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Nonlinear travelling waves in ferroelectrics

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We investigate nonlinear travelling waves, solving the equations of motion of a diatomic chain model in the continuum limit. The polarizability of one sublattice is assumed to be nonlinear, leading to a local on-site ϕ^4_- potential. Besides periodic nonlinear waves, previously discovered in a monatomic linear chain, we find kink solutions describing the static and dynamic properties of the ferroelectric domain walls, and pulse solutions. In particular, travelling-pulse excitons are described and seen to carry a large dipole moment.

I. INTRODUCTION

In previous papers[1,2] it has been shown that displacive-type ferroelectric phase transitions can be described in terms of a shell model with nonlinear polarizability at the chalcogenide-ion lattice site. The most important dynamical features of the three-dimensional model can be reproduced by a simple diatomic chain version. A fairly accurate description of the temperature-dependent quantities, such as the soft mode, the dielectric constant and the phonon dispersion, can be given in the self-consistent phonon approximation (SPA) provided that the three-dimensional character is taken into account in the phase-space integration. The advantage of the linear chain model is, besides its physical transparency, the possibility of studying the exact nonlinear solutions of the equations of motion.

The model Hamiltonian for the diatomic linear chain is

$$H=\tfrac{1}{2}\sum_n[m_1\dot u_{1n}^2+m_2\dot u_{2n}^2+m_e\dot v_{1n}^2+f'(u_{1n+1}-u_{1n})^2+f(v_{1n}-u_{2n-1})^2+g_2(v_{1n}-u_{1n})^2+\tfrac{1}{2}g_4(v_{1n}-u_{1n})^4]\ , \tag{1.1}$$

where u_{1n} and u_{2n} are the core displacements of ions 1 and 2 in the nth cell of the chain, m_1 and m_2 are their respective masses. The shell of ion 1, of mass m_e, has its own displacement v_{1n}. Here however it is convenient to work with the shell-core relative displacement:

$$w_{1n}=v_{1n}-u_{1n}\ . \tag{1.2}$$

f is the nearest-neighbor shell-core force constant, f' the core-core interaction between ions 1 in two adjacent cells, g_2 and g_4 are the harmonic and quartic anharmonic shell-core force constants within ion 1, respectively.

The corresponding equations of motion in the adiabatic approximation ($m_e=0$) are

$$\begin{aligned}m_1\ddot u_{1n}&=f(u_{2n}+u_{2n-1}-2u_{1n}-2w_{1n})+f'(u_{1n+1}+u_{1n-1}-2u_{1n})\ ,\\ m_2\ddot u_{2n}&=f(u_{1n}+u_{1n+1}-2u_{2n}+w_{1n}+w_{1n+1})\ ,\\ 0&=(2f+g_2)w_{1n}+g_4w_{1n}^3-f(u_{2n}+u_{2n-1}-2u_{1n})\ .\end{aligned} \tag{1.3}$$

The SPA treatment of the above equations of motion describes the ferroelectric transition in different regimes, including the quantum regime with the logarithmic corrections, and the saturation effects in the high-temperature limit. It also provides T_c as function of physical parameters such as the ionic masses (isotope effect) and shell-core force constants g_2 and g_4, i.e., the nonlinear polarizability.[1,2]

With regard to the exact solvability of Eqs. (1.3) we note that this kind of equations contains, even in the continuum limit, essential complications when compared to the ϕ^4 model, and belongs in any case to the class of equations to which general methods like the spectral transform[3,4] or the Bäcklund transformations[5] are not applicable.

Nevertheless certain special solutions besides kinks, of the kind occurring in ϕ^4 models, have been found for the lattice case in the form of nonlinear periodic waves and have been called periodons.[6,7] These nonlinear periodic waves which exist also in the static limit, are shown to assist the mode softening in antiferroelectric transitions, such as in K_2SeO_4.[8] In this paper we show that, in the continuum limit, Eqs. (1.3) admit exact travelling solutions as they reduce to a single Bernoulli equation (Sec. II). We find, in addition to nonlinear periodic waves and a variety of kinks, also travelling pulses, which do not occur in ϕ^4 models.

The present classification and analysis of travelling wave solutions in the continuum limit is aimed at clarifying the nature of solutions in the lattice case, even if the question whether continuum nonperiodic solutions keep stable in the lattice case remains open. The discretization problem has recently been tackled by Pnevmatikos *et al.*[9] in the case of monoatomic and diatomic chains with intersite anharmonicity. Most of the periodic and nonperiodic solutions, discussed in Secs. III and IV, respectively, have a clear physical meaning, and are likely to exist also in the lattice case, possibly with a modified form and a finite lifetime. For instance, the existence of nonlinear periodic waves, proved for the lattice,[6–8] can be inferred from the set of oscillating solutions found in the continuum limit (Sec. III).

Travelling pulses, found for both ferroelectric and paraelectric phases (Sec. IV), are particularly intriguing because of their capability of carrying energy and large dipole moments associated with the local nonlinear polarization (Sec. V).

II. SOLUTIONS IN THE CONTINUUM LIMIT

In the continuum limit the nonlinear equations of motion (1.3) for the model diatomic linear chain can be given a wide class of exact solutions in the form of travelling waves. The continuum limit allows in principle for a classification of the solitary solutions which do not have periodic character. However, also slowly varying periodic solitary solutions can be inferred from the present analysis. A rigorous treatment for the lattice case has been given elsewhere.[7,8]

Here, we look for solutions in the travelling wave form:

$$\begin{aligned} u_{1n+1}(t+2a/v)&=u_{1n}(t)\ ,\\ u_{2n+1}(t+2a/v)&=u_{2n}(t)\ ,\\ w_{1n+1}(t+2a/v)&=w_{1n}(t)\ , \end{aligned} \tag{2.1}$$

where a is the interionic distance and v the phase velocity. In the continuum limit we use the expansion with respect to $\tau=2a/v$

$$u_{1n\pm1}(t)=u_{1n}(t)\pm\tau\dot u_{1n}(t)+\tfrac{1}{2}\tau^2\ddot u_{1n}(t)\ , \tag{2.2}$$

and similarly for $u_{2n\pm1}(t)$ and $w_{1n\pm1}(t)$. By eliminating u_{1n} and u_{2n} from the equations of motion, we obtain a single equation at the arbitrary site n for the internal shell-core coordinate $w_{1n}\equiv w$:

$$\ddot w(1+\beta-3\beta w^2/w_F^2)+6\beta w\dot w^2/w_F^2 +(g_2/M)w(1-w^2/w_F^2)=0\ , \tag{2.3}$$

where

$$w_F\equiv\pm(-g_2/g_4)^{1/2} \tag{2.4}$$

represent the minima of the double-well potential. Furthermore,

$$\beta\equiv\frac{g_2}{2f}\ \frac{1}{1-v_2^2/v^2}\ , \tag{2.5}$$

$$\frac{1}{M}\equiv\frac{1}{m_1(1-v_1^2/v^2)}+\frac{1}{m_2(1-v_2^2/v^2)}\ , \tag{2.5'}$$

and

$$v_1\equiv a(4f'/m_1)^{1/2}\ ,\quad v_2\equiv a(2f/m_2)^{1/2} \tag{2.6}$$

are the two limiting acoustic velocities at the critical temperature (i.e., for $g_T\to0$; see Ref. 2); Eq. (2.4) is of Bernoulli type; it can be integrated by setting $q(w)\equiv\dot w^2$ [and hence $q'(w)\equiv 2w$]. The first integral of motion turns out to be

$$\tfrac{1}{2}\mu\dot w^2=-\frac{\mu}{2M}\ \frac{V(w^2)-V(w_0^2)}{(1+\beta-3\beta w^2/w_F^2)^2}\ , \tag{2.7}$$

where $\pm w_0$ are two turning points, $\mu\equiv m_1m_2/(m_1+m_2)$ is the diatomic cell reduced mass and

$$V(w^2)=g_2w^2[1+\beta-\tfrac{1}{2}(1+4\beta)w^2/w_F^2+\beta w^4/w_F^4]\ . \tag{2.8}$$

The right-hand side of (2.7) defines the effective potential for the shell-core displacement:

$$U(w)=\frac{1}{2}\ \frac{\mu}{M}\ \frac{V(w^2)-V(w_0^2)}{(1+\beta-3\beta w^2/w_F^2)^2}\ . \tag{2.9}$$

Solving with respect to time, we have

$$t=\tfrac{1}{2}(-M)^{1/2}\int^{w^2}dx\frac{1+\beta-3\beta x/w_F^2}{[x(x-w_0^2)R(x)]^{1/2}}\ , \tag{2.10}$$

where the lower integration limit is omitted due to the arbitrariness of the time-scale zero; and

$$R(x)\equiv[V(x)-V(w_0^2)]/(x-w_0^2)\equiv ax^2+bx+c \tag{2.11}$$

is a quadratic expression of x with coefficients

$$a=\beta g_4^2/g_2\ , \tag{2.12}$$

$$b=\tfrac{1}{2}g_4(1+4\beta)\ , \tag{2.13}$$

$$c=g_2(1+\beta)+bw_0^2\ . \tag{2.14}$$

At the turning points, $R(w_0^2)$ is factorized as

$$R(w_0^2)=\frac{dV(w_0^2)}{dx}=g_2(1-w_0^2/w_F^2)(1+\beta-3\beta w_0^2/w_F^2)\ . \tag{2.15}$$

III. PERIODIC SOLUTIONS

Physical solutions of periodic type can be obtained from Eq. (2.10) in the domains where $(x-w_0^2)R(x)$ and $-M$ have the same sign. Slowly oscillating solutions are found for small v and, should the limit $v\to0$ exist, we have static nonlinear oscillations (static periodic waves). If w_1^2 and w_2^2 are the roots of $R(x)$, i.e.,

$$R(w^2)=\beta(g_4^2/g_2)(w^2-w_1^2)(w^2-w_2^2)\ , \tag{3.1}$$

one finds that at low velocity real solutions can only occur, whatever the order of the three turning points w_0^2, w_1^2, and w_2^2, for either $w^2\le\min(w_0^2,w_1^2,w_2^2)$, or for w^2 between the two larger values. Here we investigate only the solutions obeying the first condition (oscillations across the origin), since they form a continuous set with respect to the parameter v, whereas the solutions coming from the second condition may possibly have a physical meaning only for exceptional values of v (see Sec. IV B). We also assume $w^2\le w_0^2<w_1^2<w_2^2$, since any permutation of the turning points leaves the discussion unchanged. The right-hand number of Eq. (2.10) can be expressed in terms of elliptic integrals of first and third kind. For the present discussion, however, a series representation of the integral is more expedient. Setting $w/w_0=\cos y$, performing the expansion

$$\frac{1+\beta-3\beta w^2/w_F^2}{R^{1/2}(w^2)} =\frac{1+\beta-3\beta w_0^2/w_F^2}{R^{1/2}(w_0^2)}\left[1+\sum_{m=1}^{\infty}a_m\sin my\right]\ , \tag{3.2}$$

where a_m are certain coefficients, and using the factorization (2.15), we obtain from (2.10)

$$\Omega t = -\arccos\left[\frac{w}{w_0}\right] - \sum_{m=1}^{\infty} \frac{a_m}{m}\beta \mathcal{P}_m\left[\frac{w}{w_0}\right], \quad (3.3)$$

where

$$\Omega = \left[\frac{g_2}{M}\frac{1-w_0^2/w_F^2}{1+\beta-3\beta w_0^2/w_F^2}\right]^{1/2} \quad (3.4)$$

and

$$\mathcal{P}_m(z) \equiv 1-\cos(m\arccos z) \quad (3.5)$$

are polynomials that vanish at $z=1$. Slow travelling periodic waves are found as asymptotic solutions for $v \to 0$; in this case Eq. (3.4) transforms into the condition

$$\Omega\tau \equiv 2ak = \left[-\frac{2g_2}{f^*}\right]^{1/2}\left[1-\frac{w_0^2}{w_F^2}\right]^{1/2}, \quad (3.6)$$

where $f^* \equiv 2ff'/(f+2f')$ is an effective force constant. These are travelling periodic waves of wave vector k, having a k-dependent amplitude

$$w_0^2 = w_F^2\left[1+\frac{2f^*}{g_2}a^2k^2\right]. \quad (3.7)$$

It is very interesting to note that one can recover the lattice results for static periodic waves from the present continuum treatment by considering the factor $2a^2k^2$ in (3.7) as the lowest order term in the expansion of $1-\cos(2ak)$. From the substitution $2a^2k^2 \to 1-\cos(2ak)$ and from the commensurate periodic wave condition $2ak = 2\pi/N$ for integer N, we obtain the various wave amplitudes $w_{0,N}^2$

$$\begin{aligned} w_{0,1}^2 &= w_{0,\infty}^2 = w_F^2, \\ w_{0,2}^2 &= \left[1+\frac{2f^*}{g_2}\right]w_F^2, \\ w_{0,3}^2 &= \left[1+\frac{3f^*}{2g_2}\right]w_F^2, \\ w_{0,4}^2 &= \left[1+\frac{f^*}{g_2}\right]w_F^2, \\ w_{0,5}^2 &= \left[1+\left[2\sin^2\frac{\pi}{5}\right]\frac{f^*}{g_2}w_F^2\right], \\ w_{0,6}^2 &= \left[1+\frac{f^*}{2g_2}\right]w_F^2, \end{aligned} \quad (3.8)$$

etc. These solutions coincide with those obtained by Büttner and Bilz[6] for the monoatomic case, where the effective force constant f_r corresponds identically to $\frac{1}{2}f^*$. The first solution ($N=1,\infty$) gives the ferroelectric case, for $N=2$ we have the ordinary antiferroelectric case, while for $N \geq 3$ we have commensurate periodic wave solutions.

Clearly, for $v=0$ the asymptotic solutions (3.3)–(3.5) exist as *static periodic waves.* Since g_2 is negative and f^* positive, the travelling periodic wave amplitude is always smaller than the ferroelectric amplitude and larger than the antiferroelectric one, namely $w_{0,2}^2 < w_{0,N}^2 < w_{0,\infty}^2$.

IV. NONPERIODIC SOLUTIONS

Physical solutions of nonperiodic type can exist when the integral (2.10) diverges for some value of w^2. In order for a nonintegrable pole to occur, the quartic expression $w^2(w^2-w_0^2)R(w^2)$ at the denominator must have a pair of coincident zeros. Single zeros correspond to ordinary turning points at finite time.

There are two distinct classes of solutions corresponding to the conditions $R(w_0^2)=0$ and $R(0)=0$. Their asymptotic extrema are $w=\pm w_F$ *(ferroelectric solutions)* or $w=0$ *(paraelectric solutions),* respectively. Any other choice of coincident zeros can be reduced to one of the above cases.

A. Ferroelectric solutions

If one of the roots of $R(x)$ is w_0^2, we have

$$w_0^2 = w_F^2 \quad \text{or} \quad w_F^2(1+\beta)/3\beta\,. \quad (4.1)$$

Due to the factor $1+\beta-3\beta x/w_F^2$ in (2.10), only the first value of w_0^2 yields a divergence in time, and is here considered. Thus, Eq. (2.10) becomes

$$\Omega_F t = \int^{w^2/w_F^2} \frac{dy}{1-y}\,\frac{1+\frac{3}{2}A_F(1-y)}{y^{1/2}[1+A_F(1-y)]^{1/2}}, \quad (4.2)$$

where we have set

$$A_F \equiv \frac{2\beta}{1-2\beta} = -\frac{g_2}{f}\,\frac{v^2}{v_2^2-(1-g_2/f)v^2} \quad (4.3)$$

and

$$\Omega_F \equiv \left[\frac{2g_2}{M(1-2\beta)}\right]^{1/2}. \quad (4.4)$$

Here the asymptotic extrema of the motion $w_0 = \pm w_F$ are maxima of the effective potential (Fig. 1, left). Also ordinary turning points, occurring where $\partial t/\partial w$ has an integrable divergence, exist at

$$\bar{w} = \pm w_F\left[1+\frac{1}{A_F}\right]^{1/2} = \pm\frac{w_F}{(1-2\beta)^{1/2}}, \quad (4.5)$$

provided that either $A_F > 0$ or ≤ -1.

1. Static and slowly propagating solutions

For static and slowly propagating solutions (small v), A_F is positive, so that no turning point is encountered in the motion between the two asymptotic values $\pm w_F$. These solutions are travelling kinks (K) which do exist also in the static limit, $v \to 0$ *(ferroelectric domain wall).* A necessary condition is

$$v^2 < v_2^2/(1-2\gamma), \quad (4.6)$$

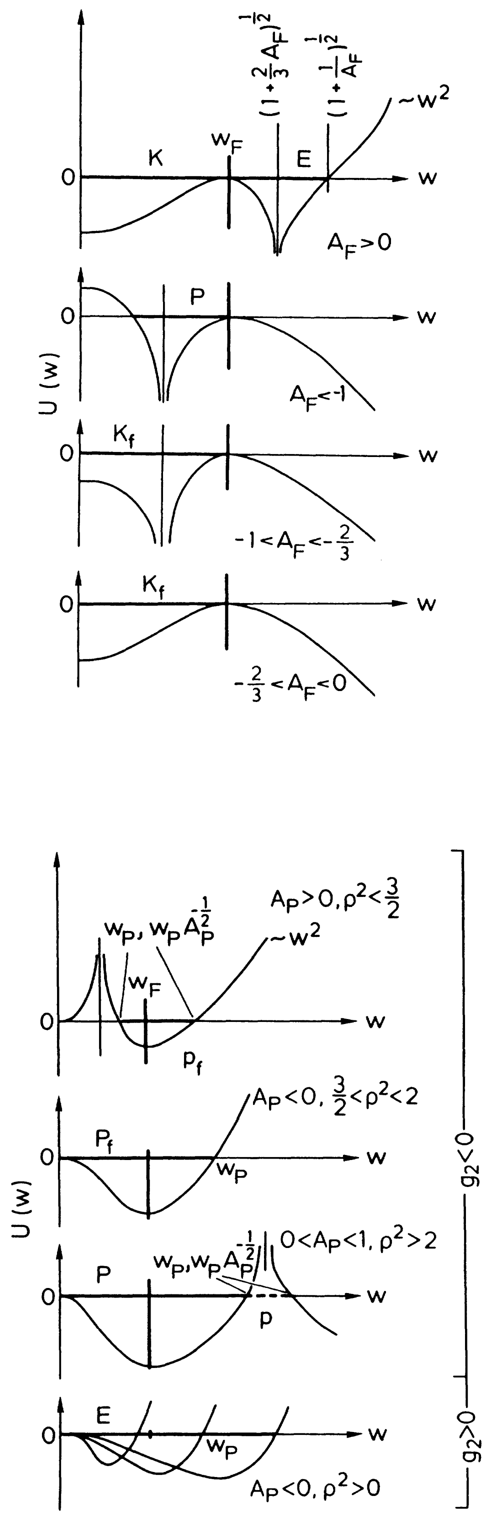

FIG. 1. Effective potentials for ferroelectric waves (above) and paraelectric waves (below). K, slow kinks; E, pulse excitons; P, pulses; K_f, fast kinks; P_f, fast pulses; p_f, fast periodic waves; p, slow periodic waves. The parameters A_F and A_P are defined in the text.

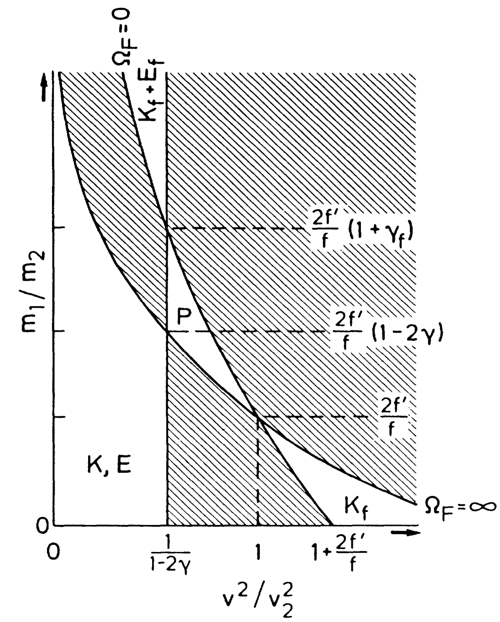

FIG. 2. Existence domains for ferroelectric waves (white areas) as functions of the mass ratio m_1/m_2 and the relative velocity v/v_2.

with $\gamma \equiv g_2/2f$. Moreover, the existence of real turning points $\bar{w}^2 > w_F^2$ allows also for pulse solutions of amplitude $|\bar{w}| - |w_F|$, starting from and arriving to the ground-state polarization. If the local shell motion far beyond the ferroelectric equilibrium is conceived as being associated with some electronic excitation, such pulse solutions can be regarded as travelling excitons (*pulse excitons:* E). However, the larger the excitation, the slower the pulse translation. For $\bar{w}^2 \to \infty$, $v \to 0$, which means that a local ionization process does not propagate at all. The effective potential and the existence domain for these solutions, as well as for those discussed in the next paragraphs, are shown in Figs. 1 and 2, respectively.

2. *Large velocity solutions*

For large values of the ratio m_1/m_2, i.e., for

$$m_1/m_2 > (2f'/f)(1+\gamma_f)$$

with (4.7)

$$\gamma_f \equiv -g_2/f^* ,$$

and in the restricted region $0 < 2\beta < 1$ ($A_F > 0$), there are solutions having either kink or pulse exciton character. Here, however, their velocity is larger than v_1 and therefore we speak of fast kinks and pulse excitons ($K_f + E_f$). These solutions have formally the same expression as slow kinks and pulse excitons (K + E), the only difference being in the value of the parameter Ω_F, namely in the velocity.

3. *Ferroelectric pulse solutions*

For

$$v_2^2/(1-2\gamma)<v^2<v_1^2(1+2f'/f) \ , \tag{4.8}$$

we have $0\le\bar{w}^2\le w_F^2$. No kink is possible, but just a pulse consisting in a frustrated attempt to reverse locally the polarization *(ferroelectric pulse:* P*)*. These solutions, however, exist in a restricted domain of the mass ratio m_1/m_2, as illustrated in Fig. 2. It is, in any case, necessary that

$$2f'/f\le m_1/m_2\le(2f'/f)(1+\gamma_f) \ . \tag{4.9}$$

4. *Fast kink solutions*

For $v\ge v_2$, and again in a restricted region of the mass ratio m_1/m_2 (in any case $m_1/m_2<2f'/f$, where $-1<A_F<0$ and $\bar{w}$ is imaginary), we have exclusively *fast kinks* K_f.

Ground-state kinks and pulse excitons are described by the same implicit equation

$$\Omega_F t=2\ \ln\frac{y^{1/2}+[1+A_F(1-y)]^{1/2}}{|(1-A_F)(1-y)|^{1/2}} -\tfrac{3}{2}A_F^{1/2}\arcsin\left[1-\frac{2A_F y}{1+A_F}\right] \ , \tag{4.10}$$

with

$$y\equiv w^2/w_F^2 \ , \quad A_F\ge 0 \ . \tag{4.11}$$

Slow solutions ($v\to 0$) take a simpler form since A_F is in this case a small quantity and the arcsin term can be neglected. Slow kinks and pulse excitons for $|A_F|\ll 1$ are, respectively, given by

$$\frac{w}{w_F}\cong\frac{1+A_F-(1-A_F)e^{-\Omega_F t}}{[(1-A_F)^2(1+e^{-\Omega_F t})^2+4A_F]^{1/2}} \ , \tag{4.12}$$

$$\frac{w}{w_F}\cong\frac{1+A_F+(1-A_F)e^{-\Omega_F t}}{[(1-A_F)^2(1-e^{-\Omega_F t})^2+4A_F]^{1/2}} \ . \tag{4.13}$$

The asymptotic pulse amplitude is correctly given by $w_F(1+A_F^{-1})^{1/2}\simeq w_F/A_F^{1/2}$. The above expressions give the exact solutions in the static limit ($A_F=0$), respectively, expressed by the hyperbolic tangent and cotangent of $\Omega_F t/2$. Thus the slowly moving kink describing the motion of the Bloch domain wall along the diatomic chain is approximately given by

$$w_{1n}=\left[-\frac{g_2}{g_4}\right]^{1/2}\tanh[\tfrac{1}{2}\Omega_F(t-2an/v)] \ , \tag{4.14}$$

$$u_{1n}=-\frac{2g_2}{M_1\Omega_F^2}w_{1n} \ , \tag{4.15}$$

$$u_{2n}=\frac{g_2}{M_2\Omega_F^2}(w_{1n}+w_{1n-1}) \ . \tag{4.16}$$

Using the asymptotic dispersion relation

$$\Omega_F^2\sim(\gamma_f/a^2)v^2 \ , \tag{4.17}$$

we obtain, for $\Omega_F\to 0$, the shape of the static domain wall

$$w_{1n}=(-g_2/g_4)^{1/2}\tanh(\gamma_f^{1/2}n) \ , \tag{4.18}$$

$$u_{1n}=-w_{1n}/(1+2f'/f) \ , \tag{4.19}$$

$$u_{2n}=\tfrac{1}{2}(w_{1n}+w_{1n-1})/(1+f/2f') \ . \tag{4.20}$$

The width of the static domain wall in cell size units is

$$2\gamma_f^{-1/2}=2(-f^*/g_2)^{1/2}=2(f^*/g_4)^{1/2}w_F \ . \tag{4.21}$$

As v^2 grows from zero to any finite value delimiting the K + E region (Fig. 2), namely either v_1 or $v_2(1-2\gamma)^{-1/2}$, the width Γ of the moving kink decreases from the static value (4.21) to zero according to the expression

$$\Gamma=2\frac{(1-v^2/v_1^2)^{1/2}[1-(1-2\gamma)v^2/v_2^2]^{1/2}}{\gamma_f^{1/2}(1-v^2/v_0^2)^{1/2}} \ , \tag{4.22}$$

where

$$v_0\equiv a(2f+4f')^{1/2}/(m_1+m_2)^{1/2} \tag{4.23}$$

is the ordinary transverse sound velocity. The hybridization of TA with the soft TO branch at the transition has the effect of depressing the sound velocity from v_0 to either v_1 or v_2, so that either v_1 or $v_2(1-2\gamma)^{-1/2}$ (or both) are smaller than v_0. Thus the kink undergoes a sort of relativistic contraction where the limiting velocity, however, is not v_0, but $v_\infty\equiv\min[v_1,v_2(1-2\gamma)^{-1/2}]$.

Examples of exact kink solutions are shown in Fig. 3 for various values of A_F. The contraction does not appear because the abscissa argument $t-2an/v$ has been conveniently multiplied by Ω_F (which diverges with A_F as $v\to v_\infty$). Even in the exact case, however, there is no significant distortion of the kink shape with respect to the antisymmetric hyperbolic tangent valid in the static limit.

In Fig. 4 the pulse excitons for a few positive values of A_F are displayed. For decreasing velocity ($A_F\to 0$), the amplitude diverges, whereas the width tends slowly to zero. Ferroelectric pulses restricted to the domain (4.8) where $A_F<-1$, as well as fast kinks, are represented by the two-logarithm form

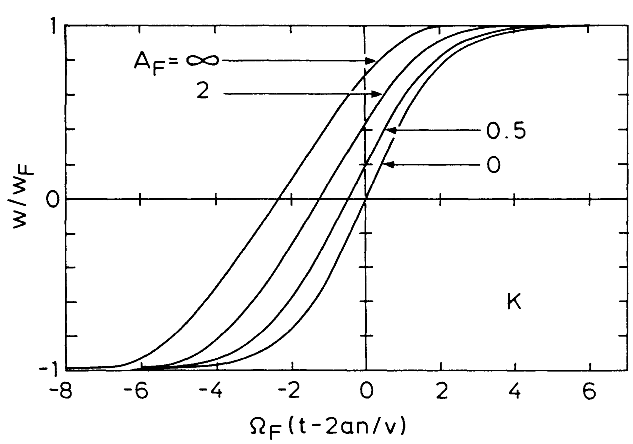

FIG. 3. Slow kinks in the ferroelectric phase for different values of the parameter A_F. A_F increases with the velocity. $A_F=0$ corresponds to the static kink.

$$\Omega_F t = 2\ln\left[\frac{y^{1/2}+[1+A_F(1-y)]^{1/2}}{|(1-A_F)(1-y)|^{1/2}}\right] - 3(-A_F)^{1/2}\ln\left|\frac{(-A_F y)^{1/2}+[1+A_F(1-y)]^{1/2}}{(1-A_F)^{1/2}}\right| . \tag{4.24}$$

The divergent part comes exclusively from the first logarithm, so that there is always a choice of the model parameters such that the second logarithm is small. In this case the ferroelectric pulse is also given by (4.12) [*not* (4.13)]: for $A_F<1$, w/w_F can never change sign, but it clearly takes a pulse form. Figure 5 shows a few examples of ground-state ferroelectric pulses. They are rather flat and broad, their width diverging as $A_F \to -1$. The limit $A_F=-1$ corresponds to an infinitely broad pulse spanning $w=0$ to w_F, whose descending half has gone to infinity. In this way we enter the fast-kink domain: examples for $A_F=-0.5$, -0.6, and -0.8 are shown in Fig. 6.

Pulses of E and P type and fast kinks K_f for $-1<A_F\le -\frac{2}{3}$ show an interesting feature produced by the negative divergence in their effective potentials (Fig. 1). They have pairs of points of vertical slope (indicated by horizontal arrows in Figs. 4–6), where the shell relative velocity is divergent. This is the way these solutions mimic the virtual electronic transitions involved in locally large polarization waves.

B. Paraelectric solutions

$R(x)$ has a vanishing root, namely $R(0)=0$. This requires

$$V(w_P^2)/w_P^2=0 , \tag{4.25}$$

or equivalently that the third coefficient (2.14)

$$c(w_P^2,\tau^2)=0 . \tag{4.26}$$

In this case we have a single asymptotic value $w^2=0$, whereas w_P ($\neq 0$) is an ordinary turning point. Thus the physical solutions of this class are pulses travelling across the paraelectric phase *(paraelectric pulses).*

Inspection of the effective potentials associated with paraelectric solutions (Fig. 1, at right) shows that under certain conditions oscillating solutions do occur in addition to paraelectric pulses. These are just the periodic solutions existing for special values of the velocity which have been disregarded in the discussion of Sec. III. Figure 7 depicts the existence condition of paraelectric solutions, for either $g_2<0$ (above) or $g_2>0$ (below), in the form of a dispersion relation between the velocity and the amplitude w_P:

$$\frac{v^2}{v_2^2}=\frac{2-\rho^2}{2\gamma\rho^4-(1+4\gamma)\rho^2+2(1+\gamma)} , \quad \rho\equiv\frac{w_P^2}{w_F^2} . \tag{4.27}$$

Slow (P) and fast (P_f) pulse solutions occur where the frequency constant

$$\Omega_P\equiv\left[-\frac{4g_2}{M(1+\beta)}\right]^{1/2} \tag{4.28}$$

is real (heavy lines); periodic waves (p,p_f), where Ω_P is imaginary (broken lines). This plot corresponds to the case $v_2>v_1$; it is an easy matter to redraw it for the less common case $v_1>v_2$.

For $g_2<0$ real solutions occur for either $v^2>v_2^2$ or $v^2<v_2^2/(1+8\gamma)$ and correspond to slow, large-amplitude waves and fast, small-amplitude waves, respectively. In both domains we have either periodic waves or pulses. From the effective potential we see that fast solutions are centered around w_F, where the shell displacement reaches the maximum velocity. Also slow pulses are around w_F.

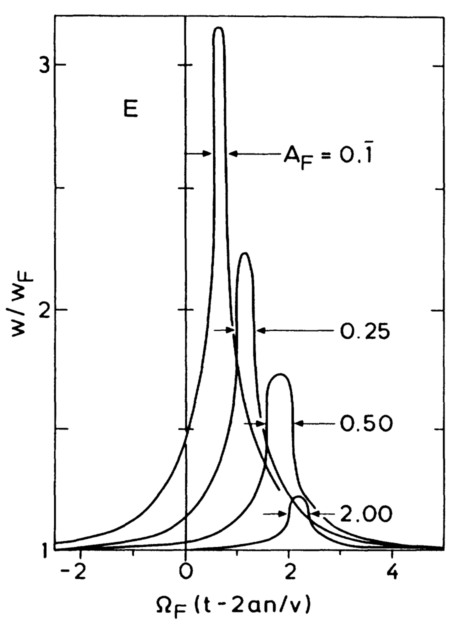

FIG. 4. Pulse excitons in the ferroelectric phase for different values of the parameter A_F. At the limit $A_F=0$ we have a static, infinitely high and narrow peak, corresponding to the ionization limit with its relaxation field. The arrows indicate isolated points of vertical slope.

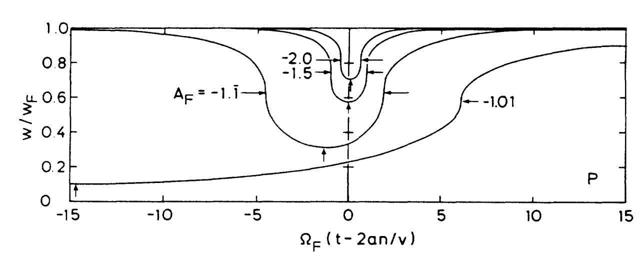

FIG. 5. Pulse waves in the ferroelectric phase. At the limit $A_F=-1$ the pulse becomes infinitely large and transforms into a fast kink. Horizontal arrows indicate isolated points of vertical slope.

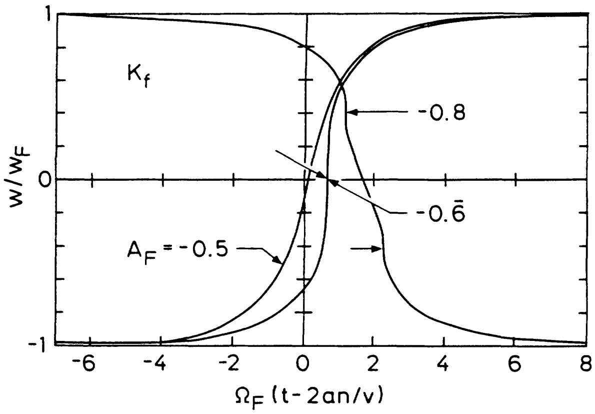

FIG. 6. Fast kinks in the ferroelectric phase. For $A_F < -\frac{2}{3}$ there are two isolated points of vertical slope, at $A_F = -\frac{2}{3}$ one in the center, for $-\frac{2}{3} < A_F < 0$ the kink has a finite slope everywhere.

The effective potential for slow periodic waves is the opposite of the one for slow pulses; slow periodic oscillations occur between w_P and $w_P A_P^{-1/2}$, where

$$A_P \equiv \rho^2 \beta/(1+\beta) , \tag{4.29}$$

and have divergent shell velocity when passing through the singularity of the potential falling between the two extrema. We note that such slow periodic waves would in principle admit a static limit; here, however, A_P vanishes and the amplitude is divergent. In any case, these solutions, centered much above the shell-potential minimum w_F, are to be regarded as unstable, and no longer considered.

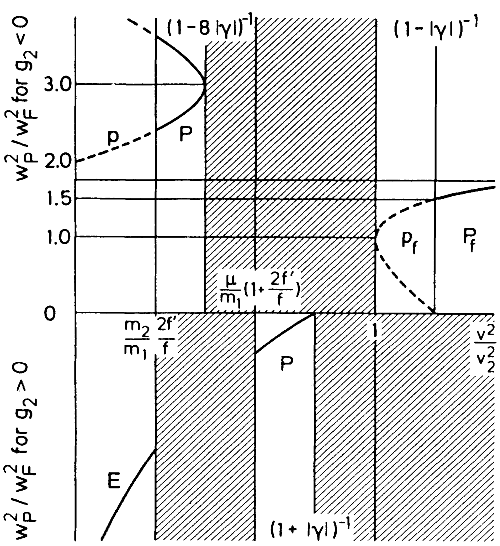

FIG. 7. Existence condition for paraelectric waves with either $g_2 < 0$ (above) or $g_2 > 0$ (below): heavy lines for pulse solutions; broken lines for periodic waves.

1. *Fast periodic waves*

Fast periodic waves are described by the solutions

$$|\Omega_p| t = 2 \arctan \left[\frac{y-1}{1-A_P y} \right]^{1/2} \pm 6 \frac{A_P^{1/2}}{\rho^2} \arctan \left[\frac{A_P(y-1)}{1-A_P y} \right]^{1/2} , \tag{4.30}$$

with $y \equiv w^2/w_P^2$, and the sign chosen on the basis of the physical requirement of a monotonically increasing time. The period is then given by

$$T = \frac{2\pi}{|\Omega_P|} \left[1 \pm 3 \frac{A_P^{1/2}}{\rho^2} \right] . \tag{4.31}$$

Two examples of periodic waves, one for $w_P < w_F$ ($w_p = 0.38 w_F$, $A_P = 0.1$) and one for $w_P > w_F$ ($w_P = 1.2 w_F$, $A_P = 8$) are given in Fig. 8.

Let us consider the limiting solution for $w_P \to w_F$, the amplitude tends to zero and we approach a harmonic oscillation of frequency and wave vector, respectively, given by

$$w = \begin{cases} (2f/m_2)^{1/2} \\ (f/2m_2)^{1/2} \end{cases} , \quad k = \begin{cases} G/\pi = 1/a \\ G/2\pi = 1/(2a) \end{cases} , \tag{4.32}$$

where $G = \pi/a$ is the reciprocal lattice constant and upper (lower) values are used according to the sign choice in (4.30).

The phonon frequency (4.32) clearly belongs to the optical branch at the critical temperature, which is degenerated into an acoustic branch of velocity v_2. In the absence of dispersion, as required in the present continuum limit, the respective wave vector deviates slightly from $\frac{2}{3}$ or $\frac{1}{3}$ of the reduced Brillouin zone. For $\rho^2 \to 1.5$ $[v^2/v_2^2 \to (1-|\gamma|)^{-1}]$ the period goes to infinity together with A_P and the travelling periodic wave degenerates into an infinitely broad pulse. Then for $v^2/v_2^2 \to (1-|\gamma|)^{-1}$ we have fast pulses of decreasing width, corresponding to negative A_P.

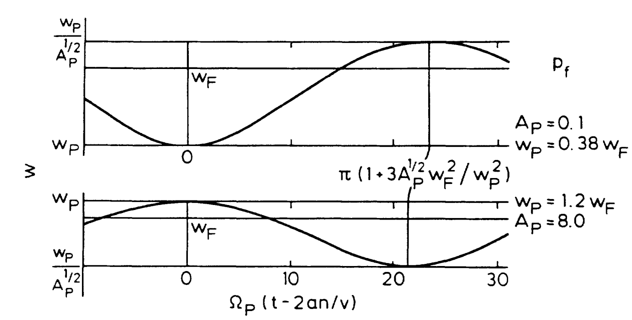

FIG. 8. Fast paraelectric periodic waves for $w_P \to w_F$; the periodic wave tends to the ferroelectric phonon at the critical temperature.

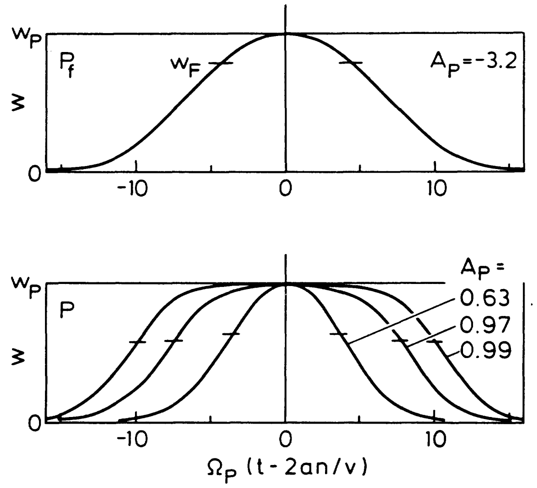

FIG. 9. Fast (above) and slow (below) paraelectric pulses. For $A_P \rightarrow 1$ the slow pulse becomes infinitely wide and degenerates into a kink-antikink pair. The marks indicate the amplitude w_F. Pulses P and E for $g_2 > 0$ are similar to P_f.

2. *Fast pulses*

Fast pulses (P_f) are expressed by a combination of inverse circular and hyperbolic tangents:

$$\Omega_P t = 2 \operatorname{arctanh} \left[\frac{1-y}{1-A_P y} \right]^{1/2} \pm 6 \frac{(-A_P)^{1/2}}{\rho^2} \arctan \left[A_P \frac{1-y}{1-A_P y} \right]^{1/2} . \quad (4.33)$$

Despite the complicated form, they have a fairly regular shape (Fig. 9, above) and a width which contracts for increasing velocity.

3. *Slow pulses*

Slow pulses (P) for $g_2 < 0$ have, unlike P_f, a positive A_p and a double inverse hyperbolic tangent form given by

$$\Omega_p t = 2 \operatorname{arctanh} \left[\frac{1-y}{1-A_P y} \right]^{1/2} \pm 6 \frac{A_P^{1/2}}{\rho^2} \operatorname{arctanh} \left[A_P \frac{1-y}{1-A_P y} \right]^{1/2} . \quad (4.34)$$

A few solutions are illustrated in Fig. 9 (below) for values of A_P approaching unity. The limit $A_P = 1$, corresponding to $w_p = \sqrt{3} w_F$, is particularly interesting because the pulse degenerates in a pair of *infinitely apart kink and antikink,* having a stepwise shape.

4. *Paraelectric solutions for $g_2 > 0$*

The paraelectric solutions are perhaps more interesting in the case $g_2 > 0$ (single-well anharmonic potential), where they exist for either

$$v \le v_1 \ , \quad v_0 \le v \le v_2 \ , \quad (4.35)$$

and have the character of pulse excitons (E) and ordinary pulses (P), respectively. They have $A_P < 0$ and are formally expressed also by (4.33). For $v < v_1$ we may consider the static limit, $v \rightarrow 0$, $A_p \rightarrow -\infty$, in which the amplitude w_P / w_F diverges and the width vanishes. We may regard this limit as an ionization limit, as for the case of ferroelectric pulse excitons.

For $v_0 \le v \le v_2$ we are in the small amplitude range, where $w_P \ll w_F$ and $|A_P| \ll 1$. In this case we can approximate the solution with the more familiar soliton form:

$$W = w_P \operatorname{sech}^2(\tfrac{1}{2}\Omega_P t) \ . \quad (4.36)$$

This pulse, however, travels in the paraelectric phase with a velocity larger than the ordinary acoustic transverse velocity v_0, and is known in the literature to be unstable (see, e.g., Ref. 10).

V. CONCLUDING REMARKS

The diatomic layer model with nonlinear polarizabilities besides providing a microscopic description of the ferroelectric phase transition in the self-consistent phonon approximation, predicts some interesting nonlinear features such as the existence of periodic waves, the statics and dynamics of the Bloch walls in the ferroelectric phase, and the possibility of pulse travelling waves.

In particular the so-called pulse excitons, which admit as a static limit the local ionization, are seen to carry an integrated dipole moment which increases with decreasing velocity (in the ionization limit the dipole moment would be infinite or the shell would be infinitely apart; of course the theory based on an expansion in w^2 breaks down for overly large displacements). We can give an estimation for the dipole moment per unit shell charge p, carried by a pulse exciton in the ferroelectric phase in the case $v \ll v_1, v_2$. This is obtained by integrating the E solutions of Fig. 4:

$$p = \frac{v w_F}{2a\Omega_F} \int_{-\infty}^{+\infty} d\zeta \frac{w}{w_F} \ , \quad (5.1)$$

where ζ is the dimensionless abscissa variable. For small velocities the integral is numerically found to be $\simeq (4A_F)^{-1/2}$, and therefore

$$p \simeq (-ff^*/8g_2 g_4)^{1/2} (v_2/v) \ . \quad (5.2)$$

For example in $SrTiO_3$, using the values of the parameters which fit the experimental phonon branches in the SPA,[2] we find, for $v/v_2 = 0.3$, the value $p = 6.3$ nm, which is a fairly large value as compared to the polarization induced by ordinary optical phonons.

Travelling pulse solutions might have applications in a variety of systems. For example, polarization waves carrying large dipole moments, and consequently large amounts of energy, have been considered to play a crucial role in biomolecules.[11]

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[1]R. Migoni, H. Bilz, and D. Bäuerle, Phys. Rev. Lett. **37**, 1155 (1976).

[2]H. Bilz, A. Bussmann, G. Benedek, H. Büttner, and D. Strauch, Ferroelectrics **25**, 339 (1980); A. Bussmann-Holder, H. Bilz, and P. Vogl, *Dynamical Properties of IV-VI Compounds* (Springer, Berlin, 1983), p. 51. A systematic account of the theory in the self-consistent phonon approximation is to be given in two forthcoming papers.

[3]F. Calogero and A. Degasperis, *Spectral Transform and Solitons: Tools to Solve and Investigate Nonlinear Evolution Equations* (North-Holland, Amsterdam, 1982, 1986), Vols. 1 and 2.

[4]F. Calogero, in *Statics and Dynamics of Nonlinear Systems*, edited by G. Benedek, H. Bilz, and R. Zeyher (Springer, Heidelbeg, 1983), p. 7.

[5]C. Rogers and W. F. Shadwich, *Bäcklund Transformations and Their Applications* (Academic, New York, 1982).

[6]H. Büttner and H. Bilz, J. Phys. (Paris) Colloq. **C6**, C6-111 (1981).

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

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

[9]S. Pnevmatikos, N. Flytzanis, and M. Remoissenet, Phys. Rev. B **33**, 2308 (1986).

[10]S. Aubry, J. Chem. Phys. **64**, 3392 (1976).

[11]H. Bilz, H. Büttner, and H. Fröhlich, Z. Naturforschung **366**, 208 (1981).