Dynamics of domain walls in ferrodistortive materials. I. Theory

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(Received 1 September 1978)

A theoretical study of domain walls in uniaxial displacive ferrodistortive systems is presented. We start from a generalized Langevin equation of motion for the movements of the ions, which includes dissipative terms and external fields, in addition to anharmonic and strain-force terms. We obtain large- and small-amplitude solutions corresponding to domain walls and the usual soft-mode phonons, respectively. We show that apart from translation the domain walls are absolutely stable solutions of our equation and that in external fields they reach a unique terminal velocity. The linear dependence of the velocity on the field allows us to define a temperature-dependent mobility which is related to the diffusion coefficient for the wall. Furthermore, we calculate analytically the dynamic structure factor due to domain walls and soft-mode phonons. We find that the Brownian motion of the domain walls leads to a very narrow Rayleigh peak. As we show in the second paper of this series, our model is useful in correlating and interpreting experiments in this field.

I. INTRODUCTION

In this article we investigate the dynamics of domain walls in certain systems that exhibit structural phase transitions. Such a phase transformation is associated with an instability in the lattice displacement pattern when a crystal is cooled below its critical temperature T_c. From the many materials found to undergo such transitions, several classes have been identified.[1,2] We restrict our study to *displacive* crystals whose lattice displacements change only gradually between neighboring unit cells.

Our theory describes domain-wall motion and its effect on scattering *below* T_c. This contrasts with the many studies of these materials near their critical point.[3–8] In the ferrodistortive regime the systems display two (or more) degenerate ordered states corresponding to different displacement patterns. Depending on preparation, the crystal may be entirely in a state of uniform structure, or in a state with coexisting domains,[9] separated by walls.

Experimentally, domain walls may be observed in a number of ways: although they may be very narrow, their position in a crystal can be seen optically, either directly[10] if the medium is optically active, or generally by the use of an etching agent.[11] The effects of domain-wall motion can be seen in scattering[12,13] and polarization[14,15] experiments. Due to the intrinsic interest of multidomain crystals and their use in electronic applications,[16,17] many such experiments have been carried out in recent years.

Here, we develop a model which allows us to correlate and interpret many of the observations. A complete theoretical description of domain walls is quite difficult since the walls are large-amplitude distortions of high energy. Perturbation and mode-mode coupling techniques,[18] while quite successful in describing low-amplitude fluctuations, are inadequate in treating domain walls.[19,20] We choose therefore a simple model which allows a clear conceptual understanding of *both* the large- and small-amplitude dynamics involved. The second article in this series demonstrates in detail how our model can be interpreted and successfully applied to ferroelectric crystals.

The essential features of our model are as follows: We employ a single degree of freedom to describe the collective ferrodistortive displacement corresponding to the *soft mode*.[1,21–24] The overall crystalline anharmonicity produces the soft mode and also couples this vibrational degree of freedom to many other lattice modes. For this reason we dispense with a Hamiltonian formulation appropriate to conservative systems[19,20] and begin with an equation of motion incorporating the essential phenomenological behavior. Our equation of motion may be viewed as the *projection* from the set of all lattice vibrational modes onto one component u of the soft mode. The interaction between this degree of freedom and the rest of the lattice is introduced through a force derived from an anharmonic crystalline-field potential, a random fluctuating force, and a damping term. The anharmonic potential is characteristic of the average coupling when all other lattice ions assume their equilibrium positions. In the soft-mode model this effective potential is temperature dependent.[1,23] The fluctuating force and damping are related to the thermal motion of the lattice, and account for the nonconservative, dissipative nature of the mode. The lattice modes are thus assumed to constitute a bath in the usual Langevin sense.[25] We allow also for coupling to an external (electric) field.

So as to perform all of our calculations analytically, we specialize the model to one spatial dimension. As we shall see in the second paper of this series, (see following paper) one can account for a variety of physical phenomena in ferrodistortive systems despite this restriction. Thus when we consider a point x on the spatial axis $\hat{x}$, we are in fact referring to an entire plane of atoms through x, normal to $\hat{x}$. For ease of discussion in the following sections we sometimes refer to a mass m in a unit cell centered at point x. However, for physical applications one must keep in mind that the displacements are due to the collective motion of atoms in planes, which can be described as the movement of effective particles of mass m. Moreover, domain walls are not merely segments of a line as the simple one-dimensional formalism suggest at first glance, but rather *volumes* whose surfaces have such small curvature as to be treated as planes.

Other one-dimensional equations of motion have been proposed by Aubry,[20] and Krumhansl and Schrieffer[19] for crystals undergoing structural phase transitions. Our model differs substantially from these in three ways. First, our dissipative model leads to a damped domain-wall motion. For a fixed applied field the walls have a unique terminal velocity.[26] In contrast, the walls in conservative models accelerate to acoustic velocities for any applied field. Second, our model is designed for three-dimensional uniaxial ferrodistortive materials. Our spatial coordinate is normal to the ordering axis, domain walls are parallel to this axis[9,14] and the displacement refers to the positions of planes of atoms. Other models have been generally restricted to quasi-one-dimensional systems and have assumed that the spatial coordinate lies along the ordering axis and that the domain walls are normal to the axis. Third, we assume that domain walls are not equilibrium excitations, but long-lived metastable states. The number of walls is taken to be constant and depends on the history of the sample. The domain walls of our theory are high-energy features which are not readily created or destroyed thermally except very near T_c.

This work addresses questions related to other fields. There is a formal analogy between domain walls in ferroelectrics and the ferromagnetic Bloch domain walls, which were studied extensively[27]; also the description of one-dimensional dislocations is similar.[28] However, as pointed out in Ref. 29, there are considerable differences in the behavior of ferroelectric and of Bloch domain walls, understandably so, since the microscopic interactions responsible for them are physically very different. From the theoretical side our work is akin to a number of recent treatments of the damped-soliton problem[30]; however, the approaches are in each case different from ours (see reference citation for further comments).

The paper is structured as follows: In Sec. II we discuss the motion of domain walls in uniaxial, displacive ferrodistortive materials and introduce our equation of motion. We indicate the physical origin of each of the terms in the equation and remark that in structure it corresponds to a generalized Langevin equation. In the following Secs. III–V, we derive the *dynamical* properties of domain walls in the model and obtain expressions for a number of experimentally accessible quantities.

Section III considers the macroscopic motion of a domain wall in the presence of an external field. We show that a wall initially accelerated by an external field attains a terminal velocity of propagation. At low external field this velocity is linearly proportional to the field and vanishes at zero field. This allows us to define a mobility. We also examine the stability of the planar domain walls to small perturbations in the displacement coordinate. We find that due to the explicit inclusion of damping (providing an energy-dissipating mechanism), the domain wall is *absolutely* stable to all perturbations apart from a shift in position. This marginal stability is a consequence of the translational invariance of our equation of motion. From the stability analysis we explore the interaction between the quasiharmonic excitations and the domain walls. With each domain wall the density of phonon states changes since two-phonon modes become bound to it. The first mode corresponds to the translational mode of the wall while the second one is an oscillating perturbation of the domain-wall profile.

In Sec. IV we consider in detail the effect of thermal fluctuations on the domain wall in the absence of an external field. We show that the mean position of the wall undergoes Brownian motion. We derive the form of the *diffusion coefficient* for the domain wall and demonstrate its simple relation to the wall *mobility*. The wall, which is the Brownian particle of a generalized Langevin equation, is a large-amplitude, coherent, nonlinear modulation of the individual oscillator displacements.

In Sec. V we derive the form of the dynamic structure factor $S(k,\omega)$ for ferrodistortive systems both in the absence and presence of domain walls. $S(k,\omega)$ decomposes into contributions from the Brownian motion of the domain walls, from the bound-state oscillation of the wall, and from the soft-phonon mode. We derive the temperature dependence of the central peak, which is the dominant elastic-scattering feature below T_c. We prove that Brownian motion of domain walls does not contribute significantly to the critical scattering. We also deduce the temperature dependence of the domain-wall transport coefficients.

In Sec. VI we summarize our results. Analytical details are presented in two appendices. In Appendix A we show that both short-range electrostatic interactions and crystalline-elastic-strain effects lead to equations of motion for the displacement which are formally identical. In Appendix B we provide the calculation of $S(k, \omega)$.

In the second article we show how the model can be applied to two prototypic ferroelectric materials, lead germanate, and antimony sulphoiodide. The model parameters are determined from available experimental data and are shown to have reasonable values. Using *no adjustable parameters* we calculate for lead germanate the wave number and temperature dependence of the low-temperature central peak in the neutron-scattering spectra. The domain-wall width, in $Pb_5Ge_3O_{11}$, derived from the central-peak intensity data,[12] is also determined. These results are in *quantitative* agreement with experimental data. The integrated intensity of this peak is shown to depend linearly on the (temperature-independent) domain-wall density. The calculated wall density agrees well with the average domain size observed directly in other samples. The temperature dependences of the domain-wall diffusion coefficient and mobility are obtained. This mobility, together with the calculated wall density, yields a correct order-of-magnitude estimate of the polarization switching time. For SbSI we evaluate the temperature and pressure dependence of the low-temperature central peak and compare it to the available data.

II. THE MODEL

This work is concerned with uniaxial ferrodistortive crystals below their critical temperature. We restrict ourselves to displacive materials, in which the lattice deformation changes gradually from one unit cell to the next.[21] In these substances one finds that adjacent domains have opposite polarization, aligned with the ferrodistortive axis $\hat{z}$. Such domains are separated by 180° walls, which lie parallel to $\hat{z}$.[9] We consider, for simplicity, planar walls normal to a direction $\hat{x}$ ($\hat{x} \perp \hat{z}$). Then, since the displacement pattern associated with the soft mode is the same in each plane perpendicular to $\hat{x}$, the overall displacement of the whole crystal can be described by a single function $u(x,t)$, where x measures the distance along $\hat{x}$.

Our basic assumption is that the soft-mode displacement pattern at a position x_i is given by the following equation of motion:

$$m\frac{\partial^2 u(x_i,t)}{\partial t^2} + m\lambda\frac{\partial u(x_i,t)}{\partial t} + Au(x_i,t) + Bu^3(x_i,t) - \tilde{C}[u(x_{i+1},t) + u(x_{i-1},t) - 2u(x_i,t)] = R(x_i,t) + F(x_i,t) \quad . \qquad (2.1)$$

In Eq. (2.1) m represents an *effective* mass, $Au + Bu^3$ is the force due to the anharmonic crystalline potential $V(u)$,

$$V(u) = \tfrac{1}{2}Au^2 + \tfrac{1}{4}Bu^4, \quad (A < 0,\ B > 0) \quad . \qquad (2.2)$$

$$\tilde{C}[u(x_{i+1},t) + u(x_{i-1},t) - 2u(x_i,t)]$$

is the electrostatic (see Appendix A) and strain force due to the neighboring particles, $m\lambda(\partial u/\partial t)$ represents the damping, $R(x_i,t)$ denotes a random fluctuating force due to the remaining lattice degrees of freedom, and $F(x_i, t)$ represents an external force. Since we restrict ourselves to displacive ferrodistortive systems, we can use the continuum representation of the lattice, to obtain an equation of motion for $u(x,t)$,

$$m\frac{\partial^2 u}{\partial t^2} + m\lambda\frac{\partial u}{\partial t} + Au + Bu^3 - mc_0^2\frac{\partial^2 u}{\partial x^2} = R(x,t) + F(x,t) \quad , \qquad (2.3)$$

where $mc_0^2 = \tilde{C}l^2$, and l is the unit-cell length (see Ref. 31).

Equation (2.3) extends the equation of motion derived by Aubry,[20] and Krumhansl and Schrieffer[19] from a Hamiltonian model for one degree of freedom in a one-dimensional lattice,

$$m\frac{\partial^2 u}{\partial t^2} + Au + Bu^3 - mc_0^2\frac{\partial^2 u}{\partial x^2} = 0 \quad . \qquad (2.4)$$

Since Eq. (2.4) is derived for a conservative system, it does not contain the dissipative term $m\lambda(\partial u/\partial t)$ and the fluctuating force $R(x,t)$. These terms take account of the nonconservative nature of the soft-mode degree of freedom and its coupling to the other lattice vibrations. We show below that these terms produce significant changes in the allowed solutions of Eq. (2.3) as compared with Eq. (2.4), and are essential for the treatment of domain-wall motion in external fields. However, the common terms in Eqs. (2.3) and (2.4) have similar meaning. The anharmonic force $Au + Bu^3$ originates from an interaction between the relevant degree of freedom and the crystal lattice and has a form Eq. (2.2) appropriate to crystals undergoing a structural phase transition. The coupling term, $mc_0^2(\partial^2 u/\partial x^2)$, accounts for elastic strain effects between neighboring unit cells, so that c_0 corresponds to a velocity.

Since the structures of Eqs. (2.3) and (2.4) are similar, it is useful to state briefly some of the results obtained by Krumhansl and Schrieffer,[19] and Aubry.[20]

The interaction potential $V(u)$ has below T_c two degenerate minima at $u = \pm u_0$, where $u_0 = (|A|/B)^{1/2}$. In a homogeneous domain $(\partial^2 u/\partial x^2 = 0)$, $u(x,t) = \pm u_0$ are steady-state solutions of Eq. (2.4) and correspond to the two degenerate ordered states of the crystal. Moreover, Eq. (2.4) has many interesting solutions in terms of the moving coordinate ξ,

$$\xi = (x - vt)(1 - v^2/c_0^2)^{-1/2} \quad . \tag{2.5}$$

Of these, the most relevant are the domain-wall solutions

$$u_w = u_0 \tanh(\alpha\xi) \quad , \tag{2.6}$$

where

$$\alpha \equiv (|A|/2m)^{1/2}/c_0 \equiv \omega_s/c_0 \quad . \tag{2.7}$$

Single domain walls, joining domains where $u = u_0$ or $u = -u_0$, are free to move with any speed between zero and c_0. In the low-amplitude limit the usual phonon modes are also solutions of Eq. (2.4), $u(\xi) = \pm u_0 + \delta u(\xi)$, with

$$\delta u(\xi) = \tilde{A} \sin(2\alpha\xi + \phi) \quad , \tag{2.8}$$

where

$$\xi = (x - vt)(v^2/c_0^2 - 1)^{-1/2}, \quad v > c_0 \quad .$$

The energy of the traveling wave solutions is velocity dependent and is found by substituting Eq. (2.8) in the Hamiltonian of Ref. 19. Krumhansl and Schrieffer,[19] and Currie *et al.*,[32] have calculated the equilibrium statistical mechanics both exactly and phenomenologically (both methods give the same result) and interpreted and exact thermodynamic functions in terms of linear (phonon) and highly nonlinear (domain-wall) contributions.

As outlined in the Introduction, in applications to ferrodistortive materials one has to consider the crystal to be in a long-lived metastable state rather than in true equilibrium. This assumes that the time scale on which the domain-wall number changes is much longer than the period of the individual oscillators. Thus, the thermal motion of the individual particles is in equilibrium with the lattice. Equation (2.3) can be viewed as a generalized Langevin equation in space and time. In Eq. (2.3), the motion of the displacement $u(x,t)$ results in energy dissipation into the remaining lattice modes. The presence of these modes in turn produces a fluctuating force on $u(x,t)$. In the usual manner,[25] we assume that this force, $R(x,t)$, is random in time and position along the one-dimensional lattice, and is Markovian. Denoting the equilibrium average by $\langle\ \rangle$, we have

$$\langle R(x,t)\rangle = 0 \quad , \tag{2.9}$$

$$\langle R(x,t)R(x',t')\rangle = C\delta(x-x')\delta(t-t') \quad . \tag{2.10}$$

Whenever the fluctuating force $R(x,t)$ appears in a linear equation of motion, we assume that the fluctuation-dissipation theorem[25] holds, so that the coefficient C of Eq. (2.10) is given by

$$C = 2k_B T m\lambda l \quad , \tag{2.11}$$

where k_B is the Boltzmann constant, $m\lambda$ is the friction coefficient of Eq. (2.3), and l is the lattice constant.

In the following sections we derive some consequences of the nonlinear Langevin equation (2.3) with particular reference to the dynamics of the domain walls.

III. MOTION IN A FIELD

In this section we investigate some of the macroscopic properties described by our Langevin equation (2.3); by macroscopic properties we mean those characteristics which are described by an equilibrium ensemble average or time average of this equation. Taking the equilibrium average of Eq. (2.3), we obtain

$$m\frac{\partial^2\langle u\rangle}{\partial t^2} + m\lambda\frac{\partial\langle u\rangle}{\partial t} + A\langle u\rangle + B\langle u\rangle^3 - F(x,t) - mc_0^2\frac{\partial^2\langle u\rangle}{\partial x^2} = 0 \quad , \tag{3.1}$$

where $\langle R(x,t)\rangle 0$ from Eq. (2.9), and we have set $\langle u^3\rangle = \langle u\rangle^3$. This last approximation assumes that fluctuations, $u - \langle u\rangle$, are small and thus Eq. (3.1) is restricted to temperatures well below T_c.

For some constant applied field E, and coupling constant (or effective "charge") e^*, each oscillator has an additional potential energy, V_e,

$$V_e = -ue^*E \quad . \tag{3.2}$$

This assumes a linear coupling to the displacement. The coefficient e^* describes the strength of the coupling between the field and displacement. Our equation of motion (3.1) becomes

$$m\frac{\partial^2\langle u\rangle}{\partial t^2} + m\lambda\frac{\partial\langle u\rangle}{\partial t} + A\langle u\rangle + B\langle u\rangle^3 - e^*E - mc_0^2\frac{\partial^2\langle u\rangle}{\partial x^2} = 0 \quad . \tag{3.3}$$

To find solutions of constant velocity we transform to the moving coordinate s,

$$s = \left[\frac{|A|}{m(c_0^2 - v^2)}\right]^{1/2}(x - vt) \quad .$$

Letting $\eta = \langle u\rangle/u_0$, we obtain from Eq. (3.3)

$$\frac{d^2\eta}{ds^2} + v'\frac{d\eta}{ds} + \eta - \eta^3 + E' = 0 \quad , \tag{3.4}$$

where

$$v' = \lambda v[m/(c_0^2 - v^2)|A|]^{1/2} \quad ,$$

$$E' = e^*EB^{1/2}|A|^{-3/2}, \quad \text{and} \quad -\infty \le s \le \infty \quad .$$

Equation (3.4) has the form

$$\frac{d^2\eta}{ds^2} + v' \frac{d\eta}{ds} + F(\eta) = 0 \ , \tag{3.5}$$

where

$$F(\eta) = -(\eta - a)(\eta - b)(\eta - c), \quad a < c < b \ .$$

Equation (3.4) has the *unique* bounded solution[33]

$$\eta(s) = a + (b - a)[1 + \exp(\pm\beta s)]^{-1} \ , \tag{3.6}$$

where

$$\beta = (b - a)/2^{1/2} \ ,$$

and v' must have the value

$$\begin{aligned} v' &= \pm 2^{-1/2}(a + b - 2c) \\ &= \pm 2^{-1/2}(-3c) \ . \end{aligned} \tag{3.7}$$

The last relation follows from $a + b + c = 0$ since from Eq. (3.4) there is no term in η^2 in $F(\eta)$.

Equation (3.5) is well known in the contexts of population genetics[34] and nonequilibrium chemical systems.[35] More generally, when $F(\eta)$ is not a third-order polynomial in η, but there are still three distinct values of η for which $F(\eta) = 0$, Aronson and Weinberger[36] have shown that Eq. (3.5) has exactly one solution at a *unique* value of v'.

The profile $\eta(s)$ of Eq. (3.6) is a traveling domain wall with velocity given by

$$m\lambda v[m(c_0^2 - v^2)|A|]^{-1/2} = (2)^{-1/2}(-3c) \ . \tag{3.8}$$

For small external field E ($E' << 1$), it is simple to show that $c \simeq -E'$, and therefore

$$m\lambda v[m(c_0^2 - v^2)|A|]^{-1/2} = \frac{3E'}{2^{1/2}} \ . \tag{3.9}$$

The field and hence the velocity have been assumed to be small ($v << c_0$), so that Eq. (3.9) gives

$$\begin{aligned} v &= \frac{3c_0}{\lambda|A|}\left(\frac{B}{2m}\right)^{1/2} e^*E \\ &\equiv \mu e^*E \ , \end{aligned} \tag{3.10}$$

where we have defined the domain-wall mobility μ as

$$\mu = \frac{3c_0}{\lambda|A|}\left(\frac{B}{2m}\right)^{1/2} \ . \tag{3.11}$$

For an applied field the domain wall moves with a unique constant velocity determined by the field. In the absence of a field, the domain wall is stationary; this is the *only* possible solution. For no external field, Eq. (3.1) is

$$m\frac{\partial^2\langle u\rangle}{\partial t^2} + m\lambda\frac{\partial\langle u\rangle}{\partial t} + A\langle u\rangle + B\langle u\rangle^3 - mc_0^2\frac{\partial^2\langle u\rangle}{\partial x^2} = 0 \ . \tag{3.12}$$

For a steady state we have

$$A\langle u\rangle + B\langle u\rangle^3 - mc_0^2\frac{\partial^2\langle u\rangle}{\partial x^2} = 0 \ .$$

This has the steady-state solutions of interest

$$\langle u\rangle \equiv \pm u_0 = \pm\left(\frac{|A|}{B}\right)^{1/2} \ ,$$

and (3.13)

$$\langle u\rangle \equiv \pm u_w(x - x_0) \ ;$$

$$u_w(x) = u_0 \tanh(\alpha x) \ , \tag{3.14}$$

These stationary solutions are clearly the same as those obtained if damping is absent. The domain-wall solution $u_w(x)$ is but one of the class obtained without damping factor in Ref. 19. There it was shown that domain walls moving with any constant velocity between zero and c_0 satisfy the equations of motion. We find, however, that when the damping coefficient does not vanish all solutions of Ref. 19, except that stationary ones, are transient and disappear.

Equation (3.10) shows a linear response of the wall velocity to the field. We envisage a wall, initially at rest, accelerating in the field to some terminal velocity. The shape of the wall gradually distorts into its final form, with faster walls having a steeper slope [see Eq. (3.6) and Fig. 1].

In order to prove the last remarks, we now show that the wall [Eq. (3.6)] is a *stable* solution[37] of Eq. (3.3), that is, any small perturbation of the wall will eventually vanish, rather than grow or persist. Until now we have only shown that the wall is a solution of the ordinary differential Eq. (3.5). We now verify that, for reasonable initial conditions, the system

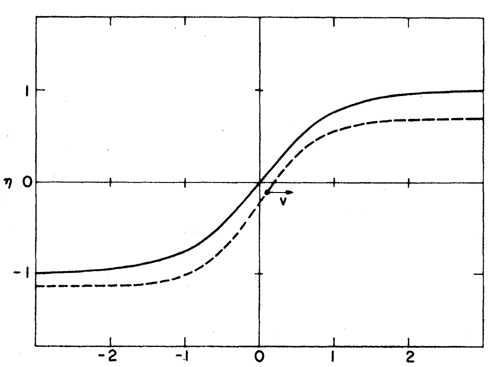

FIG. 1. Domain profile η, Eq. (3.6), at rest (——) and moving at a terminal velocity of $\vec{v}/c_0 = \pm 0.7\hat{x}$ in an applied field (- -), vs αx, Eq. (2.7). Note that the moving wall is steeper at its center and that the asymptotic values are shifted by the field.

given by Eq. (3.3) will approach its terminal form. The case of zero field is first discussed in detail and a qualitative discussion of the stability of the domain-wall solution in an external field is presented. In the absence of an external field, we can write the displacement $u(x,t)$,

$$u(x,t)=u_w(x)+\delta u(x,t) \quad , \tag{3.15}$$

where we assume that at time $t=0$ the wall is localized at $x=0$.

For small deviations the linearized equation of motion is

$$m\frac{\partial^2\delta u}{\partial t^2}+m\lambda\frac{\partial\delta u}{\partial t}-mc_0^2\frac{\partial^2\delta u}{\partial x^2} +2|A|(1-\tfrac{3}{2}\,\mathrm{sech}^2\alpha x)\delta u=0 \quad , \tag{3.16}$$

where we have used Eqs. (3.3) and (3.14). This equation can be solved by recognizing that the related equation

$$\left[m\frac{\partial^2}{\partial t^2}+2|A|[1-\tfrac{3}{2}\,\mathrm{sech}^2(\alpha x)]-mc_0^2\frac{\partial^2}{\partial x^2}\right]y=0 \tag{3.17}$$

is exactly soluble.[38]

Letting $y(x,t)=e^{i\omega t}f(x)$, gives

$$\left[-m\omega^2+2|A|[1-\tfrac{3}{2}\,\mathrm{sech}^2(\alpha x)]-mc_0^2\frac{\partial^2}{\partial x^2}\right]f=0 \quad . \tag{3.18}$$

Equation (3.18) has the form of a Schrödinger equation with a potential of the form $-\mathrm{sech}^2(\alpha x)$. Figure 2 depicts this potential and the eigenfunctions of the associated Schrödinger equation. There are two bound states and an infinite set of continuum solutions given by

$$y_1(x,t)=e^{i\omega_1 t}f_1(x) \quad ,$$
$$\omega_1=0,\quad f_1=N_1\,\mathrm{sech}^2(\alpha x) \quad , \tag{3.19}$$

$$y_2(x,t)=e^{i\omega_2 t}f_2(x),$$
$$\omega_2^2=3\omega_s^2,\quad f_2=N_2\frac{\sinh(\alpha x)}{\cosh^2(\alpha x)} \quad , \tag{3.20}$$

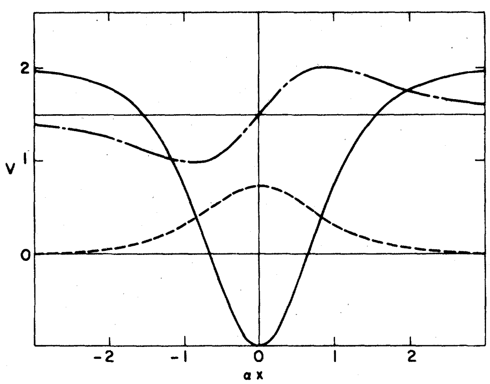

FIG. 2. Plot of the potential $V(\alpha x)$ [——] in the effective Schrödinger equation (3.18). Also shown are the two bound-state eigenfunctions $y_1(\alpha x)$ [- - -] and $y_2(\alpha x)$ [-·-·] drawn over their corresponding energies. The drawings are made for $|A|=1$, $\alpha=2^{-1/2}$, and $m=1$.

$$y_l(x,t)=e^{i\omega_l t}f_l(x),\quad \omega_l^2=4\omega_s^2+\omega_s^2 l^2 \quad ,$$
$$f_l(x)=N_l e^{il\alpha x}[3\tanh^2(\alpha x)-(1+l^2) +3il\tanh(\alpha x)],\quad -\infty\le l\le\infty \quad , \tag{3.21}$$

and $\omega_s^2=|A|/2m$. N_l is a normalization factor. The continuum functions, $f_l(x)$, correspond to plane waves distorted in the region of the potential. Both bound states correspond to disturbances localized on the domain wall.

The normalization factors N_i are defined by, for the bound states,

$$\int_{-\infty}^{\infty} f_i f_i^*\,dx=1 \quad , \tag{3.22a}$$

for the continuum states,

$$\lim_{L\to\infty}\frac{1}{2L}\int_{-L}^{L} f_l f_l^*\,dx=1 \quad . \tag{3.22b}$$

Since the normalized functions $f_i(x)$ are the eigenvectors of an Hermitian operator, they form a complete, orthonormal set for bounded functions $g(x)$. We use this fact to set

$$\delta u(x,t)=s_1(t)y_1(x,t)+s_2(t)y_2(x,t) +\int_{-\infty}^{\infty}dl\,s_l(t)y_l(x,t) \quad . \tag{3.23}$$

Substituting this expansion in Eq. (3.16) and using Eq. (3.17) gives

$$m\left[\frac{d^2s_1}{dt^2}+2i\omega_1\frac{ds_1}{dt}+i\omega_1\lambda s_1+\lambda\frac{ds_1}{dt}\right]e^{i\omega_1 t}f_1+m\left[\frac{d^2s_2}{dt^2}+2i\omega_2\frac{ds_2}{dt}+i\omega_2\lambda s_2+\lambda\frac{ds_2}{dt}\right]e^{i\omega_2 t}f_2 +\int_{-\infty}^{\infty}dl\,m\left[\frac{d^2s_l}{dt^2}+2i\omega_l\frac{ds_l}{dt}+i\omega_l\lambda s_l+\lambda\frac{ds_l}{dt}\right]e^{i\omega_l t}f_l(x)=0 \quad . \tag{3.24}$$

Then by the orthonormality of the $\{f_i(x)\}$, we have

$$\frac{d^2 s_j}{dt^2} + (\lambda + 2i\omega_j)\frac{ds_j}{dt} + i\omega_j \lambda s_j = 0, \quad j = 1, 2, l \quad . \tag{3.25}$$

This has the general solutions

$$\begin{aligned} s_j(t) &= C_1 e^{-\gamma_1 t} + C_2 e^{-\gamma_2 t} \ , \\ \gamma_{1,2} &= i\omega_j + \tfrac{1}{2}[\lambda \pm (\lambda^2 - 4\omega_j^2)^{1/2}] \\ &\equiv i\omega_j + \mu_{1,2} \ . \end{aligned} \tag{3.26}$$

From Eq. (3.19) to Eq. (3.26) we see that $\delta u(x,t)$ is a linear combination of terms $e^{-\mu_k t} f_j(x)$, $k = 1, 2$. The real parts of μ_1 and μ_2 are strictly positive unless $\omega_j = 0$ and then μ_2 is zero. The first bound state has $\omega_1 = 0$. Therefore, the perturbation $\delta u(x,t) \to 0$ as $t \to \infty$ except for the component of $\delta u(x,t)$ associated with the lowest bound state $y_1(x)$. So,

$$u(x,t) \underset{t\to\infty}{\longrightarrow} u_w(x) + C_2 y_1(x) \ ,$$

[see Eq. (3.26) for $\omega_1 = 0$],, where y_1 is given by

$$y_1(x) = \Omega \frac{du_w}{dx}, \quad \Omega = (\tfrac{4}{3} u_0^2 \alpha)^{-1/2} \ .$$

Therefore, we have

$$u(x,t) \underset{t\to\infty}{\longrightarrow} u_w(x + C_3), \quad C_3 = C_2 \Omega \ , \tag{3.27}$$

since only small perturbations are considered. We see that the ground-state perturbation $y_1(x)$ involves translating the domain wall uniformly. Clearly, in our infinite one-dimensional model the position of the wall [that value of x where $u_w(x) = 0$] is arbitrary and $u_w(x)$ is indistinguishable from $u_w(x + C_3)$. There is no restoring force which will return the domain wall to its original position. The translational invariance of Eq. (3.12) leaves the position of the domain wall indeterminate. In all other respects the wall is stable due to the inclusion of damping.

The stability of traveling waves in the presence of a field follows in a similar manner. Setting $u(x,t) = u_w(\xi) + \delta u(\xi,t)$ we arrive at an equation for $\delta u(\xi,t)$ analogous to Eq. (3.16). This can be solved in similar fashion to give solutions for $\delta u(\xi,t)$ which in moderate fields vanish as $t \to \infty$.

The macroscopic dynamics and structure of moving domain walls described by this model can be tested by measurement of wall mobility. The linear response in wall velocity with applied field, Eq. (3.9), can be used to estimate the damping coefficient λ. In Sec. IV we investigate further dynamical properties of the domain walls and relate these to the damping coefficient.

IV. DIFFUSION OF A DOMAIN WALL

In Sec. III we have shown how the inclusion of energy dissipation from the degree of freedom $u(x,t)$ led to a domain wall whose average velocity vanished in the absence of any driving field. However, this average velocity takes no account of the random fluctuating force $R(x,t)$, since $\langle R(x,t)\rangle = 0$. Here, we demonstrate that the effect of this force is to move the domain wall in random fashion, so that while $\langle v\rangle = 0$, the velocity autocorrelation function $\langle v(t)v(0)\rangle$ does not vanish.

Consider now Eq. (2.3) for the displacement $u(x,t)$. We recall that in the absence of an external field $\langle u\rangle = u_w(x)$, Eq. (3.14) so that we set

$$u(x,t) = u_w(x) + \delta u(x,t) \ . \tag{4.1}$$

For small fluctuations, Eq. (2.3) can be linearized to obtain, in similar fashion to Eq. (3.16),

$$m\frac{\partial^2 \delta u}{\partial t^2} + m\lambda \frac{\partial \delta u}{\partial t} - mc_0^2 \frac{\partial^2 \delta u}{\partial x^2} + 2|A|[1 - \tfrac{3}{2}\operatorname{sech}^2(\alpha x)] \times \delta u = R(x,t) \ . \tag{4.2}$$

We can again expand $\delta u(x,t)$ in terms of the set of functions $\{y_j(x,t)\}$ and find an equation corresponding to Eq. (3.25),

$$\frac{d^2 s_j}{dt^2} + (\lambda + 2i\omega_j)\frac{ds_j}{dt} + i\omega_j \lambda s_j = \int_{-\infty}^{+\infty} \frac{1}{m} R(x,t) y_j^*(x,t)\, dx \equiv Q_j(t) \ , \tag{4.3}$$

where $j = 1, 2, l$. The first member of this basis set y_1 is associated with translation of the wall. Since all other y_j's are orthogonal to y_1, they do not contribute to the displacement of the wall as a whole. Concentrating on the y_1 term alone, Eq. (4.3) becomes ($\omega_1 = 0$),

$$\frac{d^2 s_1}{dt^2} + \lambda \frac{ds_1}{dt} = Q_1(t) \ . \tag{4.4}$$

Then, as in Eq. (3.27)

$$\begin{aligned} u(x,t) &= u_w(x) + s_1(t)\,\Omega \frac{du_w}{dx} \\ &= u_w(x + \Omega s_1(t)), \quad \Omega = (\tfrac{4}{3} u_0^2 \alpha)^{-1/2} \ , \end{aligned} \tag{4.5}$$

since $s_1(t)$ is assumed small compared to α^{-1}.

Now, we define this position of the domian wall as that value of the coordinate $x_w(t)$ for which

$$u(x_w(t)) = 0 \ . \tag{4.6}$$

This corresponds to the center of the wall. Then, from Eq. (4.5)

$$x_w(t) = -\Omega s_1(t) \ , \tag{4.7}$$

since we chose [see Eq. (3.14)] $u_w(0)=0$. The instantaneous wall velocity is $v(t)$ such that

$$v(t) = \frac{dx_w(t)}{dt} = -\Omega \frac{ds_1(t)}{dt} \tag{4.8}$$

and, with Eq. (4.4),

$$\frac{dv(t)}{dt} + \lambda v(t) = -\Omega Q_1(t) \ . \tag{4.9}$$

From Eqs. (2.9), (2.10), and (4.3) we obtain,

$$\langle Q_1(t) \rangle = 0 \ , \tag{4.10}$$

$$\langle Q_1(t) Q_1(t') \rangle = \frac{1}{m^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} y_1(x) y_1(x') \times \langle R(x,t) R(x',t') \rangle \, dx \, dx'$$

$$= \frac{C}{m^2} \delta(t-t') \tag{4.11}$$

so that, using Eqs. (2.7), (2.11), and (3.17),

$$\Omega^2 \langle Q_1(t) Q_1(t') \rangle = \frac{2k_B T \lambda}{m^*} \delta(t-t') \tag{4.12}$$

where we defined

$$m^* \equiv m \left[\frac{4u_0^2 \omega_s}{3c_0 l} \right] \ . \tag{4.13}$$

Equations (4.9), (4.10), and (4.12) are the Langevin equations[25] describing the Brownian motion of the domain wall through the lattice. The diffusion coefficient associated with this motion is given by the Einstein relation[25]

$$D = \int_0^{\infty} \langle v(t) v(0) \rangle dt = \frac{k_B T}{m^* \lambda} \tag{4.14}$$

since, from Eq. (4.9),[39]

$$v(t) = -\Omega e^{-\lambda t} \int_{-\infty}^{t} e^{\lambda \tau} Q_1(\tau) \, d\tau \tag{4.15}$$

and thus, with Eqs. (4.10) and (4.11),

$$\langle v(t) v(0) \rangle = \frac{k_B T}{m^*} e^{-\lambda t} \ . \tag{4.16}$$

The diffusion coefficient D and the mobility of the wall in a field, Eq. (3.11), are therefore related by

$$\frac{D}{\mu} = \tfrac{1}{2} k_B T \frac{l}{u_0} \ . \tag{4.17}$$

The wall-position autocorrelation function follows directly from Eq. (4.16):

$$\langle [x_w(\tau) - x_w(0)]^2 \rangle = 2[\langle x_w(0) x_w(0) \rangle - \langle x_w(\tau) x_w(0) \rangle]$$

$$= 2 \int_0^{\tau} d\tau_1 \int_0^{\tau_1} d\tau_2 \langle v(\tau_2) v(0) \rangle$$

$$= 2D \left[\tau + \frac{e^{-\lambda \tau} - 1}{\lambda} \right] \ . \tag{4.18}$$

The diffusive and forced motions of the wall are both determined by the damping of the individual oscillators. Unlike the usual retardation of a particle moving in a fluid, the force is not acting directly on the coordinate of motion x_w but rather on $u(x,t)$ through the damping proportional to the velocity of the ion displacement. The ion displacement need not be aligned with the coordinate axis $\hat{x}$; still the cooperative motion experiences the same damping and is characterized by the effective mass m^*.

While the wall motion is clearly a consequence of the cooperative ion displacements, we consider the issue in reverse. What effect does this diffusing wall have on the fluctuating ion positions? The natural quantity to evaluate is the fluctuation or power spectrum for the system since this is measured in a light or neutron-scattering experiment. In Sec. V we consider this fluctuation spectrum in a crystal at low temperature, and low density of domain walls randomly distributed throughout the system.

V. DYNAMIC STRUCTURE FACTOR

This section gives the results for the dynamic structure factor for a crystal composed of many domains, randomly distributed. We require that each domain be sufficiently large so that the domain walls do not interact, corresponding to an ideal gas. This limitation is necessary in order to employ the results of Sec. III where it was assumed that each wall resided in an effectively infinitely long system. Since the walls are localized to within several unit cells, the noninteracting planar wall limit obtains when each domain is on average some few thousands of lattice constants across. The fact that the domain walls are randomly distributed ensures that all average properties are translationally invariant.

We start by considering the displacement correlation function

$$S(x,x',t,t') \equiv \langle u(x,t) u(x',t') \rangle \ . \tag{5.1}$$

This quantity is related to the density correlation function which is measured in neutron-scattering experiments. The displacement correlation function can also be observed in light scattering experiments which probe the time- and space-dependent polarization correlation function, provided that u is a deviation from a nonsymmetrical state or that the refractive index is not an even function of u.

Since Eq. (5.1) is time and translationally invariant

$$S = S(x-x', t-t') \ . \tag{5.2}$$

To evaluate the contribution of $u(x,t)$ to the scattering intensity, we calculate $S(k,\omega)$,

$$S(k,\omega) = \lim_{\epsilon\to 0} 2\,\mathrm{Re}\left\{\int_0^\infty e^{iz(t-t')} S(k,t-t')\, d(t-t')\right\} \ ,$$

$$z = \omega + i\epsilon \ , \tag{5.3a}$$

where

$$S(k,t-t') = \int_{-\infty}^{\infty} e^{-ik(x-x')} \times \langle u(x,t)u(x',t')\rangle\, d(x-x') \ , \tag{5.3b}$$

and k and ω are the changes in the wave number and frequency of the scattered particles, respectively; k is related to the scattering angle. The total observed scattering intensity contains contributions proportional to $S(k,\omega)$. For comparison, we first consider the case where there are no domain walls. Such a situation would be realized if the crystal were first subjected to a high static field. Setting

$$u(x,t) = \pm u_0 + \delta u(x,t) \ , \tag{5.4}$$

we have

$$\langle u(x,t)u(x',t')\rangle = u_0^2 + \langle \delta u(x,t)\,\delta u(x',t')\rangle \ . \tag{5.5}$$

The fluctuation $\delta u(x,t)$ obeys the linearized equation of motion

$$m\frac{\partial^2 \delta u}{\partial t^2} + m\lambda\frac{\partial \delta u}{\partial t} - mc_0^2\frac{\partial^2 \delta u}{\partial x^2} + 2|A|\,\delta u = R(x,t) \ , \tag{5.6}$$

where $u_0^2 = |A|/B$ was used. Equation (5.6) leads to the dynamic structure factor for phonons

$$S(k,\omega) = \frac{C/m^2}{[\omega^2-\omega_0^2(k)]^2+\lambda^2\omega^2} + (2\pi)^2 u_0^2\,\delta(k)\,\delta(\omega) \ , \tag{5.7}$$

where we have $C = 2k_B T m l\lambda$, Eq. (2.11), and

$$\omega_0^2(k) = \frac{2|A|}{m} + c_0^2 k^2 \ . \tag{5.8}$$

In Eq. (5.7) the second term simply represents the single Bragg scattering peak in the forward direction associated with the homogeneous crystal. The first term represents the scattering from the phonon modes with frequencies $\omega_0(k)$ of the one-dimensional chain of oscillators. The phonon contribution $S_1(k,\omega)$ is sketched in Fig. 3. Depending on λ the phonon spectrum is overdamped (maximum at $\omega = 0$ for large λ) or underdamped (with two distinct maxima). Eq. (5.7) fulfills the two sum rules

$$I_1(k) = \frac{1}{2\pi}\int_{-\infty}^{\infty} S(k,\omega)\, d\omega = \frac{k_B T l}{m\,\omega_0^2(k)} \ , \tag{5.9}$$

and

$$J_1(k) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \omega^2 S(k,\omega)\, d\omega = \frac{k_B T l}{m} \ , \tag{5.10}$$

where only the first term in Eq. (5.7) was considered. The phonon dispersion relation is given by

$$\omega_0^2(k) = J_1(k)/I_1(k) \ . \tag{5.11}$$

Now we return to the problem posed by the presence of domain walls. In the limit of low-wall density we can assume that their form is that derived in Sec. III, where each wall resided in a system of infinite extent. Around a wall centered at $x = x_0$ we set

$$u(x,t) = u_w(x-x_0) + \delta u(x,t) \ . \tag{5.12}$$

To find $\delta u(x,t)$ we expand it in terms of the set $\{y_j(x-x_0)\}$ [see Eq. (3.19) to Eq. (3.23)], and solve the Eq. (4.3) for the time-dependent coefficients $s_j(t)$.

As shown in Sec. III the set $\{y_j\}$ contains two bound states and an infinite number of continuum states. In Appendix B we calculate $S(k,\omega)$. The continuum states obey the same dispersion relation as Eq. (5.8) and, in the limit of low-wall density, reduce to the usual phonon modes [see Eq. (5.7)]. The contribution from the second bound state y_2 and for the part of $S(k,\omega)$ due to the first bound state are presented. The dynamic structure factor is

$$S(k,\omega) = S_1(k,\omega) + S_2(k,\omega) + S_3(k,\omega) \ , \tag{5.13}$$

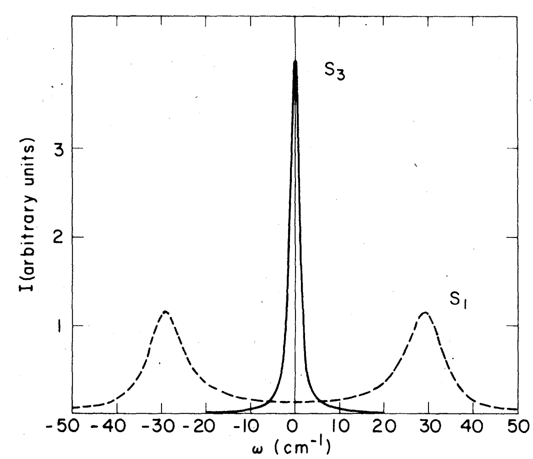

FIG. 3. Sketches of the two contributions $S_1(k,\omega)$ [- - - -] Eq. (5.14) and $S_3(k,\omega)$ [———] Eq. (5.16) for a fixed k value chosen so that the Rayleigh peak has a width $2Dk^2 = 2$ cm^{-1}. The phonon frequency and damping have been set to $\omega_0(k) = 30$ cm^{-1} and $\lambda = 10$ cm^{-1}, respectively. The relative intensities of S_1 and S_3 are arbitrary in this plot.

where

$$S_1(k,\omega)=\frac{C/m^2}{[\omega^2-\omega_0^2(k)]^2+\lambda^2\omega^2}\ , \tag{5.14}$$

$$S_2(k,\omega)=n_w\frac{3}{2\alpha}\left[\frac{\pi k}{\alpha}\operatorname{sech}\left(\frac{\pi k}{2\alpha}\right)\right]^2 \times\frac{C/m^2}{(\omega^2-3\omega_s^2)^2+\lambda^2\omega^2}\ , \tag{5.15}$$

$$S_3(k,\omega)=n_w\left[\frac{u_0\pi}{\alpha}\operatorname{csch}\left(\frac{\pi k}{2\alpha}\right)\right]^2\frac{2Dk^2}{\omega^2+(Dk^2)^2}\ , \tag{5.16}$$

and n_w is the number density of domain walls (the inverse of the average domain length).

We discuss now the contributions to the scattering intensity due to the bound states. $S_2(k,\omega)$ arises from the mode of frequency $(3)^{1/2}\omega_s$ [Eq. (3.20)], which is an asymmetric modulation of the domain wall (see Fig. 2). Since this is a local mode, its frequency is independent of k. The line shape of this mode is determined by the same damping as the phonon modes [see Eq. (5.14)]. The integrated intensity of this peak is low in comparison with that of the soft mode. We have

$$I_2(k)=\frac{1}{2\pi}\int_{-\infty}^{\infty}S_2(k,\omega)\,d\omega$$
$$=n_w\frac{1}{2\alpha}\left[\frac{\pi k}{\alpha}\operatorname{sech}\left(\frac{\pi k}{2\alpha}\right)\right]^2\frac{k_BTl}{\omega_s^2 m}$$
$$\simeq\frac{n_w}{2\alpha}\frac{\pi^2k^2}{\alpha^2}\frac{k_BTl}{\omega_s^2m}\left(\text{for small }\frac{k}{\alpha}\right)$$
$$=2\frac{n_w}{\alpha}\frac{\pi^2k^2}{\alpha^2}I_1(0)\ . \tag{5.17}$$

Here α is the reciprocal-wall length, so that k is at most of the order of α($k\sim10^{-3}$ Å^{-1} for light and $k\lesssim 0.1$ Å^{-1} for neutron scattering). However we have $n_w \ll \alpha$, so that $I_2 \ll I_1(0)$.

The term $S_3(k,\omega)$, arising from the Brownian motion of the wall, is a quasielastic Lorentzian peak (with a maximum at $\omega=0$) similar to the usual Rayleigh peak encountered in scattering from fluids. This feature has a line shape of width $2Dk^2$. For light scattering, where k is very small, this central peak is extremely narrow in comparison with the phonon peak. In neutron scattering, k is of the order of α; still if D is sufficiently small the linewidth $2Dk^2$ remains below experimental resolution. When the linewidth is very narrow the peak height is large, since the integrated intensity is

$$I_3^{(k)}=\frac{1}{2\pi}\int_{-\infty}^{\infty}S_3(k,\omega)\,d\omega=n_w\left(\frac{u_0\pi}{\alpha}\operatorname{csch}\frac{\pi k}{2\alpha}\right)^2$$
$$=4n_w\frac{u_0^2}{k^2},\ \text{for small } k\ , \tag{5.18a}$$
$$=6n_w\frac{\omega_0(k)c_0}{\lambda Dk^2}I_1(k)\ . \tag{5.18b}$$

Thus, when Dk^2 is very small and the wall density n_w is not too low, the central peak may be intense in comparison with the phonon mode. Contributions to the dynamic structure factor are illustrated in Fig. 3 for particular values of the model parameters that yield a clearly distinguishable central peak and an underdamped phonon mode.

The second-order phase transformation for ferrodistortive materials occurs in association with a soft-phonon mode whose frequency for $k=0$ vanishes at T_c as[1]

$$\omega_0^2(T)/\omega_0^2(0)=(T_c-T)/T_c\ . \tag{5.19}$$

Also, in first-order phase transformations below T_c, the frequency of a particular phonon mode obeys

$$\omega_0^2(T)/\omega_0^2(0)=(T_A-T)/T_A\equiv t_A\ , \tag{5.20}$$

with $T_A > T_c$. At T_c the quantity $\omega_0^2(T)$ drops discontinuously. Equation (5.20) includes Eq. (5.19) for $T_A=T_c$.

The static lattice displacement pattern is also temperature dependent,

$$u_0^2(T)/u_0^2(0)=t_A\ . \tag{5.21}$$

The empirical behavior [Eqs. (5.20) and (5.21)] is incorporated in our phenomenological model by setting

$$A(T)/A(0)=t_A\ . \tag{5.22}$$

This yields a temperature-dependent barrier in the double minimum crystalline potential $V(u)$ [see Eq. (2.2)]. The barrier shrinks as $T\to T_A$ from below and vanishes at T_A.

It is easily seen from Eq. (4.13) that the effective mass of the domain wall is

$$m^*(T)/m^*(0)=t_A^{3/2} \tag{5.23}$$

and the domain-wall width d ($\equiv\alpha^{-1}$) is given by

$$\frac{d(T)}{d(0)}=t_A^{-1/2} \tag{5.24}$$

as $T\to T_A$ from below.

Using Eqs. (5.22) and (5.23) we can determine the temperature dependence of the transport coefficients D and μ, and hence of the total dynamic structure factor, assuming $\lambda(T)$ to be known. We obtain

$$D(T) = Tt_A^{-3/2}\frac{k_B}{m^*(0)\lambda(T)} \tag{5.25}$$

and

$$\mu(T) = t_A^{-1}\frac{2u_0(0)}{lm^*(0)\lambda(T)} \quad . \tag{5.26}$$

The temperature dependence of the important features of $S(k,\omega)$ can now be deduced. The integrated intensity of the phonon peaks I_1 increases as Tt_A^{-1} while the integrated intensity of the central peak I_3 decreases as t_A [see Eq. (5.18a)]; here, we assume that the wall density does not change. The central Rayleigh peak derived here will be the dominant feature in the scattering spectrum at low temperatures, where it appears as a very narrow, very intense mode. In the framework of the linear analysis this Brownian wall motion does not contribute to the critical scattering ($T = T_c$). The central peak obtained herein appears to correlate very well with the low-temperature spectrum of ferrodisplacive crystals.[12]

V. CONCLUSION

We have studied the dynamics of domain walls in uniaxial displacive ferrodistortive materials. We introduced a phenomenological Langevin equation of motion for the displacement field. This equation has terms deriving from an anharmonic double well potential, a damping and random fluctuating force through which energy is dissipated, a spatial coupling arising from elastic strain or electromagnetic interactions, and an external field. The coefficient of the harmonic part of the potential term and the damping coefficient depend parametrically on temperature and pressure. The low-amplitude solutions to the equation of motion reproduce all of the characteristics of the soft-mode optical phonons. The large amplitude solutions correspond to walls between differently ordered domains. The domain boundaries are coherent features which are absolutely stable with respect to small fluctuations and whose average shape depends on the mean velocity at which they propagate through the crystal. The wall solutions are obtained by treating the nonlinearity exactly and not as a perturbation of a harmonic crystal. The nonlinearity also gives rise to an interaction between the soft-mode phonons and the walls resulting in two-phonon states becoming bound to each wall. One bound state gives rise to an oscillation of the wall profile while the second one is associated with wall translation. We show that the domain-wall dynamics are those of a Brownian particle in a bath. In the absence of a field the wall undergoes a diffusive motion for which we calculate the corresponding diffusion coefficient D. In an external field the wall reaches a terminal velocity proportional to the applied field from which we determine the mobility μ. The constants μ and D are linearly related; this follows from the fluctuation dissipation law. Our theory shows how these transport coefficients for the macroscopic domain walls are derivable from the parameters of the microscopic phenomenological equation of motion. Combining the exact results for the classes of large and small amplitude excitations we calculate analytically the dynamic structure factor corresponding to these solutions. We find that the diffusive Brownian motion of the domain walls leads to a Rayleigh quasielastic peak whose width at wave vector k is $2Dk^2$. The next paper shows how all these theoretical results compare with the observed properties of two classes of ferroelectric substances.

ACKNOWLEDGMENTS

The authors are grateful to Professor R. Silbey and Professor J. W. Cahn for very valuable discussions during the course of this work. This study was supported in part by the NSF and AFOSR. M.A.C. acknowledges the support of the CSIRO. The assistance of the Deutsche Forschungsgemeinschaft through a research grant is gratefully acknowledged by A.B. J.F.C. thanks the NRC of Canada for support and the Department of Materials Science at M.I.T. where part of this work was done.

APPENDIX A

Our equation of motion (3.3) may be readily viewed as arising from the strain forces in the crystal. In this Appendix we show that the inclusion of electrostatic interactions leads to precisely the same form for Eq. (3.3), but with renormalized coefficients. Hence, our solution is more general than the structure of Eq. (3.3) may suggest.

Consider $eW(u_1,\ldots,u_i,\ldots)$ to be the electrostatic potential energy due to the ions at positions $u_1,\ldots u_i,\ldots$. The total electrostatic field at u_i is

$$E_{\text{ext}} + E_{\text{nn}} \tag{A1}$$

with E_{ext} the external field and E_{nn} the field due to the neighboring atoms. In the following we assume that the potential W decays very rapidly with distance, so that only the next neighbors contribute.

If the displacements from equilibrium are small, the total energy associated with u_i is

$$-eE_{\text{ext}}u_i - e^2\frac{1}{2}\left(\frac{\partial^2 W}{\partial u_{i-1}\partial u_i}\Big|_{\text{eq}}u_{i-1} + \frac{\partial^2 W}{\partial u_i\partial u_{i+1}}\Big|_{\text{eq}}u_{i+1}\right)u_i \quad . \tag{A2}$$

Because of the translational symmetry of the crystal

$$\frac{\partial^2 W}{\partial u_{i-1}\partial u_i}\Big|_{\rm eq}=\frac{\partial^2 W}{\partial u_i \partial u_{i+1}}\Big|_{\rm eq}$$

and we set

$$\tfrac{1}{2}e\frac{\partial^2 W}{\partial u_{i-1}\partial u_i}\Big|_{\rm eq}=\kappa \ .$$

Moreover,

$$u_{i-1}+u_{i+1}=(u_{i-1}-u_i)-(u_i-u_{i+1})+2u_i$$

which in the continuum limit corresponds to $l^2\partial^2 u/\partial x^2+2u(x)$. Equation (A2) thus has the form

$$-eE_{\rm ext}u-e\kappa\left[l^2 u\frac{\partial^2 u}{\partial x^2}+2u^2\right] \ . \tag{A3}$$

Since the Euler-Lagrange equations of motion are

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot u}=\frac{\partial \mathcal{L}}{\partial u}-\frac{\partial}{\partial x}\left[\frac{\partial \mathcal{L}}{\partial(\partial u/\partial x)}\right]+\frac{\partial^2}{\partial x^2}\left[\frac{\partial \mathcal{L}}{\partial(\partial^2 u/\partial x^2)}\right] , \tag{A4}$$

Eq. (A3) leads to additional terms in Eq. (3.3). A simple way to account for them is to change

$$mc_0^2 \rightarrow mc_0^2+2el^2\kappa \ , \tag{A5}$$

$$A \rightarrow A-4el^2\kappa \ , \tag{A6}$$

$$E \rightarrow E_{\rm ext} \ . \tag{A7}$$

One should remark that Eq. (A6) also leads to a change in T_A [see Eq. (5.22)].

APPENDIX B

To calculate the dynamic structure factor we set

$$u(x,t)=u_w(x-x_0)+\delta u(x,t) \ . \tag{B1}$$

We expand $\delta u(x,t)$ in terms of the set $\{y_j(x-x_0)\}$ appropriate to a wall centered at $x=x_0$ [see Eq. (3.19) to Eq. (3.23)] and solve the Eq. (4.3) for the time-dependent coefficients $s_j(t)$. The solution is

$$s_j(t)=-(\gamma_1-\gamma_2)^{-1}\times\left[e^{-\gamma_1 t}\int_{t_0}^{t}e^{\gamma_1\tau}Q_j(\tau)\,d\tau-e^{-\gamma_2 t}\int_{t_0}^{t}e^{\gamma_2\tau}Q_j(\tau)\,d\tau\right] , \tag{B2}$$

where

$$\gamma_{1,2}=i\omega_j+\tfrac{1}{2}[\lambda\pm(\lambda^2-4\omega_j^2)^{1/2}] \equiv i\omega_j+\mu_{1,2} \tag{B3}$$

Now, to calculate the correlation $\langle\delta u(x,t)\delta u(x',t')\rangle$ we expand $\delta u(x',t')$ in the basis set $\{y_j{}^*(x'-x_0)\}$.

Denoting the expansion (3.23) in abbreviated form

$$\delta u(x',t')=\int s_j{}^*(t')y_j{}^*(x',x_0,t')\,dj \ , \tag{B4}$$

we have

$$\langle\delta u(x,t)\delta u(x',t')\rangle_{x_0}=\left\langle\int s_i(t)y_i(x,x_0,t)\,di\times\int s_j{}^*(t')y_j{}^*(x',x_0,t')\,dj\right\rangle \tag{B5}$$

where $\langle\ \rangle_{x_0}$ represents an equilibrium average over all degrees of freedom except the position x_0 of the domain wall. Clearly, we have

$$\langle\delta u(x,t)\delta u(x',t')\rangle_{x_0}=\int\int y_i y_j{}^*\langle s_i(t)\ s_j{}^*(t')\rangle\,di\,dj \ . \tag{B6}$$

Using Eq. (B2) the properties of the random fluctuating force and the orthonormality of the set $\{y_i\}$, we find

$$\langle s_i(t)s_j{}^*(t')\rangle=\delta_{ij}e^{-i\omega_i(t-t')}T_i(t-t') \ , \tag{B7}$$

where

$$T_i(t-t')=(\mu_1^2-\mu_2^2)^{-1}\times\left[\frac{e^{-\mu_2(t-t')}}{\mu_2}-\frac{e^{-\mu_1(t-t')}}{\mu_1}\right]\frac{C}{2m^2} \ , \tag{B8}$$

and δ_{ij} is the Kronecker delta function. Thus we have

$$\langle\delta u(x,t)\delta u(x',t')\rangle_{x_0}=[f_1(x-x_0)f_1(x'-x_0)]T_1(t-t')+[f_2(x-x_0)f_2(x'-x_0)]T_2(t-t')+\int_{\infty}^{\infty}|f_i(x-x_0)f_i(x'-x_0)|\,T_i(t-t')\,di \ . \tag{B9}$$

Finally, we regain the translational invariance of the sytem by averaging over the domain-wall position x_0. We have

$$\langle\delta u(x,t)\delta u(x',t')\rangle=\lim_{L\to\infty}\frac{1}{2L}\int_{-L}^{L}\langle\delta u(x,t)\delta u(x',t')\rangle_{x_0}\,dx_0 \ , \tag{B10}$$

where L is the length of the lattice. Then for small but nonvanishing domain-wall density n_w we write

$$\langle \delta u(x,t)\delta u(x',t')\rangle = n_w \int_{-\infty}^{\infty} [f_1(x-x_0)f_1(x'-x_0)T_1 + f_2(x-x_0)f_2(x'-x_0)T_2]\,dx_0 + \int_{\infty}^{\infty} T_i \left\{ \lim_{L\to\infty} \frac{1}{2L}\int_{-L}^{L} f_i(x-x_0)f_i^*(x'-x_0)\,dx_0 \right\} di \quad . \tag{B11}$$

We can now readily evaluate the power spectrum $S(k,\omega)$. Let us consider first the second term in Eq. (B11) associated with the continuum basis functions. From Eq. (3.21) we see that the continuum functions f_j are composed of a plane wave term $e^{ij\alpha(x-x_0)}$ and a part *localized* to the domain wall. In the limit as $L\to\infty$

$$\frac{1}{2L}\int_{-L}^{L} f_j(x-x_0)f_j^*(x'-x_0)\,dx_0 \to \frac{1}{2L}\int_{-L}^{L} e^{ij\alpha(x-x')}\,dx_0 = e^{ij\alpha(x-x')} \quad . \tag{B12}$$

Then, the contribution to $S(k,\omega)$ from the second term is

$$2\,\mathrm{Re}\int_0^{\infty} e^{iz(t-t')}\,d(t-t')\int_{-\infty}^{\infty} dj \int_{-\infty}^{\infty} e^{-ik(x-x')}e^{ij\alpha(x-x')}\,d(x-x')\,T_j(t-t')$$
$$= 2\,\mathrm{Re}\int_0^{\infty} e^{iz(t-t')}\,d(t-t')\int_{-\infty}^{\infty} dj\, T_j(t-t')\delta(j-k/\alpha)$$
$$= 2\mathrm{Re}\int_0^{\infty} e^{iz(t-t')}T_{k/\alpha}(t-t')\,d(t-t') \quad .$$

Integrating we obtain

$$S_1(k,\omega) = \frac{C/m^2}{[\omega^2-\omega_0^2(k)]^2+\lambda^2\omega^2} \quad , \tag{B13}$$

as $\omega_{k/\alpha}^2 = \omega_s^2(4+k^2/\alpha^2) = \omega_0^2(k)$. Here we have used the definitions (2.7) and (5.8).

We have simply regained the same phonon spectrum that appears when domain walls are absent. The neglect of the *localized* part of the modes $f_j(x-x_0)$ was equivalent to ignoring the small perturbation of the usual phonon modes caused by a low density of domain walls.

Now, the first term in Eq. (B11) is associated with oscillations of $u(x,t)$ which are localized to the wall, as can readily be seen from Eqs. (3.19) and (3.20) for f_1 and f_2. These two contributions are phonon modes arising from the presence of domain walls. Their contributions to $S(k,\omega)$ are given by $S_2(k,\omega)$ and $S_3(k,\omega)$, corresponding to the modes f_2 and f_1, respectively,

$$S_{3,2}(k,\omega) = 2\,\mathrm{Re}\int_0^{\infty} e^{iz(t-t')}T_{1,2}(t-t')\,n_w \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f_{1,2}(x-x_0)f_{1,2}(x'-x_0)e^{-ik(x-x')}\,dx_0\,d(x-x') \tag{B14}$$
$$= 2\,\mathrm{Re}\int_0^{\infty} e^{iz(t-t')}T_{1,2}(t-t')\,n_w|F_{1,2}(k)|^2 \quad , \tag{B15}$$

where $F_{1,2}(k)$ is the Fourier transform of $f_{1,2}(x)$,

$$F_{1,2}(k) = \int_{-\infty}^{\infty} e^{-ikx}f_{1,2}(x)\,dx \quad . \tag{B16}$$

The second mode, associated with f_2, is an asymmetric fluctuation of the wall with frequency ω_2, $\omega_2 = (3)^{1/2}\omega_s$ (see Fig. 2). Its contribution to $S(k,\omega)$ is $S_2(k,\omega)$,

$$S_2(k,\omega) = \frac{n_w C/m^2}{(\omega^2-3\omega_0^2/4)^2+(\lambda\omega)^2}|F_2(k)|^2 = n_w\frac{C}{m^2}\frac{3\pi k^2}{2\alpha^3}\mathrm{sech}^2\left(\frac{\pi k}{2\alpha}\right) \times \left[\left(\omega^2-\frac{3\omega_0^2}{4}\right)^2+(\lambda\omega)^2\right]^{-1} \quad . \tag{B17}$$

Let us now consider the first discrete term $S_3(k,\omega)$. From Eq. (B7) $T_1(t-t')$ is given by $\langle s_1(t)s_1(t')\rangle$, which, according to Eq. (4.7) is related to $\langle x_w(t)x_w(t')\rangle$; thus $T_1(t-t')$ grows linearly with $(t-t')$ at long times [see Eq. (4.18)]. However, since

$$\delta u \lesssim u_0, \quad \langle \delta u(x,t)\delta u(x',t)\rangle \lesssim u_0^2$$

the correlation function cannot grow indefinitely. We have already encountered this problem in Sec. III; there our equation for $\delta u(x,t)$, Eq. (4.2), was valid only for small δu. At large times $t-t'$ the wall moves considerably and $\delta u(x,t)$ must be large near the wall. While this does not affect our evaluation of the velocity autocorrelation in Sec. IV, here we must find some other means of evaluating the displacement autocorrelation. In Eq. (4.5), the wall motion is described by

$$u(x,t) = u_w(x) + \Omega s_1(t)\frac{du_w}{dx}, \text{ for small } s_1(t) \quad \text{(B18)}$$

$$= u_w(x + \Omega s_1(t))$$

$$= u_w(x - x_w(t)) \quad . \quad \text{(B19)}$$

The breakdown of Eq. (B18) for large $s_1(t)$ causes the divergence of $T_1(t-t')$. We assume that Eq. (B19) applies regardless of whether $s_1(t)$ is large or small. Equation (B19) is an appropriate description of the domain wall when all fluctuations of the domain wall are ignored *except* its diffusing position. Such fluctuations are accounted for by the usual phonon modes in the limit as $n_w \rightarrow 0$, and by the second discrete term. Therefore, we now consider the contribution to $S(k,\omega)$ stemming from the term $S_3(k,\omega)$. Using Eqs. (B19) and (5.3b) we have

$$S_3(k,t-t') \equiv n_w \int_{-\infty}^{\infty} e^{-ik(x-x')} \int_{-\infty}^{\infty} \langle u_w(x-[x_w(t)+x_0])\, u_w(x'-[x_w(t')+x_0])\rangle\, dx_0\, d(x-x') \quad . \quad \text{(B20)}$$

A simple change of variables, $y = x' - [x_w(t') + x_0]$ and $z = (x - x') + y - [x_w(t) - x_w(t')]$, gives

$$S_3(k,t-t') = n_w |u_w(k)|^2 \langle e^{-ik[x_w(t)-x_w(t')]}\rangle \quad , \quad \text{(B21)}$$

where

$$u_w(k) = \int_{-\infty}^{\infty} u_w(x) e^{-ikx} dx$$

$$= -iu_0 \frac{\pi}{\alpha} \operatorname{csch}\left(\frac{\pi k}{2\alpha}\right) \quad . \quad \text{(B22)}$$

To calculate $\langle e^{-ik[x_w(t)-x_w(t')]}\rangle$ we observe that from Eq. (4.8) follows:

$$\langle e^{-ik[x_w(t)-x_w(t')]}\rangle = \left\langle \exp\left[-ik\int_{t'}^{t} v(\tau)\, d\tau\right]\right\rangle$$

$$= \left\langle \exp\left[-ik\int_{0}^{t-t'} v(\tau)\, d\tau\right]\right\rangle . \quad \text{(B23)}$$

The last expression can be evaluated readily if we assume $R(x,t)$, Eqs. (2.9) to (2.11), to be a Gaussian process. Then only the second cumulant, $K_2(t-t')$ is nonvanishing, and[40]

$$\left\langle \exp\left[-ik\int_{0}^{t-t'} v(\tau)\, d\tau\right]\right\rangle = e^{K_2(t-t')} \quad , \quad \text{(B24)}$$

where

$$K_2(t-t') = -k^2 \int_0^{t-t'} d\tau_1 \int_0^{\tau_1} d\tau_2 \langle v(\tau_1) v(\tau_2)\rangle$$

$$= -k^2 D\lambda \int_0^{t-t'} d\tau_1 \int_0^{\tau} d\tau_2\, e^{-\lambda(\tau_1-\tau_2)}$$

$$= -k^2 D\left((t-t') + \frac{e^{-\lambda(t-t')}-1}{\lambda}\right) \quad \text{(B25)}$$

$$= -k^2 D(t-t') \quad \text{for } t-t' > \lambda^{-1} \quad . \quad \text{(B26)}$$

Thus, for time differences larger than λ^{-1} we have

$$\langle e^{-ik[x_w(t)-x_w(t')]}\rangle = e^{-Dk^2(t-t')} \quad . \quad \text{(B27)}$$

$S_3(k,t-t')$ is then given by

$$S_3(k,t-t') = n_w |u_w(k)|^2 e^{-Dk^2(t-t')} \quad . \quad \text{(B28)}$$

Finally, the frequency transform $S_3(k,\omega)$ is, using Eq. (B22)

$$S_3(k,\omega) = n_w \frac{u_0^2 \pi^2}{\alpha^2} \operatorname{csch}^2\left(\frac{\pi k}{2\alpha}\right) \frac{2Dk^2}{\omega^2 + (Dk^2)^2} \quad . \quad \text{(B29)}$$

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