a polarization perturbation p related by $p \simeq P_0\theta$ in the case of small rotations (Ref. 28). However, one must be rather cautious regarding the physical reality of the above-devised model since, clearly, such a model accounts only for what happens *along* the chain. But when dipoles experience sufficiently large rotations, the assumed one-dimensional nature of the medium is broken and interactions with neighboring parallel chains (Ref. 28) should be taken into account. This would greatly complicate the picture and the algebra. We prefer to let the coefficients e, K, and $\mathcal{X}$ rather be unspecified so that a wider class of interactions than those accounted for in the previous paragraphs could be included in these if necessary.

In the case of rotations θ's of small amplitude about the equilibrium orientation $\theta=0$, and making the required expansion of the electrostatic energy up to terms of the order of θ_n^4 and considering only a linear electromechanical coupling, Eqs. (2.12b) and (2.12c) reduce to

$$\rho\ddot{v}=\hat{C}_{\perp}\frac{\partial^2 v}{\partial x^2}-e\frac{\partial\theta}{\partial x}\ , \tag{2.14a}$$

$$J\ddot{\theta}=K\frac{\partial^2\theta}{\partial x^2}+2\chi(\theta-\tfrac{2}{3}\theta^3)+e\frac{\partial v}{\partial x}\ . \tag{2.14b}$$

A nonlinear term in θ^3 remains in the second of these equations. This term is equivalent to considering the rotational motion of electric dipoles in a double-well potential $V(\theta)=E_0(\frac{1}{3}\theta^2-\frac{1}{2})^2$. A previous study considering such a potential has concluded in favor of the existence of solutions in the form of solitons.[37] The stability analysis of these waves has shown that only the stable wave could correspond to the motion of a domain wall separating two domains in the ferroelectric crystal.

Consider now the following simultaneous changes of functions and variables:

$$\begin{gathered}\phi=2\theta,\quad \bar{v}=2v\sqrt{2}\chi/J\ ,\\ t=\tau\sqrt{J/2\chi},\quad x=X\sqrt{K/2\chi}\ .\end{gathered} \tag{2.15}$$

In an obvious manner we set

$$\hat{V}_L^2=\frac{J\hat{C}_{\parallel}}{\rho K},\quad \hat{V}_T^2=\frac{J\hat{C}_{\perp}}{\rho K},\quad \eta=\frac{e}{2}\sqrt{J/K}\ . \tag{2.16}$$

The new set $(u,\bar{v},\phi)$ of functions satisfies the following system:

$$\frac{\partial^2 u}{\partial\tau^2}-\hat{V}_L^2\frac{\partial^2 u}{\partial X^2}=0\ , \tag{2.17a}$$

$$\frac{\partial^2 v}{\partial\tau^2}-\hat{V}_T^2\frac{\partial^2\bar{v}}{\partial X^2}=-\eta\frac{\partial}{\partial X}(\sin\phi)\ , \tag{2.17b}$$

$$\frac{\partial^2\phi}{\partial\tau^2}-\frac{\partial^2\phi}{\partial X^2}-\sin\phi=\eta\frac{\partial\bar{v}}{\partial X}\cos\phi\ . \tag{2.17c}$$

It is not difficult to show that Eqs. (2.17) admit the following Lagrangian density:

$$\mathscr{L}=\frac{1}{2}\left[\left[\frac{\partial\bar{v}}{\partial\tau}\right]^2+\left[\frac{\partial\phi}{\partial\tau}\right]^2\right]-\frac{1}{2}\left[\hat{V}_T^2\left[\frac{\partial\bar{v}}{\partial X}\right]^2+\left[\frac{\partial\phi}{\partial X}\right]^2\right]$$

$$-(1+\cos\phi)+\eta(\sin\phi)\frac{\partial\bar{v}}{\partial X}\ . \tag{2.18}$$

Now let $\mathscr{L}=0$ for $\bar{v}=0$ and $\phi=\pm\pi$. Equivalently, on introducing the following conjugate quantities:

$$\vec{\Pi}=(\Pi_1,\Pi_2)\ ,\ \vec{\rho}=(\rho_1,\rho_2)\ ,$$

$$\Pi_1=\frac{\partial\mathscr{L}}{\partial(\partial\bar{v}/\partial\tau)}=\frac{\partial\bar{v}}{\partial\tau},\quad \Pi_2=\frac{\partial\mathscr{L}}{\partial(\partial\phi/\partial\tau)}=\frac{\partial\phi}{\partial\tau}\ , \tag{2.19}$$

$$\rho_1=\frac{\partial\mathscr{L}}{\partial(\hat{V}_T\partial\bar{v}/\partial X)}=-\hat{V}_T\frac{\partial\bar{v}}{\partial X},\ \rho_2=\frac{\partial\mathscr{L}}{\partial(\partial\phi/\partial X)}=-\frac{\partial\phi}{\partial X}\ ,$$

we can introduce the Hamiltonian

$$\mathscr{H}=\tfrac{1}{2}(\vec{\Pi}^2+\vec{\rho}^{\,2})+1+\cos\phi+(\eta/\hat{v}_T)\rho_1\sin\phi\ . \tag{2.20}$$

The associated canonical equations read thus

$$\begin{aligned}&\frac{\partial\Pi_1}{\partial\tau}+\hat{V}_T\frac{\partial\rho_1}{\partial X}=-\eta\frac{\partial}{\partial X}(\sin\phi)\ ,\\ &\frac{\partial\rho_1}{\partial\tau}+\hat{V}_T\frac{\partial\Pi_1}{\partial X}=0\ ,\\ &\frac{\partial\Pi_2}{\partial\tau}+\frac{\partial\rho_2}{\partial X}=\sin\phi-(\eta/\hat{V}_T)\rho_1\cos\phi\ ,\\ &\frac{\partial\rho_2}{\partial\tau}+\frac{\partial\Pi_2}{\partial X}=0\ ,\\ &\frac{\partial\bar{v}}{\partial\tau}=\Pi_1\ ,\\ &\frac{\partial\phi}{\partial\tau}=\Pi_2\ .\end{aligned} \tag{2.21}$$

This last formalism proves to be useful in studying a numerical scheme for the solution of the system (2.17b) and (2.17c) under various initial conditions for ϕ and $\bar{v}$ (in the problem of the collision of solitons in particular).

III. SOLITONS

A. Transformation of the equations

Consider Eqs. (2.17b) and (2.17c) in which we write v instead of $\bar{v}$ to simplify the notation. Some obvious properties of such equations can be emphasized. Let (v,ϕ) be a solution. Then both $(-v,-\phi)$ and $(v,\pi-\phi)$ are also solutions, and thus $(-v,\pi+\phi)$ is also a solution. Obviously, ϕ is defined mod$2k\pi$ and the system (2.17b) and (2.17c) has the elementary solution

$$v=v_0=\text{const},\quad \phi=k\pi,\ k\in\mathbb{Z}\ . \tag{3.1}$$

We look for solutions in the form of propagative waves, that is, functions of the only variable $\xi=QX-\Omega\tau$, where Q and Ω may be referred to as a pseudo wave number and a pseudo circular frequency which must satisfy a certain dispersion relation. In this case the system (2.17) yields

$$(\Omega^2-\hat{\Omega}_L^2)\frac{d^2u}{d\xi^2}=0,\quad \hat{\Omega}_L^2\equiv\hat{V}_L^2Q^2\ . \tag{3.2a}$$

$$(\Omega^2-\hat{\Omega}_T^2)\frac{d^2v}{d\xi^2}=-\eta Q\frac{d}{d\xi}(\sin\phi),\quad \hat{\Omega}_T^2\equiv\hat{V}_T^2Q^2\ , \tag{3.2b}$$

$$(\Omega^2-Q^2)\frac{d^2\phi}{d\xi^2}-\sin\phi=\eta Q\frac{dv}{d\xi}\cos\phi\ . \tag{3.2c}$$

The first of these obviously provides the dispersion relation

$$\Omega=\pm\hat{\Omega}_L\ . \tag{3.3}$$

Equation (3.2b) integrates once with respect to ξ to give

$$(\Omega^2-\hat{\Omega}_T^2)\frac{dv}{d\xi}=-\eta Q\sin\phi \tag{3.4}$$

on the condition that $(dv/d\xi)=0$ if $\phi=k\pi$ and $\Omega\neq\pm\hat{\Omega}_T$. This will have to be checked *a posteriori* once ϕ is known.

Now, on substituting $(dv/d\xi)$ from Eq. (3.4) into Eq. (3.6), we obtain

$$(\Omega^2-Q^2)\frac{d^2\phi}{d\xi^2}=\sin\phi-\gamma(\Omega,Q)\sin(2\phi)\ , \qquad (3.5)$$

where

$$\gamma(\Omega,Q)=\frac{\eta^2}{2}\frac{Q^2}{\Omega^2-\hat{\Omega}_T^2}\ . \qquad (3.6)$$

We note that Eq. (3.5) is entirely equivalent to the partial differential equation

$$\frac{\partial^2\phi}{\partial\tau^2}-\frac{\partial^2\phi}{\partial X^2}=\sin\phi-\gamma\sin(2\phi)\ , \qquad (3.7)$$

whenever we consider solutions $\phi=\phi(\xi)$. Forgetting for the moment that the solution of Eq. (3.7) depends on Ω and Q, we note that Eq. (3.7) is formally a *double sine-Gordon equation* [not exactly, in fact, since the double sine-Gordon equation usually studied involves $\sin(\phi/2)$ and *not* $\sin(2\phi)$! (cf. Refs. 38—40)]. If we carry solutions $\phi(\xi)$ in Eq. (3.7), then we recover Eq. (3.5). But the latter possesses a first integral (energy integral) given by

$$(\Omega^2-Q^2)\left[\frac{dQ}{d\xi}\right]^2+V(\phi)=E_0\ , \qquad (3.8a)$$

$$V(\phi)=2\cos\phi-\gamma\cos(2\phi)\ , \qquad (3.8b)$$

where E_0 is the integration constant which can be related to the total energy of the system under consideration. Equation (3.8a) represents the motion of a particle of mass Ω^2-Q^2 in a periodic potential $V(\phi)$—of period 2π—but here the "mass" may be negative in some cases. In a general manner, Eq. (3.7), hence Eqs. (3.8) as well, has periodic propagative solutions which depend on the energy E_0. This is an interesting property which can be eventually connected with the motion of electric dipoles in an incommensurate phase (see the introduction). Indeed, in such a phase, dipoles oscillate with a period which is *not* commensurate with the lattice spacing. Here, however, we shall consider the case of Eq. (3.7) or (3.8) which present solutions with $E_0=-2$.

An initial remark is in order before proceeding to the solution of Eq. (3.7). Consider the following "Lorentz transformation"

$$X\rightarrow X'=\frac{QX-\Omega\tau}{(Q^2-\Omega^2)^{1/2}},\quad \tau\rightarrow\tau'=\frac{Q\tau-\Omega X}{(Q^2-\Omega^2)^{1/2}}\ . \qquad (3.9)$$

Then both Eq. (3.7) and the corresponding Lagrangian density are invariant in such a transformation. This is of interest because it allows one to work out the problem in a frame *co-moving* with the wave at a velocity Ω/Q. This property can also be exploited in the study of stability of soliton waves.[41]

B. Solution

In order to solve Eq. (3.7) we introduce the following operator:[42,43]

$$D_X^m D_\tau^n(a,b)=\left[\left[\frac{\partial}{\partial X}-\frac{\partial}{\partial X'}\right]^m\left[\frac{\partial}{\partial\tau}-\frac{\partial}{\partial\tau'}\right]^n\times[a(X,\tau)b(X',\tau')]\right|_{X'=X,\tau'=\tau}\ . \qquad (3.10)$$

Let us first envisage solutions in the form

$$\phi=2\tan^{-1}(f/g)\ , \qquad (3.11)$$

where both f and g are functions of X and τ. Now set

$$X=Y+T,\ \tau=T-Y\ , \qquad (3.12)$$

so that we can rewrite Eq. (3.7) in the form

$$\frac{\partial^2\phi}{\partial Y\partial T}=-\sin\phi+\gamma\sin(2\phi)\ . \qquad (3.13)$$

Accounting for the definition (3.11), we have

$$\frac{\partial^2\phi}{\partial Y\partial T}=2[f\cdot gD_YD_T(f\cdot f-g\cdot g)-(f^2-g^2)D_YD_T(f\cdot g)]\times(f^2+g^2)^{-2}\ .$$

On using this and Eq. (3.11), we can rewrite Eq. (3.13) as

$$[2\gamma f\cdot g-D_YD_T(f\cdot g)](f^2-g^2)+[D_YD_T(f^2-g^2)+(f^2-g^2)](f\cdot g)=0\ . \qquad (3.14)$$

We look for solutions of this equation such that the following decomposition holds well (μ is not known as yet):

$$D_YD_T(f\cdot g)=\mu f\cdot g\ ,$$
$$D_YD_T(f^2-g^2)=-(f^2+g^2)+(\mu-2\gamma)(f^2-g^2)\ . \qquad (3.15)$$

This system presents a certain symmetry insofar as f and g are concerned. Consider now functions f and g, permitting expansions of the following type:

$$f=1+\delta^2f_2+\delta^4f_4+\cdots\ ,$$
$$g=\delta g_1+\delta^3g_3+\cdots\ , \qquad (3.16)$$

where δ is an arbitrary parameter. At zeroth order we obtain

$$\mu=1+2\gamma\ , \qquad (3.17)$$

while at the first order

$$\frac{\partial^2g_1}{\partial Y\partial T}=\mu g_1\ . \qquad (3.18)$$

We seek a solution of the latter in the form (the choice is not unique)

$$g_1(Y,T)=\exp z,\ z=\alpha Y-\beta T,\ \alpha\beta=-\mu\ . \qquad (3.19)$$

The constants α and β can be related to Q and Ω by the intermediary of Eqs. (3.12). This gives

$$\alpha=Q+\Omega,\ \beta=\Omega-Q\ . \qquad (3.20)$$

On substituting from Eq. (3.20) into Eq. (3.18) and accounting for Eqs. (3.17) and (3.19), we obtain the dispersion relation as

$$\Omega^2-Q^2=-(1+2\gamma)\ . \tag{3.21}$$

Finally, at the second order in δ, taking the results of previous orders—Eqs. (3.17) and (3.18)—into account, we have

$$\frac{\partial^2 f_2}{\partial Y\,\partial T}=-g_1^2\ . \tag{3.22}$$

With (3.19) this yields

$$f_2=\frac{-\exp(2z)}{4(1+2\gamma)}\ . \tag{3.23}$$

Taking $f_{2p}=0$ and $g_{2p+1}=0$ for $p\geq 2$, we can show that the expansions (3.16) converge and the *exact* solution of Eq. (3.17) or (3.13) is finally obtained as

$$\phi=-2\tan^{-1}\left[\frac{\sinh\xi'}{(1+2\gamma)^{1/2}}\right], \tag{3.24}$$

where

$$\xi'=\xi-\tfrac{1}{2}\ln\left[\frac{4(1+2\gamma)}{\delta}\right]. \tag{3.25}$$

This solution holds only for $1+2\gamma>0$, which is satisfied on account of the dispersion relation (3.21) and of the expression (3.6) of γ. As $\xi'\rightarrow-\infty$, $\phi\rightarrow+\pi$ and for $\xi'\rightarrow\infty$, $\phi\rightarrow-\pi$; the term $\xi_0=\delta\ln(1+2\gamma)/4$ may be viewed as a constant arbitrary phase.

Another solution of the problem is obtained by looking for a solution of Eq. (3.17) or (3.13) in the form

$$\phi=\pi+\bar{\phi}\ , \tag{3.26}$$

where $\bar{\phi}$ satisfies Eq. (3.13) but with $\sin\phi$ replaced by $-\sin\bar{\phi}$. The resulting computations are identical to the previous ones and the results are a dispersion relation

$$\Omega^2-Q^2=1-2\gamma \tag{3.27}$$

and a solution

$$\phi=\pi-2\tan^{-1}\left[\frac{\sinh\xi'}{(1-2\gamma)^{1/2}}\right] \tag{3.28}$$

with

$$\xi'=\xi-\frac{1}{2}\ln\left[\frac{4(1-2\gamma)}{\delta}\right]. \tag{3.29}$$

This last solution is valid if $(1-2\gamma)>0$, which holds true by virtue of Eq. (3.27).

The "dispersion relations" (3.21) and (3.27) are of the utmost interest. They can be rewritten in full as $(\Omega_F^2\equiv 1+Q^2)$

$$[\Omega^2-(\Omega_F^2-2)](\Omega^2-\hat{\Omega}_T^2)+\eta^2Q^2=0 \tag{3.30a}$$

and

$$[\Omega^2-\Omega_F^2](\Omega^2-\hat{\Omega}_T^2)+\eta^2Q^2=0\ , \tag{3.30b}$$

respectively. In Fig. 3 the uncoupled solutions of the linear problem are represented in broken lines (cf. Refs. 8 and 28): branch (a) of equation $\Omega=\hat{\Omega}_T$ is the transverse acoustic branch while branch (b) of equation $\Omega_F^2=1+Q^2$ is the ferroelectric mode. The branches (c) and (d) correspond to the solutions of the dispersion relation (3.30a) or (3.21) while branches (e) and (f) correspond to those of the dispersion relation (3.30b) or (3.27). In the first case (c) is such that $\Omega<Q$ while curve (d) is very close to $\hat{\Omega}_T$, up to terms of order η^2, so that the corresponding soliton propagates practically at the speed of a transverse acoustic mode. As for curves (e) and (f), for both we have $\Omega>Q$ and they are *conjugate* to those obtained in the linear framework (Refs. 8 and 28).

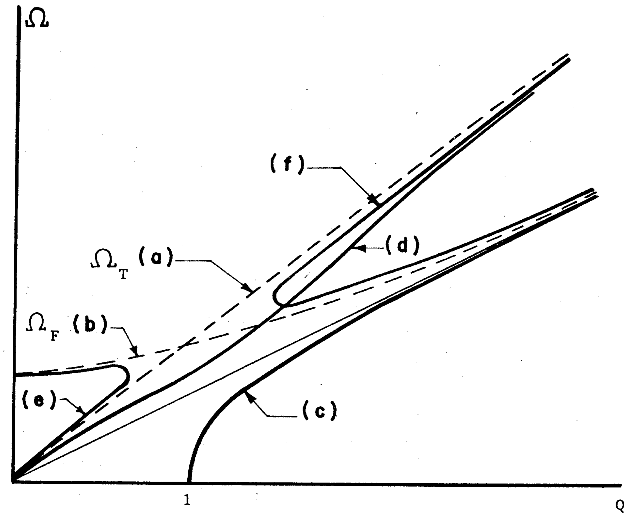

FIG. 3. Dispersion relation for single soliton. (c) and (d): solutions of Eq. (3.30a). (e) and (f): solutions of Eq. (3.30b).

(i) Stability. Of the two solutions (3.24) and (3.28) (we could also consider coshz' instead of sinhz'), the most interesting one is the stable one. A stability criterion for the sine-Gordon equation of the type (3.7) is given by (cf. Ref. 41)

$$\Omega<Q,\quad \frac{d\phi}{d\xi}\leqq 0\ . \tag{3.31}$$

Only the solution corresponding to the branch (c) in Fig. 3 is thus stable. This is analytically described by Eq. (3.24). Moreover, only this solution has a physical significance. However, it must also be noticed that solutions (3.24) and (3.28) have been obtained by substituting $-X$ for X in the system (2.11)—because of the fact that X depends on temperature. Had we kept $+X$ we would have obtained the same solutions (3.24) and (3.28) but with γ replaced by $-\gamma$ and the two dispersion relations (3.30) interchanged. Then the stable solution would have been (3.24). This must not be overlooked when giving a physical interpretation to the solutions.

(ii) Other form of the solution (3.24). The solution (3.24), as well as (3.28) for that matter, can be given another form by decomposing the $\tan^{-1}$ operator. We arrive thus at the expression

$$\phi=-2\tan^{-1}(e^{\xi+\Delta})+2\tan^{-1}(e^{-\xi+\Delta})\ , \tag{3.32}$$

or, else,

$$\phi=\pi-2\tan^{-1}(e^{\xi+\Delta})-2\tan^{-1}(e^{\xi-\Delta}) \tag{3.33}$$

with

$$\xi = QX - \Omega\tau, \quad \Delta = -\frac{1}{2}\ln\left[\frac{4(1+2\gamma)}{\delta}\right]. \tag{3.34}$$

In the form (3.32) or (3.33), the simple soliton solution to the double sine-Gordon equation (3.7)—coupled case, $\gamma \neq 0$—decomposes in the sum of two simple soliton solutions. Taken separately, each of these is analogous to the simple soliton solution of the *usual* sine-Gordon equation (case $\gamma = 0$) up to a factor 2 in front of $\tan^{-1}$ operators. Note also that for $\gamma = 0$, the solutions (3.32) and (3.33) reduce to the classical case of the solution of the usual sine-Gordon equation (Ref. 41).

It is of interest to evaluate the stress field generated by the soliton solution. This field is defined by

$$\sigma = -\hat{V}_T^2 \frac{\partial v}{\partial X} + \eta \sin\phi . \tag{3.35}$$

Owing to Eqs. (3.4) and (3.24), this yields

$$\sigma = \eta \frac{\Omega^2\sqrt{1+2\gamma}}{\Omega^2 - \hat{\Omega}_T^2} \frac{\sinh\xi'}{\sqrt{1+2\gamma} + \sinh^2\xi'} . \tag{3.36}$$

The same type of result obtains for the soliton solution (3.28).

Finally, Eq. (3.34) can be integrated in order to provide the elastic displacement that corresponds to the motion of the wall. This, in fact, is possible because the strain compatibility conditions are satisfied in the present case. However, it would not be necessarily the case in more complex situations where one would have to consider so-called *internal* strains. The evaluation of the displacement yields

$$v - v_0 = \frac{2\eta Q}{(\Omega^2 - \hat{\Omega}_T^2)} \left[\frac{1+2\gamma}{-2\gamma}\right]^{1/2} \tanh^{-1}\left[\frac{\cosh(\xi - \xi_0)}{\sqrt{-2\gamma}}\right] \tag{3.37}$$

and

$$v - v_0 = \frac{-2\eta Q}{(\Omega^2 - \hat{\Omega}_T^2)} \left[\frac{1-2\gamma}{-2\gamma}\right]^{1/2} \tan^{-1}\left[\frac{\cosh(\xi - \xi_0)}{\sqrt{-2\gamma}}\right] \tag{3.38}$$

for the solutions (3.24) and (3.28), respectively.

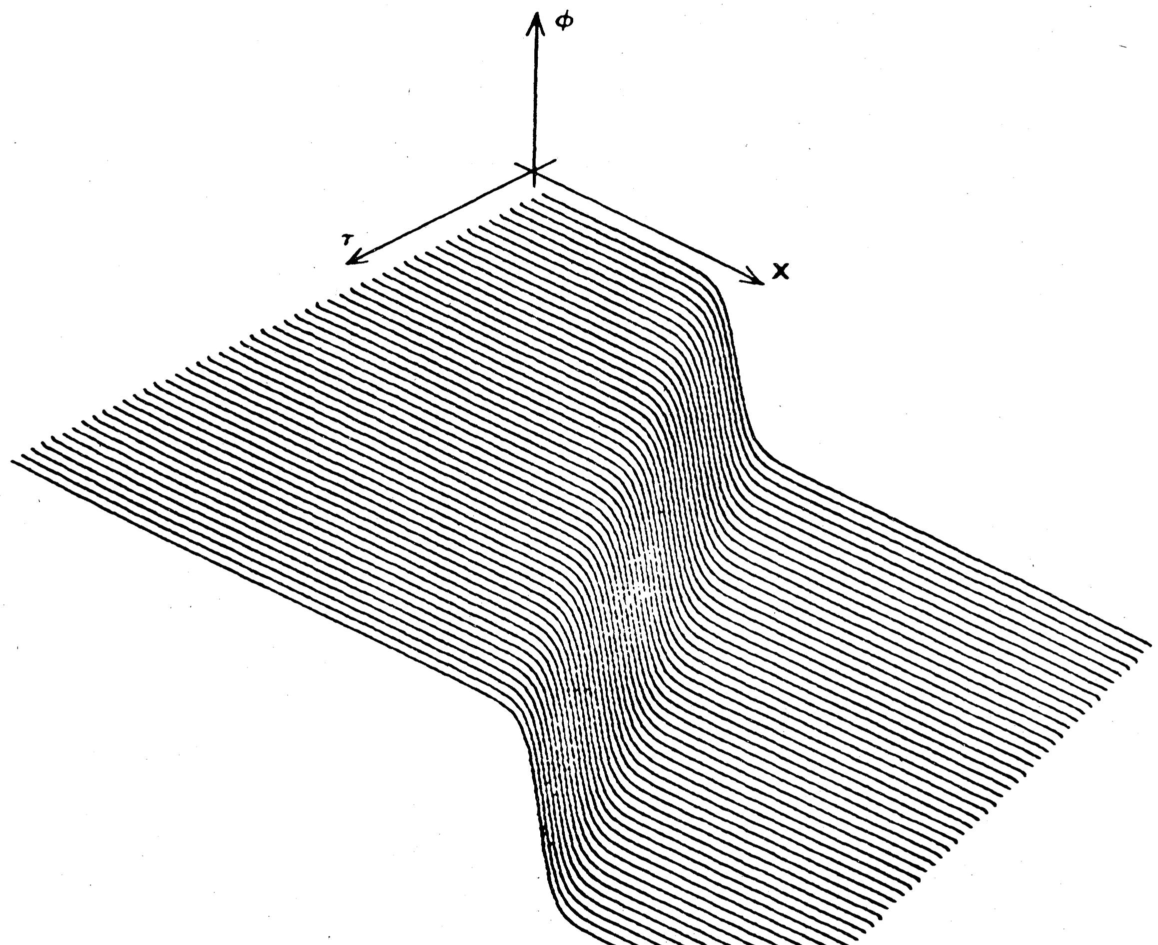

FIG. 4. Ferroelectric soliton (polarization angle).

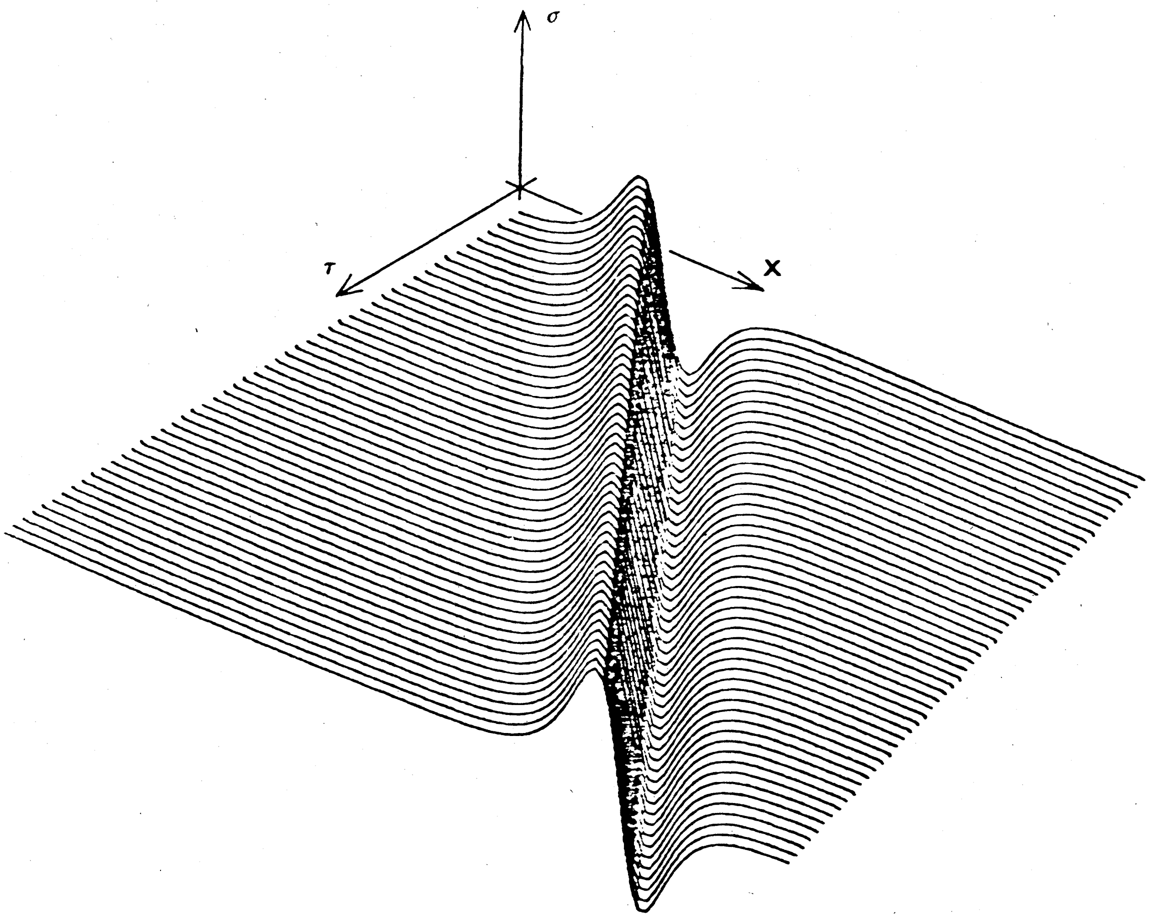

FIG. 5. Soliton in stress accompanying the single ferroelectric soliton.

Numerical evaluations of the space-time graphs of the solutions (3.24), (3.35), and (3.37) are given in Figs. 4, 5, and 6. Physically, the solution sketched out in these graphs corresponds to the motion of a wall that separates two domains, with $\phi \to \pi$, $\theta \to \pi/2$ for $X \to -\infty$ and $\phi \to -\pi$, $\theta \to -\pi/2$ for $X \to +\infty$. The spatial region where changes occur drastically determines the *thickness* of the wall. The corresponding stress in Fig. 5 is obviously essentially nonzero in the immediate vicinity of the wall. It is proportional to the electromechanical coupling parameter η. Similarly, the displacement in Fig. 6 is essentially nonzero in the spatial region of the wall, presenting a maximum where the solution of Fig. 4 presents a point of inflexion. Clearly, a *nonlinear* stress wave is generated by the wall motion between two domains, via electromechanical couplings, although the medium considered is strictly linear from the point of view of elasticity.

C. Evaluation of energies

Before relating the previous mathematics to some physical situation, we evaluate and compare the various energies involved in the system at hand. First, the total energy is evaluated. Then, in the static case we get an idea of the wall energy per unit area and compare it to known ferroelectric cases. The wall thickness is also determined.

The total energy is obtained by summing up the Hamiltonian density (2.20), i.e.,

$$E = \int_{-\infty}^{+\infty} \mathscr{H}(\vec{p}, \vec{\Pi}, \phi) dX .$$

After a somewhat lengthy calculation one obtains

$$E = -\frac{2}{Q} \left\{ \left[\left[\frac{\Omega^2 + \hat{\Omega}_T^2}{\Omega^2 - \hat{\Omega}_T^2} \right] + \frac{\Omega^2 + Q^2}{1+2\gamma} \right] \left[\frac{1+2\gamma}{-2\gamma} \right]^{1/2} \tan^{-1} \left[\left[\frac{-2\gamma}{1+2\gamma} \right]^{1/2} \right] - (1+2\gamma) \left[\frac{\Omega^2 + Q^2}{1+2\gamma} + \frac{3\Omega^2 - \hat{\Omega}_T^2}{\Omega^2 - \hat{\Omega}_T^2} \right] \right\} . \tag{3.39}$$

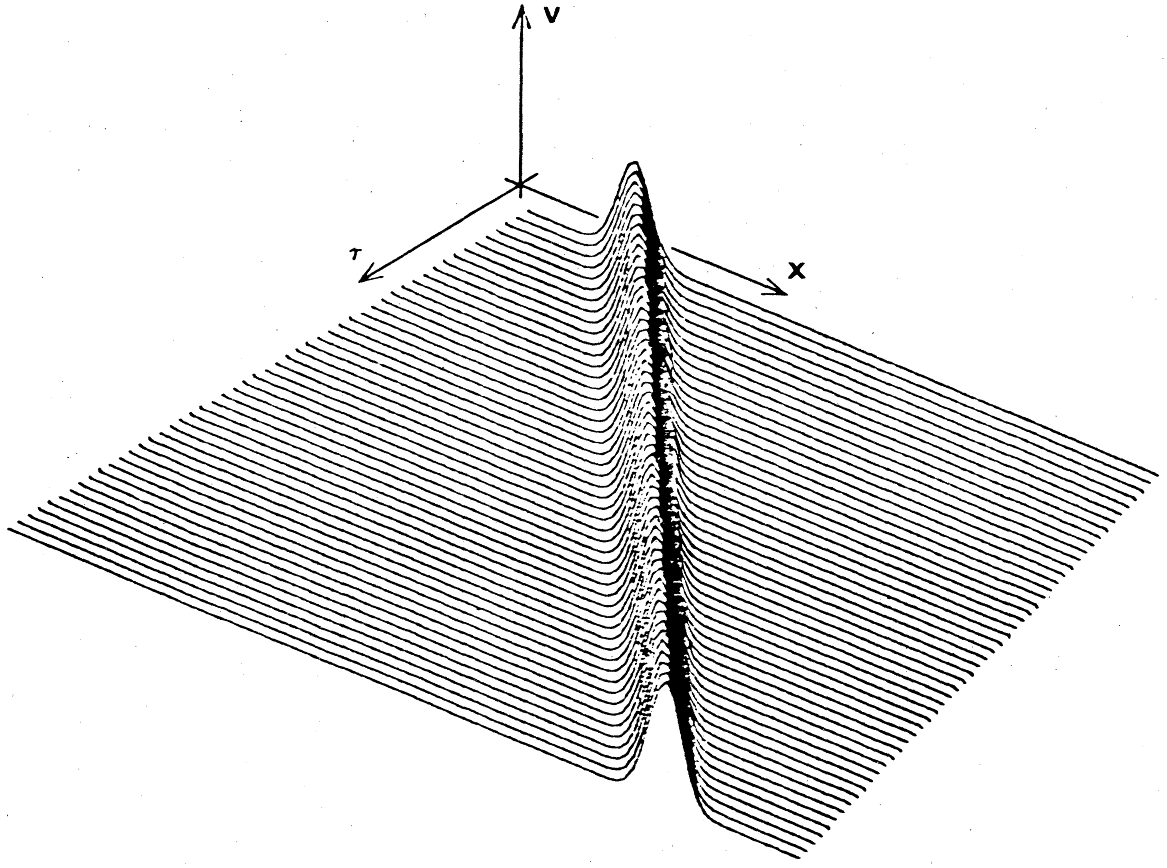

FIG. 6. Soliton in displacement corresponding to Figs. 4 and 5.

Notice that the term γ of Eq. (3.6) is involved in the result (3.39). This depends on η, hence on electromechanical couplings. The elastic contribution is felt through the presence of the "elastic" frequency $\hat{\Omega}_T$. If one neglects electromechanical couplings ($|\gamma| \ll 1$ or $\eta \ll 1$), then Eq. (3.39) simplifies noticeably to give the extremely simple result

$$E = 8Q \ . \tag{3.40}$$

In this case everything occurs as if both elastic and coupling energies were zero; only the electric-dipole energy remains.

Returning to the general case (3.39), we consider small γ's so that an expansion to the first order in γ yields

$$E = 8Q + \frac{16\gamma}{3Q^2}\left[2 + Q^2 + \frac{\Omega^2}{2(\hat{\Omega}_T^2 - \Omega^2)}\right] + O(\gamma^2) \ . \tag{3.41}$$

We must still account for the dispersion relation [Eq. (3.30a)] and extract from it only the *stable* solution. To the first order in η^2 in Eq. (3.41) we may take $\Omega^2 \equiv Q^2 - 1$ so that

$$\gamma = \frac{\eta^2 Q^2}{\hat{\Omega}_T^2 - (\hat{\Omega}_F^2 - 2)} \ ,$$

and E depends only on the pseudo wave number Q and the parameters $\hat{V}_T$ and η of the model.

In order to evaluate the wall energy, we consider the *static* version of the coupled equations (2.12b) and (2.12c). That is, in dimensional notation,

$$\begin{gathered}
\hat{C}_\perp \frac{d^2 v}{dx^2} = \frac{e}{2}\frac{d}{dx}(\sin 2\theta) \ , \\
K\frac{d^2\theta}{dx^2} = -\chi \sin(2\theta) - e\frac{dv}{dx}\cos(2\theta) \ .
\end{gathered} \tag{3.42}$$

The corresponding total energy of the system reads

$$\begin{aligned}
E = \int_{-\infty}^{+\infty} \Bigg\{ & \frac{1}{2}\left[K\left[\frac{d\theta}{dx}\right]^2 + \hat{C}_\perp\left[\frac{dv}{dx}\right]^2\right] \\
& + \frac{\chi}{2}(1+\cos 2\theta) + \frac{e}{2}(\sin 2\theta)\frac{dv}{dx}\Bigg\} dx \ .
\end{aligned} \tag{3.43}$$

The change

$$\bar{v} = 2v(\hat{C}_\perp/K)^{1/2}, \quad \bar{e} = e(2\hat{C}_\perp\chi)^{-1/2} \tag{3.44}$$

and transformations (2.15) allow one to return to nondimensional notation if needed. On computing the energy (3.43), we obtain thus

$$E = 4\left[\frac{1}{\bar{e}}\tan^{-1}\left[\frac{\bar{e}}{(1-\bar{e}^2)^{1/2}}\right] + (1-\bar{e}^2)^{1/2}\right] \ . \tag{3.45}$$

Suppose that $\bar{e} \ll 1$, which is generally the case, and we return to dimensional units. Then Eq. (3.45) yields

$$\Sigma \simeq \tfrac{1}{4}[2\mathcal{X}K(1-\bar{e}^2)]^{1/2} , \tag{3.46}$$

an expression which compares with the one for Néel walls in ferromagnets. Notice that the electromechanical coupling has the effect of increasing the wall energy. Returning now to microscopic parameters of the lattice from which $\mathcal{X}$ and K were defined and considering the expression (2.5) for ϵ, we have

$$\Sigma \simeq \frac{a(1-\bar{e}^2)^{1/2}}{\pi\epsilon_0\sqrt{2}}\left[\frac{P_0}{a^3}\right]^2, \quad \bar{e}^2 = \frac{2\epsilon}{\hat{C}_{\perp}a^3} . \tag{3.47}$$

This is an interesting expression. Indeed, in accord with Eq. (3.46), we have an energy which has the same expression as the one obtained for Néel walls in ferromagnets.[44] This analogy holds even more if we notice that the present model is equipped with microscopic dipoles of constant magnitude which experience a rotation in a plane orthogonal to the plane of the wall (in contradistinction with the case of Bloch walls in ferromagnets[44]). On the other hand, Eq. (3.47) is formally the same as the one obtained for a ferroelectric wall in classical cases (Zirnov's model[45]). The energy Σ depends quadratically on P_0/a^3. The coefficients K and $\mathcal{X}$ which, respectively, account for dipolar interactions and resemble a temperature-dependent electric susceptibility, are involved. In addition, a corrective factor $(1-\bar{e}^2)^{1/2}$ is due to electromechanical couplings. However, passing from Eq. (3.46) to Eq. (3.47) is rather questionable and the expression (3.47) must be considered as approximate and the question arises of the interpretation of the energies in terms of phase transition. A numerical estimate with $\mathcal{X} \simeq 5\times 10^{10}\ \mathrm{J\,m^5\,C^{-4}}$ and $K \simeq 1.04\times 10^{-11}\ \mathrm{C^2/fm}$ [The evaluation of K was made from the fourth equation of (2.13) in reduced units: $K \simeq 2.0\times 10^{12}$ MKS (r.u.)$^{-2}$ with one r.u.$=2\pi/a$ for the example of NaNO$_2$] gives $\Sigma \simeq 10^{-3}$ J/m^2 and the electromechanical coupling coefficient is such that $\bar{e}^2 \simeq 5.0\times 10^{-3}$. The latter coefficient has a marked influence for materials with high electromechanical coupling parameters.

If we now return to the solutions of Eqs. (3.42), in nondimensional notation we obtain

$$\phi = -2\tan^{-1}\left[\frac{\sinh(QX-Z_0)}{(1-\bar{e}^2)^{1/2}}\right], \quad Q^2 = 1-\bar{e}^2 . \tag{3.48}$$

This is obtained by adopting the coefficients of the dynamical case. A short computation allows one to show that the corresponding mechanical stress is zero so that we can say that, at equilibrium, the wall separating two ferroelectric domains is described by Eq. (3.48) and the material presents no prestresses although electromechanical couplings are still felt through $\bar{e}$. If the latter is discarded, we obviously recover a solution analogous to the one obtained for Bloch walls in ferromagnets[46] (ordinary sine-Gordon equation[46]). The wall thickness may be defined by $\delta = Q^{-1}$ so that in dimensional notation we have

$$\delta = \pi\left[\frac{K}{2\mathcal{X}(1-\bar{e}^2)}\right]^{1/2} . \tag{3.49}$$

Reintroducing the definitions of K and $\mathcal{X}$ in terms of microscopic parameters, this reads thus

$$\delta \simeq \frac{\pi a}{(1-\bar{e}^2)^{1/2}} \tag{3.50}$$

or $\delta = O(a)$. Electromechanical couplings have the effect of increasing the wall thickness. Here also, Eq. (3.50) is quite approximate and gives only an order of magnitude. In general we must check the hypothesis expressed in Eq. (2.11), which implies that $\delta \gg a$. However, Eq. (3.49) yields $\delta \simeq 5.4\times 10^{-2}\ \mu$m.

Only the static case has been considered in the above calculations. This does not restrict the analysis since a Lorentz transformation (3.9) allows one to revert to the case of a wall in uniform motion.

IV. PHYSICAL INTERPRETATIONS

A. Domain walls

The model presented above finds a physical interpretation in the case of ferroelectrics such as NaNO$_2$ [SC(NH$_2$)$_2$ is another example]. For such a crystal in its paraelectric phase microscopic dipoles associated with the NO$_2$ group are directed in a random manner, but with an equal probability, along the axes $\vec{b}$ and $-\vec{b}$. The Na$^+$ ions can occupy two positions, with equal probabilities, on the axis $\vec{c}$ orthogonal to $\vec{b}$ (cf. Refs. 24 and 47). The paraelectric and ferroelectric phases are separated by an incommensurate phase in the temperature interval 162.5–164.0 °C.[48] Insofar as domains are concerned, x-ray scattering topography shows that domain walls are parallel to the (100) plane.[49–50] On the other hand, in the static case, Eq. (3.48), with $\phi = 2\theta$, shows that θ varies between $\pi/2$ and $-\pi/2$ and that the rotation of the dipole $\vec{P}$ occurs essentially in the layer of thickness δ. This means that dipoles oriented parallel to $\vec{b}$ are reversed after passage of the wall and are then oriented parallel to $-\vec{b}$. This "rotation" takes place in a plane perpendicular to the wall. Measurements give a wall thickness of the order of 0.3–1 μm (this corresponds to about 2500 lattice spacings!) and is very important for a ferroelectric since, for BaTiO$_3$, the thickness is about $(2\text{–}5)\times 10^{-3}\ \mu$m for a 180° wall and $10^{-2}\ \mu$m for a 90° wall.[45] We can say that the stable solution (3.24), in effect, corresponds to the motion of a wall separating two domains in a ferroelectric crystal of the type of NaNO$_2$. However, other theories,[50–51] in order to explain the important wall thickness, divide the wall in several buffer layers between 180° domains. An intermediate region, wherein microscopic dipoles perform discrete rotations in accord with several equilibrium states, is "sandwiched" between two metastable regions. But neither x-ray nor electron-microscopy experiments seem to confirm this hypothesis for the moment. The explanation of such an important thickness could be sustained by a distortion effect of the crystal structure within the wall. Therefore, a nonnegligible influence of strains along the $\vec{a}$ and $\vec{b}$ axes of the crystal could manifest itself. Altogether, however, the wall motion must be intimately related to the type of phase transition occuring in the crystal.

B. Commensurate-incommensurate phase transition

Certain crystals such as $NaNO_2$ [but also many others such as $SC(NH_2)_2$, $BaMnF_4$, K_2SeO_4, $(NH_4)_2BeF_4$, $ThBr_4$] transit through one or several intermediate phases, so-called incommensurate phases, between the paraelectric phase and the ferroelectric one. These intermediate phases are of the utmost importance for the formation of domains.[15–16] In the high-temperature phase electric dipoles associated with the NO_2 group are disordered, but aligned either with the $\vec{b}$ or $-\vec{b}$ axis, the crystal having orthorhombic symmetry of class *Immm*. As temperature decreases the crystal enters a *modulated antiferroelectric phase*. In the latter ($T < 164\,°C$), dipoles remain aligned with $\vec{b}$, but the molecular groups NO_2 experience small-amplitude rotations about the $\vec{c}$ axis and this, in turn, creates a modulation of the (macroscopic) polarization along the $\vec{a}$ and $\vec{b}$ axes. Furthermore, this sinusoidal modulation is *not commensurate* with the lattice spacing (cf. Refs. 15, 16, and 24). In this phase the crystal symmetry is still orthorhombic but with class *I*2*mm* (symmetry of the wave vector). The phase is therefore called *incommensurate*. In general, the transition from the high-temperature (disordered) phase to the incommensurate phase occurs at a temperature T_I below which the incommensurate phase is stable and this corresponds to a structural transition toward a weaker symmetry. Stability is bounded from below by the *lock-in temperature* T_0. At this temperature the modulation follows that of the crystal lattice and we enter the *commensurate* phase. This is accompanied by the formation of domains and the motion of walls which materialize a *local order*. With the disappearance of the modulation, we recover an ordered phase where all dipoles are parallel to $\vec{b}$. This is the ferroelectric phase in which there exists a permanent electric polarization and the symmetry is orthorhombic of class *Im*2*m* (Refs. 15 and 16).

We shall examine these successive phase transformations on the basis of an elementary model which shall be easily connected with the more elaborate model described in previous sections. To that purpose we consider a plane—(x,y) or (001)—problem in which the electric polarization $\vec{P}=(P_x,P_y,0)$ is taken as *order parameter*. This does not exclude the existence of z components for mechanical and electric quantities in a real three-dimensional problem. Whenever one sets $P_x = P_0\cos\theta$ and $P_y = P_0\sin\theta$, one recovers the "micropolar" description of Sec. II. Using the Landau thermodynamical potential with additional terms accounting for elasticity and the peculiarities of the phase transitions,[20,52] we propose to write the total energy as

$$\varphi=\sum_{\alpha=0}^{6}\varphi_\alpha \tag{4.1}$$

with

$$\varphi_1=\frac{1}{2}K_1\left[\frac{dP_x}{dx}\right]^2+\frac{1}{2}K_2\left[\frac{dP_y}{dx}\right]^2 , \tag{4.2a}$$

$$\varphi_2=\tfrac{1}{2}\alpha_1P_x^2+\tfrac{1}{2}\alpha_2P_y^2+\tfrac{1}{4}\beta_1P_x^4+\tfrac{1}{4}\beta_2P_y^4+\tfrac{1}{2}\gamma P_x^2P_y^2 , \tag{4.2b}$$

$$\varphi_3=\delta_1P_x\frac{dP_y}{dx}+\delta_2P_y\frac{dP_x}{dx} , \tag{4.2c}$$

$$\varphi_4=\tfrac{1}{2}(c_{11}e_{xx}^2+c_{22}e_{yy}^2+c_{66}e_{xy}^2+2c_{12}e_{xx}e_{yy}) , \tag{4.2d}$$

$$\varphi_5=\begin{cases}\varphi_5^{inc}=h_{11}P_xe_{xx}+h_{12}P_xe_{yy}+h_{26}P_ye_{xy} ,\\ \varphi_5^{c}=h_{21}P_ye_{xx}+h_{22}P_ye_{yy}+h_{16}P_xe_{xy} ,\end{cases} \tag{4.2e}$$

$$\begin{aligned}\varphi_6={}&q_{12}P_y^2e_{xx}+q_{11}P_x^2e_{xx}+q_{12}P_y^2e_{yy}\\ &+q_{21}P_x^2e_{yy}+2q_{66}P_xP_ye_{xy} ,\end{aligned} \tag{4.2f}$$

where φ_0 is a reference energy, φ_1 is the interdipole exchange energy, φ_2 is the electric anisotropy energy, φ_4 is the elastic energy, φ_5 is the piezoelectric energy which takes two possible forms depending on whether we are in the incommensurate phase or in the ferroelectric phase, φ_6 is the energy of electrostriction, and φ_3 is the interaction energy between polarization and its gradient. This last contribution is essential for the description of the incommensurate phase. It already appears in other circumstances such as the description of the optical rotatory power of certain dielectrics.[53] Here, however, its role is totally different. In fact, if one sets $\delta_2=-\delta_1$, one recovers for φ_3 the so-called *Lifshitz invariant* sometimes considered in theories of the incommensurate phase.[52–54] Here e_{ij} represents the strains, c_{ij} are the moduli of elasticity, h_{ij} are the coefficients of piezoelectricity, and q_{ij} are the coefficients of electrostriction. Two order parameters are in fact considered, the polarization $\vec{P}$ being a primary order parameter and the strain providing a secondary order parameter. Working in the (001) plane *a priori* eliminates elasticity and electromechanical couplings that take place in other planes and which *do* exist for the present symmetry. The final results, however, are not altered by this *a priori* simplification. Furthermore, all field quantities appearing in potentials (4.2) depend only on x (along the $\vec{a}$ axis). The coefficient α_2, dielectric susceptibility along the $\vec{b}$ axis, depends on temperature according to the law[1]

$$\alpha_2=\alpha_0(T-T_0) , \tag{4.3}$$

the other coefficients being assumed practically independent of T. The total energy of the system reads

$$\Phi=\frac{1}{2L}\int_{-L}^{+L}\varphi\,dx . \tag{4.4}$$

Minimization of this expression on account of Eqs. (4.2) and setting $2\delta=\delta_1-\delta_2$, yields the equations that govern P_x and P_y:

$$K_1\frac{d^2P_x}{dx^2}-2\delta\frac{dP_y}{dx}-\alpha_1P_x-\beta_1P_x^3-\gamma P_xP_y^2-2q_{11}e_{xx}P_x-2q_{21}P_xe_{yy}-2q_{66}P_ye_{xy}-\left\{\begin{matrix}+h_{11}e_{xx}+h_{12}e_{yy}\\ +h_{16}e_{xy}\end{matrix}\right\}=0 \tag{4.5a}$$

and

$$K_2\frac{d^2P_y}{dx^2}+2\delta\frac{dP_x}{dx}-\alpha_2P_y-\beta_2P_y^3-\gamma P_x^2P_y-2q_{12}P_ye_{xx}-2q_{22}e_{yy}P_y-2q_{66}e_{xy}P_x-\left\{\begin{matrix}h_{26}e_{xy}\\ h_{21}e_{xx}+h_{22}e_{yy}\end{matrix}\right\}=0\ , \tag{4.5b}$$

while the stress field in domains and walls is given by

$$\sigma_{xx}=c_{11}e_{xx}+c_{12}e_{yy}+q_{12}P_y^2+q_{11}P_x^2+\left\{\begin{matrix}h_{11} & P_x\\ h_{21} & P_y\end{matrix}\right\}=0\ , \tag{4.6a}$$

$$\sigma_{yy}=c_{12}e_{xx}+c_{22}e_{yy}+q_{22}P_y^2+q_{21}P_x^2+\left\{\begin{matrix}h_{12} & P_x\\ h_{22} & P_y\end{matrix}\right\}=0\ , \tag{4.6b}$$

$$\sigma_{xy}=c_{66}e_{xy}+2q_{66}P_xP_y+\left\{\begin{matrix}h_{26} & P_y\\ h_{16} & P_x\end{matrix}\right\}=0\ . \tag{4.6c}$$

Upper and lower terms within braces in Eqs. (4.5) and (4.6) correspond to contributions of piezoelectricity in the incommensurate and ferroelectric phases, respectively. We shall assume that the medium is in equilibrium and *not* subjected to any external fields and we apply the general equations (4.5) and (4.6) to the various phases of the crystal.

1. Paraelectric phase

Then microscopic dipoles are disordered and the resulting macroscopic polarization vanishes. The medium is unstrained and thus

$$P_x=P_y=0,\quad e_{xx}=e_{yy}=e_{xy}=0\ . \tag{4.7}$$

2. Incommensurate phase

We examine at which point does the paraelectric phase disappear to leave room for another phase. To that purpose we perturbate Eqs. (4.5) and (4.6) about the basic state (4.7). The resulting linearized equations read

$$K_1\frac{d^2P_x}{dx^2}-2\delta\frac{dP_y}{dx}-\hat{\alpha}_1P_x=0\ , \tag{4.8a}$$

$$K_2\frac{d^2P_y}{dx^2}+2\delta\frac{dP_x}{dx}-\hat{\alpha}_2P_y=0\ , \tag{4.8b}$$

where we have set

$$\hat{\alpha}_1=\alpha_1+h_{11}\lambda_1+h_{12}\mu_1,\quad \hat{\alpha}_2=\alpha_2-(h_{26}^2/c_{66})\ , \tag{4.9}$$

and λ_1 and μ_1 are coefficients of P_x and P_y in the solution of Eqs. (4.6) with respect to e_{xx} and e_{yy}. Solutions of Eqs. (4.8) can be sought in the form

$$P_x=P_1\cos kx,\quad P_y=P_2\sin kx\ , \tag{4.10}$$

resulting in the following expression for the wave number k (the smallest value has been chosen):

$$k^2=\frac{2\delta^2}{K_1K_2}\left\{\left[1-\frac{K_1\hat{\alpha}_2+K_2\hat{\alpha}_1}{4\delta^2}\right]-\left[\left[1-\frac{K_1\hat{\alpha}_2+K_2\hat{\alpha}_1}{4\delta^2}\right]^2-\frac{K_1K_2\hat{\alpha}_1\hat{\alpha}_2}{4\delta^4}\right]^{1/2}\right\}. \tag{4.11}$$

Stability of the system (4.8) is guaranteed for real k's, hence real positive k^2. This induces us to define a temperature $T_{\rm I}$ by

$$\alpha_{\rm I}=\alpha_0(T_{\rm I}-T_0')=\frac{K_2}{K_1}[(\bar{\alpha})^{1/2}-(\hat{\alpha}_1)^{1/2}]^2\ , \tag{4.12}$$

where we have set

$$T_0'=T_0+(h_{26}^2/\alpha_0c_{66}),\quad (\bar{\alpha})^{1/2}=2\delta(K_2)^{-1/2}\ . \tag{4.13}$$

At $T=T_{\rm I}$ the wave number takes the value $k_{\rm I}$ such that

$$k_{\rm I}^2=(\hat{\alpha}_1\alpha_{\rm I}/K_1K_2)^{1/2}\ . \tag{4.14}$$

The temperature T_0' is "stiffened" by piezoelectricity. At $T=T_0'$, we have $\hat{\alpha}_2=0$ and $k=0$, which bounds the stability of the incommensurate phase to the temperature interval $[T_0',T_{\rm I}]$. This means that for $T>T_{\rm I}$ only the solution (4.7) is admissible. For $T=T_{\rm I}$, the paraelectric-incommensurate phase transition occurs, below which the period $2\pi/k$ of the modulation (4.10) is *not* commensurate with the lattice spacing. As T decreases further, the wave number k decreases while the period of the modulation (4.10) increases drastically as T approaches T_0' from above. The harmonic model is no longer adequate. The transition at T_0' requires anharmonicity. We shall examine in greater detail the behavior whenever k goes to zero. Substituting from Eq. (4.10) into the potential (4.4) and minimizing the latter with respect to $P_2=P_{\rm inc}$ and $P_1=\lambda P_{\rm inc}$, we obtain the value $P_{\rm inc}$ such that

$$P_{\rm inc}^2=-\frac{4}{3}\frac{\hat{\alpha}_2-\alpha_I}{\beta_1\lambda^4+\beta_2+(2\gamma\lambda^2/3)},\quad \lambda^2=K_2\alpha_I/K_1\hat{\alpha}_1 \tag{4.15}$$

while the corresponding energy reads

$$\Phi_{\rm inc}=-\frac{1}{6}\frac{(\hat{\alpha}_2-\alpha_I)^2}{\beta_1\lambda^4+\beta_2+(2\gamma\lambda^2/3)}\ . \tag{4.16}$$

Electrostriction has played *no* role in the above analysis. The energy (4.16) depends on temperature through $\hat{\alpha}_2$.

3. *Incommensurate-commensurate transition*

As the wave number k goes to zero the symmetry imposed by k disappears while the medium is not yet ferroelectric. Only the electrostrictive terms provide an electromechanical coupling in these conditions. We need not account for φ_3 any longer. In these conditions let us first consider the strain state at the limit of the domains, i.e., for $x \to \pm\infty$. Then $P_x \to 0$ and $P_y \to \pm P_0$ for a 180° wall. The strain state is given by

$$\begin{aligned} &c_{11}e^0_{xx}+c_{12}e^0_{yy}+q_{12}P_0^2=0\,,\\ &c_{12}e^0_{xx}+c_{22}e^0_{yy}+q_{22}P_0^2=0\,,\\ &c_{66}e^0_{xy}=0\,, \end{aligned} \tag{4.17}$$

from which it follows that

$$e^0_{xx}=\lambda_2P_0^2,\;\; e^0_{yy}=\mu_2P_0^2,\;\; e^0_{xy}=0\,, \tag{4.18}$$

where λ_2 and μ_2 are combinations of elasticity and electrostriction coefficients obtained in solving Eqs. (4.17) for the strains. Here, P_0 is an *unknown*. The distributions of strains both in domains and the wall are functions of x only. This is true similarly for the stresses. Therefore, e_{yy} is constant and equal to its limiting value e^0_{yy}. The other components are given by

$$\begin{aligned} &e_{xx}=-\frac{c_{12}\mu_2}{c_{11}}P_0^2-\frac{1}{c_{11}}(q_{12}P_y^2+q_{11}P_x^2)\,,\\ &e_{xy}=-2\frac{q_{66}}{c_{66}}P_xP_y\,. \end{aligned} \tag{4.19}$$

In these expressions both $e^0_{yy}=\mu_2P_0^2$ and $e^0_{xx}=-c_{12}\mu_2P_0^2/c_{11}$ are internal strains induced by the polarization in the domains. These strains do not check the usual compatibility conditions. This means that the inhomogeneous distribution of polarization within the domains and walls provides a source of *fictitious defects* (quasidislocations) induced by electrostriction. On substituting from Eqs. (4.19) into Eqs. (4.5) we obtain

$$K_1\frac{d^2P_x}{dx^2}-A_1P_x-B_1P_x^3-CP_xP_y^2=0\,, \tag{4.20a}$$

$$K_2\frac{d^2P_y}{dx^2}-A_2P_y-B_2P_y^3-CP_x^2P_y=0\,, \tag{4.20b}$$

where we have set

$$\begin{aligned} &A_1=\alpha_1+2\mu_2\left[q_{21}-q_{11}\frac{c_{12}}{c_{11}}\right]P_0^2\,,\\ &A_2=\alpha_2+2\mu_2\left[q_{22}-q_{12}\frac{c_{12}}{c_{11}}\right]P_0^2\,,\\ &B_1=\beta_1-2\frac{q_{11}^2}{c_{11}}\,,\\ &B_2=\beta_2-2\frac{q_{11}^2}{c_{11}}\,,\\ &C=\gamma-2\frac{q_{11}q_{12}}{c_{11}}-4\frac{q_{66}^2}{c_{66}}\,. \end{aligned} \tag{4.21}$$

Owing to the boundary conditions the system (4.20) has solutions

$$P_x=Q_0/\cosh(qx),\;\; P_y=P_0\tanh(qx)\,, \tag{4.22}$$

where q, Q_0, and P_0 are determined from

$$q^2=-\frac{A_2}{2K_2}\,\frac{1-(CA_1/A_2B_1)}{1+(3K_1C/2K_2B_1)}\,, \tag{4.23}$$

$$Q_0^2=P_0^2(CK_2+B_2K_1)/(CK_1+B_1K_2)\,, \tag{4.24}$$

and

$$P_0^2=-\alpha_2/\hat{\beta}_2 \tag{4.25}$$

with

$$\hat{\beta}_2=\beta_2-2\frac{q_{12}^2}{c_{11}}+2\mu_2\left[q_{22}-q_{12}\frac{c_{12}}{c_{11}}\right]. \tag{4.26}$$

This implies that $\alpha_2=\alpha_0(T-T_0)<0$, hence that $T<T_0$. The solution (4.22) corresponds to the description of a wall through which polarization evolves in a plane perpendicular to it. We therefore recover the description of Sec. II. The wall thickness is q^{-1}. In some manner, the solution (4.22) corresponds to *vectorial solitons* in the static case (compare Ref. 55). It is the limit solution of the incommensurate phase when k goes to zero. In effect, the period of modulation becomes extremely large and polarizations form domains separated by walls described by Eqs. (4.22). This means that in the neighborhood of T_0' ferroelectric domains form, demonstrating thus the ferroelectric order *within* the incommensurate phase. However, a more correct study of the nonlinear system (4.5) would require looking for anharmonic periodic solutions and then studying the limit of these solutions for an infinite period (recovering thus the notion of soliton). The structural transition of the crystal should then be described with some refinement.

The general strains (4.19) can be evaluated from the solution (4.22). We can also compute the wall energy and obtain an expression of the form

$$\Phi_w=-\nu\alpha_2^2/\alpha_I^2\,, \tag{4.27}$$

where ν is a temperature-dependent coefficient which still depends on the dielectric, mechanical, and electromechanical properties of the crystal. We assume this coefficient, whose rather complex expression can be evaluated, to be positive. The present approach to the influence of electromechanical couplings on the formation of domains clearly complements previous macroscopic theories of domains and walls[56] (see also Ref. 45) and it extends them to the case of ferroelectrics with an incommensurate phase. This approach is quite different from the one used in other theories for this type of phase.[57,58] Here, electromechanical couplings have the effect of altering both the linear and the nonlinear electric susceptibilities [see, e.g., Eqs. (4.21)] so that there can occur either a stiffening or a softening of these coefficients and this, in turn, has an influence on the wall properties [e.g., its thickness, Eq. (4.23)].

4. Commensurate-ferroelectric phase

As temperature decreases further from T_0' a state of uniform polarization spreads, yielding the ferroelectric phase. In this case the order parameter P is constant and given by (cf. Ref. 19)

$$P_x=0,\ \ P_y=P_S=(h^2-\bar{\alpha}_2)^{1/2}-h\ , \tag{4.28}$$

where we have set

$$\begin{aligned} h&=3(h_{21}a_{11}+h_{22}a_{21})/2\beta_2',\ \ \bar{\alpha}_2=\alpha_2'/\beta_2'\ ,\\ \alpha_2'&=\alpha_2-c_{11}a_{12}^2-c_{22}a_{22}^2-2c_{12}a_{11}a_{22}\\ &\quad -2h_{21}a_{12}-2h_{22}a_{22}\ ,\\ \beta_2'&=\beta_2+2c_{11}a_{11}^2+2c_{22}a_{21}^2+2c_{12}a_{11}a_{22}\\ &\quad +2q_{12}a_{11}+2q_{21}a_{21}\ . \end{aligned} \tag{4.29}$$

The strain state is defined by the following equations:

$$\begin{aligned} &c_{11}e_{xx}^0+c_{12}e_{yy}^0+q_{12}P_S^2+h_{21}P_S=0\ ,\\ &c_{12}e_{xx}^0+c_{22}e_{yy}^0+q_{22}P_S^2+h_{22}P_S=0,\ \ c_{66}e_{xy}^0=0\ . \end{aligned} \tag{4.30}$$

From the latter we extract the strain field in terms of P_S:

$$e_{xx}^0=a_{11}P_S^2+a_{12}P_S,\ \ e_{yy}^0=a_{21}P_S^2+a_{22}P_S, e_{xy}^0=0\ , \tag{4.31}$$

where the coefficients a_{11} and a_{21} can be expressed in terms of the elasticity moduli and the electrostriction coefficients while a_{12} and a_{22} involve the elasticity moduli and the piezoelectricity coefficients. The corresponding energy is given by

$$\Phi_c=\frac{1}{4}\alpha_2'P_S^2\left[1+\frac{2}{3}\frac{h\beta_2'}{\alpha_2'}P_S\right]\ . \tag{4.32}$$

P_S in Eq. (4.28) defines the spontaneous polarization. This expression is valid for $\alpha_2'<0$ and this condition defines a transition temperature for which P_S vanishes, hence $\alpha_2'=0$; that is, T_0'' such that

$$\begin{aligned} T_0''=T_0+\frac{1}{\alpha_0}(&c_{11}a_{12}^2+c_{22}a_{22}^2+2c_{12}a_{12}a_{22}\\ &+2h_{21}a_{12}+2h_{22}a_{22})\ . \end{aligned} \tag{4.33}$$

With this notation it is possible to write $\alpha_2'=\alpha_0(T-T_0'')$. If we assume that $T_0''>T_0$, then we shall say that *piezoelectricity favors the first-order incommensurate-commensurate transition.*

Let us examine the stability of the ferroelectric phase. On linearizing Eqs. (4.5) and (4.6) about the state $\{P_S,e_{xx}^0,e_{yy}^0,e_{xy}^0\}$, we obtain the following system for the perturbations in P_x and P_y:

$$\begin{aligned} &K_1\frac{d^2\tilde{P}_x}{dx^2}-2\delta\frac{d\tilde{P}_y}{dx}-\tilde{\alpha}_1\tilde{P}_x=0\ ,\\ &K_2\frac{d^2\tilde{P}_y}{dx^2}+2\delta\frac{d\tilde{P}_x}{dx}-\tilde{\alpha}_2\tilde{P}_y=0\ , \end{aligned} \tag{4.34}$$

where we have set

$$\begin{aligned} \tilde{\alpha}_1&=\alpha_1+\gamma P_S^2-[(2q_{66}P_S+h_{16})^2/c_{66}]+2(q_{11}e_{xx}^0+q_{21}e_{yy}^0)\ ,\\ \tilde{\alpha}_2&=\alpha_2+3\beta_2P_S^2+(2q_{12}P_S+h_{21})\lambda_3\\ &\quad +(2q_{22}P_S+h_{22})\mu_3+2(q_{12}e_{xx}^0+q_{22}e_{yy}^0)\ . \end{aligned} \tag{4.35}$$

In order to obtain the system (4.34) we have perturbed Eqs. (4.6) about the ferroelectric state and accounted for the state of strains. The coefficients λ_3 and μ_3 come out from this manipulation ($\tilde{e}_{xx}=\lambda_3\tilde{P}_y$, $\tilde{e}_{yy}=\mu_3\tilde{P}_y$). At this point, the stability study is identical to the one made for the incommensurate phase. Looking for harmonic solutions with factor $\exp(ikx)$, we obtain a wave number k in the same form as in Eq. (4.11) but with $\hat{\alpha}_1$ and $\hat{\alpha}_2$ replaced by $\tilde{\alpha}_1$ and $\tilde{\alpha}_2$. Stability is guaranteed for real positive k^2's. This results ultimately in $T<T_0''$; which holds true since $T<T_0'$. Therefore, the stability of the ferroelectric phase is guaranteed once we have already gone through the incommensurate-commensurate transition.[52] The latter occurs when the energies of the two phases match. This takes place at a temperature T_{II} defined by

$$\Phi_{\text{inc}}(T_{\text{II}})=\Phi_c(T_{\text{II}})\ . \tag{4.36}$$

From Eq. (4.38) we deduce that $\alpha_{\text{II}}=\alpha_0(T_{\text{II}}-T_0)$. This transition is a first-order one.

5. Recapitulation

A recapitulation of the above-described transition is in order. First we have the second-order paraelectric-incommensurate transition at temperature T_{I}. The incommensurate phase takes over for $T_0'<T\le T_{\text{I}}$ with a wave number given by Eq. (4.11). This wave number goes rapidly to zero when T approaches T_0' from above. Then for $T<T_0'$, the anharmonic model dominates if the temperature lies in the interval (T_{II},T_0). In this interval the commensurate phase is initiated with the formation of domains while the solution (4.22) holds good. Finally, for $T<T_{\text{II}}$, the stable commensurate ferroelectric phase is established with all polarizations aligned to give rise to the spontaneous polarization P_S. The existence of the incommensurate phase has the effect of smoothing out the transition between a disordered phase and an ordered phase where the order is described by a periodic solution while disorder was characterized by the incommensurability of the period. Then order dominates to yield the commensurate phase where polarization is uniform. Figure 7 gathers the various energy curves Φ_{inc}, Φ_w, and Φ_c versus the ratio $\alpha_2/\alpha_{\text{I}}$ (or T), with the various transition points. The real global energy curve is obviously less schematical. Finally, Fig. 8 gives a schematic representation of the distribution of the P_y component of the order parameter as it evolves with temperature.

Here we have given a physical interpretation of the model of ferroelectrics with a molecular group—such as $NaNO_2$—in terms of the incommensurate-commensurate phase transition. However, the model of this section is more complete than the simple one previously devised from a lattice since a continuum model allows one to easily account for material symmetry and, thus, for electromechanical couplings. If we wish to pursue the analogy between the present model and the model of Sec. II we

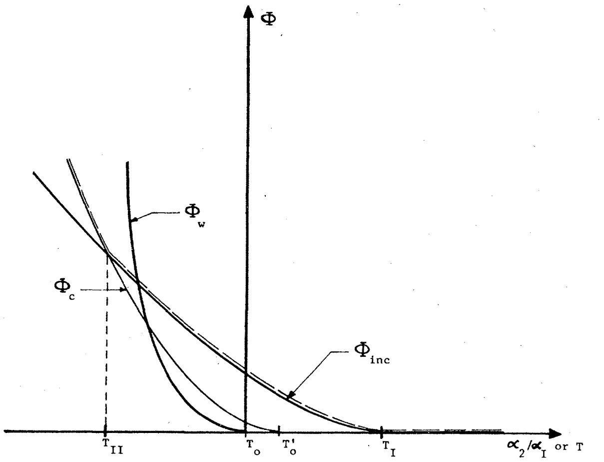

FIG. 7. Thermodynamical potential for different phases as a function of $\alpha/\alpha_{\mathrm{I}}$ and transition temperatures.

must set $P_x = P_0\cos\theta$, $P_y = P_0\sin\theta$, $e_{yy} = 0$ and then, by identifying, we note $c_{66} = \hat{C}_{\perp}$, $e = 2q_{66}P_0^2$, $\chi = \alpha_2 P_0^2/2$, $q_{12} = q_{11} = 0$, and K is replaced by $KP_0^2\,(K_1 = K_2)$, P_0^2 still being defined by Eq. (4.25) with $\hat{\beta}_2 = \beta_2 - \beta_1 = \beta$. With this notation, the energy density (4.1) reduces to the integrand of Eq. (4.3), and we find in this particular case that the wall energy (4.27) is given by

$$\Phi_w = -\frac{\alpha_2^2}{2\beta}\left[1 + \frac{4q_{66}^2}{\alpha c_{66}} P_0^2\right] . \tag{4.37}$$

This can be identified as Σ/δ, where Σ is defined in Eq. (3.46) and δ is the wall thickness (3.49). This shows how, in a certain manner, the description using two components (P_x, P_y) is equivalent to the one using the dipole orientation θ in the context of the study of walls.

The model thus devised differs either from certain models which have only one order parameter and do not account for couplings with strains (e.g., Refs. 19 and 20), or from other models with two order parameters (e.g., Refs. 17, 20, 54, 59, and 60) or else, models proposed for improper ferroelectrics.[61] In theories with two order parameters, one of the latter corresponds to the P_y component of the polarization and the other is the shear-strain component e_{xy} for the case of sodium nitrite.[62] Very early models have been proposed in order to describe the incommensurate phase of $NaNO_2$. A first model consists in a structure in microdomains in which the microscopic dipoles of a layer of (100) plane—or $(\vec{b}, \vec{c})$ plane—have the same orientation.[63] Two types of microdomains are possible, those corresponding to dipoles parallel to $\vec{b}$ and those corresponding to dipoles antiparallel to $\vec{b}$. A microdomain is made of several layers and the pattern of the two types of microdomains is periodic along $\vec{a}$. In a second model, in each layer of (100) plane there exists a local order such that the average of dipoles in this plane varies sinusoidally along $\vec{a}$. In other terms, one can say that the probability of occupying a direction parallel or antiparallel to $\vec{b}$ is a sinusoidal function of period $2\pi/k$.[64] In those models the medium is considered as an Ising system of elements $S = \pm 1$. If, in addition, one considers a global displacement of atoms within the same crystalline cell in the $\vec{b}$ direction with the same sinusoidal variation as the polarization, then one obtains a model where the transverse acoustic mode is accounted for.[65] This idea has allowed one to improve the structural factor which characterizes the x-ray diffraction by the crystal lattice. Along the same line of thought, we note that a two-mode model has been built;[47] these two modes, a polarization mode and a shear mode, may couple and cause a structural resonance at a wave number $k_0 \neq 0$, hence a possible explanation of the incommensurate phase. In our model, there are two order parameters, the polarization $\vec{P}$ with two components and the deformation. Their roles in the description of the phase transitions are obviously not equivalent. The polarization dominates the phenomena, and this directly follows from a continuum description where only reasonings related to macroscopic parameters are performed, thus eliminating *a priori* any representation in terms of order parameters issued from microscopic considerations. Note also that other theories accounting for two order parameters lead to a model which also explains the formation of domains in terms of solitons ("phasons"; for instance, Refs. 59, 60, and 66), where the latter are governed by a sine-Gordon equation quite similar to the one deduced in Sec. II above. However, physical interpretations differ. In the present case the mechanical contribution (strain)—via the electromechanical couplings—plays an important role in the study of domains and walls. Indeed, if we associate to strains a "wall" that would correspond to the crystal-lattice distortion induced by the "wall" due to polarization, we can show that the first of these walls is much thicker than the second one [if $\delta(e_{xx})$ and $\delta(e_{xy})$ are wall thicknesses corresponding to strains e_{xx} and e_{xy}, from Eqs. (4.19) we have the following estimates: $\delta(e_{xx}) \simeq 3\delta_w$ and $\delta(e_{xy}) \simeq 4\delta_w$, where δ_w is the thickness related to P_y]. This could provide an explanation for the rather important thickness observed in $NaNO_2$.[50,51] With the estimate of Sec. III $\delta_w \simeq 5.4 \times 10^{-2}$ μm, so that $\delta(e_{xx}) \simeq 0.162$ μm and $\delta(e_{xy}) \simeq 0.216$ μm. This is to be compared to wall thicknesses observed in improper ferroelectrics where

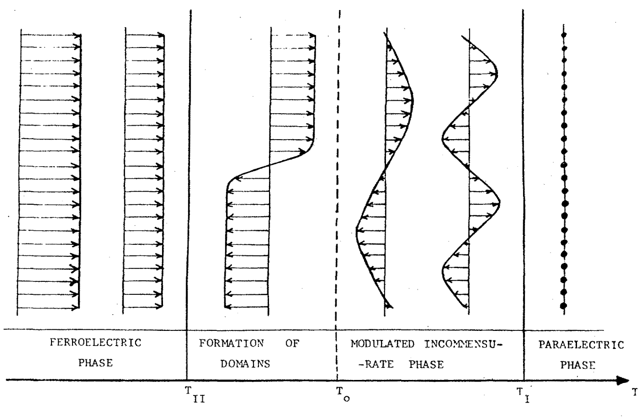

FIG. 8. Schematic representation of the evolution with temperature of the distribution of the P_y component of the order parameter (electric polarization).

strains induced by electrostriction contribute to a thickening of the walls.[56,67] This is inherent in the type of electromechanical coupling (electrostriction) which is naturally accounted for in a continuum model and that we recover in Sec. II. On the other hand, it seems, also, that strains play a certain role in the phenomenon of incommensurate phase. This fact is not excluded by x-ray diffraction experiments.[68,69]

In the present study we have excluded the action of external mechanical and electric fields. In reality, however, an electric field[62,70] and an applied stress[62] have an influence on the phase transition at the incommensurate phase [this materializes in (E,T) and (σ,T) diagrams]. A wall can be displaced by applying an electric field. The latter acts upon the electric dipoles which, in turn, generate forces which have for effect to distort the lattice, and thus to change the wall thickness. One, therefore, should evaluate a wall thickness in the presence of an applied electric field. Similar evaluations could be envisaged for applied stresses. At the level of a wall, fields are not uniform. They thus create a ponderomotive force which acts on the crystal lattice and a local electric field will characterize the polarization-lattice interactions which must have some effects on the wall behavior. Other possible refinements are as follows. In problems of walls and incommensurate phases where steep gradients in polarization and strains are observed on a length scale of the order of 10 to 100 times the lattice spacing, one should devise a *semi microscopic theory* where *second gradients of strains*[53] could be introduced in order to comprehend spatial disuniformities of the order of a few lattice spacings at the scale of walls and incommensurate structural distortions. Such a model, involved as it may be, could provide a better description of a wall structure which may be complex when walls involve microdomains. Finally, higher-order (e.g., sixth) powers of the $\vec{P}$ components could be introduced to describe more precisely the *first-order* incommensurate-commensurate transition.

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