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## Surface relaxation in crystals with spatial dispersion

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**Abstract.** Static response functions are derived for crystals with surfaces in a harmonic model showing spatial dispersion. The relaxed structure is then described by analytical formulae in crystals in which local stresses arise due to the presence of surfaces and in materials subject to macroscopic uniaxial stress with the axis either perpendicular or parallel to the surfaces. Pretransitional appearance of the new phase and the creation of antiphase domain walls in the crystals with surfaces are shown to be a consequence of thermal variation of effective force constants when the materials approach their structural phase transitions.

### 1. Introduction

The presence of surfaces engenders structural distortions extended to a larger or narrower subsurface zone of the crystal. Such a surface relaxation has been observed by low-energy electron diffraction (LEED) and x-ray diffraction under grazing angles in metals (Jona and Marcus 1988), semiconductors (Grey *et al* 1988) and other materials with both unreconstructed and reconstructed surfaces (Fu *et al* 1985). A deep and strong relaxation of the internal strain near the (001) surface of Ge and Si crystals under a uniaxial stress applied in the (110) direction has been reported by Cousins *et al* (1987).

All these phenomena reflect the reaction of the materials, which, being inhomogeneous due to the existence of their surfaces, are subject to either a local surface stress or to a homogeneous stress applied in the experiment. The surface stress comes from the inter-atomic forces, which are all balanced in the bulk but would remain non-compensated if the surface were created by just terminating the bulk structure at a given crystallographic plane. Existing models (Marcus *et al* 1988) show that the surface stress is spatially limited to several atomic layers under the surface.

The asymptotic behaviour of the strain far from the stress localised at the surface has been described recently by Allan and Lannoo (1988) in a model showing a spatial dispersion. In the present paper the static reaction of crystalline solids to any one-dimensional distribution of applied stress is obtained exactly with the use of the response function technique proposed by Zieliński (1988) and based on the surface–interface response theory developed by Dobrzynski (1986). Since the relaxation phenomena are expected to be particularly pronounced near displacive phase transitions, the parameters of the present model are chosen to illustrate the thermal evolution of the structure while a structural instability is being approached. This seems important because the surface effects of phase transitions are already being investigated (for reviews see Ipatova and

Kitaev 1985, Ernst *et al* 1987) and will certainly attract increasing interest in view of recent progress in experimental techniques.

General features of the static response functions, or Green functions, appropriate to the model are outlined in § 2 for materials displaying a non-local relation between stress and strain. The latter property, called spatial dispersion, is introduced here by phenomenological harmonic interactions of a sufficiently long, although finite, spatial range. The surface–interface response theory (Dobrzynski 1986) is then used to obtain the analytical expression for the static response function in crystals with surfaces. As a simple example of an application of the theory a perpendicular relaxation in a slab with two surfaces is studied in § 3. It is shown that a deviation of surface force constants from their values peculiar to the bulk is able to produce a surface phase transition in which the arrangement of subsurface atomic layers undergoes a modification. In § 4 the reaction of the same slab to a homogeneous strain is shown to be inhomogeneous in a certain region under the surfaces, a phenomenon which seems essential in the experiment of Cousins *et al* (1987). The corresponding local structure bears features of the soft mode when a structural instability is being approached.

## 2. Static response functions in crystals with surfaces

Knowing the crystallographic direction of the normal to the surface of interest, we shall treat the bulk crystal as an infinite succession of lattice planes perpendicular to this direction. Distortions that might occur within such planes will be, for the moment, neglected. Assuming that all the planes are identical and separated by a spacing  $a$  we shall denote by  $\mathbf{u}(l)$  the displacement vector of the  $l$ th plane and introduce new variables  $\mathbf{x}(l) = \mathbf{u}(l+1) - \mathbf{u}(l)$  proportional to the local  $l$ -dependent strain. In this notation the potential energy per unit area of the plane reads

$$\begin{aligned} E &= \frac{1}{2} \sum_{l=-\infty}^{\infty} \sum_{n=1}^M [\mathbf{u}(l+n) - \mathbf{u}(l)]^{\dagger} \boldsymbol{\beta}_n [\mathbf{u}(l+n) - \mathbf{u}(l)] \\ &= \frac{1}{2} \sum_{l=-\infty}^{\infty} \sum_{l'=l}^{l+M-1} \mathbf{x}^{\dagger}(l) \mathbf{H}(l, l') \mathbf{x}(l') \end{aligned} \quad (1)$$

where the coefficients  $\mathbf{H}(l, l')$  are  $3 \times 3$  matrices related to the force constant matrices  $\boldsymbol{\beta}_n$  through linear combinations:

$$\mathbf{H}(l, l') = \sum_{n=1}^{M-|l-l'|} n \boldsymbol{\beta}_{n+|l-l'|}. \quad (2)$$

The number  $M$  indicates the maximum range of the harmonic interactions.

The elements  $G_{\alpha\beta}(l, l')$ ,  $\alpha, \beta = 1, 2, 3$ , of the response function for the infinite crystal form, by definition, an infinite matrix inverse to the matrix of energy consisting of the elements  $H_{\alpha\beta}(l, l')$  so that

$$\sum_{l''=-\infty}^{\infty} \sum_{\alpha'=1}^3 H_{\alpha\alpha'}(l, l'') G_{\alpha'\beta}(l'', l') = \delta_{\alpha\beta} \delta_{ll'} \quad (3)$$

where  $\delta_{nm}$  is the Kronecker delta symbol.

To derive the explicit expression for the response function  $G_{\alpha\beta}(l, l')$ , it is convenient first to pass to reciprocal space in which the infinite matrix  $H_{\alpha\beta}(l, l')$  becomes block-diagonal, every  $3 \times 3$  block  $\mathbf{D}(k)$  being defined as

$$\mathbf{D}(k) = \sum_{l'-l=-M+1}^{M-1} \mathbf{H}(0, l' - l) \exp[ik\alpha(l' - l)] \quad (4)$$

for the wavevectors  $k$  from the first Brillouin zone:  $-\pi/a < k \leq \pi/a$ . Use has been made here of the translational periodicity of the matrix  $\mathbf{H}(l, l') = \mathbf{H}(0, l' - l)$ .

Evaluating the matrices  $\mathbf{G}(k) = \mathbf{D}^{-1}(k)$  inverse to these  $3 \times 3$  blocks one obtains the response function  $G_{\alpha\beta}(k)$ ,  $\alpha, \beta = 1, 2, 3$ , of the system in the wavevector representation. In view, however, of further applications of the theory to systems that are not perfectly periodic in space, it is more useful to have the response function  $G_{\alpha\beta}(l, l')$  in its original representation of positions  $l, l'$ , as defined in equation (3). The explicit form of this response function can be obtained by taking the Fourier transform of  $G_{\alpha\beta}(k)$  in the way described in detail by Zieliński (1988) (see also Mazur and Maradudin 1981). The resulting elements  $G_{\alpha\beta}(l, l')$  read

$$G_{\alpha\beta}(l, l') = \frac{1}{\det(\mathbf{H}(0, M-1))} \sum_{j=1}^{3(M-1)} \frac{A_{\beta\alpha}(z_j) z_j^{|l-l'|+3(M-1)}}{(z_j^2 - 1) \prod_{i=1, i \neq j}^{3(M-1)} (z_j - z_i)(z_j - z_i^{-1})} \quad (5)$$

where  $z_j, j = 1, \dots, 3(M-1)$ , are roots of the equation  $\det(\mathbf{D}(z)) = 0$  in which the  $3 \times 3$  matrix  $\mathbf{D}(z)$  has been obtained from the matrix  $\mathbf{D}(k)$  (equation (4)) by the substitution  $z = e^{ika}$ . All the roots involved in equation (5) have their moduli less than unity:  $|z_j| < 1$  (see the discussion below). The quantities  $A_{\alpha\beta}(z_j)$  of equation (5) are the algebraic complements of the corresponding elements  $D_{\alpha\beta}(z_j)$  of the matrices  $\mathbf{D}(z_j)$ . In other words,  $A_{\alpha\beta}(z_j)$  is obtained by multiplying by  $(-1)^{\alpha+\beta}$  the determinant of the  $2 \times 2$  matrix obtained by striking out the  $\alpha$ th row and the  $\beta$ th column of the matrix  $\mathbf{D}(z_j)$ .

The form of the Hermitian matrix  $\mathbf{D}(k)$  (equation (4)) shows that the expression for  $\det(\mathbf{D}(z))$  is symmetrical in the variable  $z$ , i.e. the powers  $z^j$  and  $z^{-j}, j = 1, \dots, 3(M-1)$ , enter here with identical real coefficients. As a consequence, all the  $2 \times 3(M-1)$  roots of the equation  $\det(\mathbf{D}(z)) = 0$  can be grouped into pairs  $z_j$  and  $z_j^{-1}$  since whenever a  $z_j$  satisfies the equation the corresponding  $z_j^{-1}$  fulfils it too. On the other hand, whenever  $|z| = 1$ , or equivalently,  $z = e^{ika}$  with a real wavevector  $k$ , the quantity  $\det(\mathbf{D}(z))$  is numerically equal to the product of the three eigenvalues of the corresponding matrix  $\mathbf{D}(k)$ . These are, at the same time, the eigenvalues of the infinite energy matrix of the elements  $H_{\alpha\beta}(l, l')$  (equation (2)). In a stable crystal all these eigenvalues for all the wavevectors must necessarily be positive and, consequently, their products must also be positive:  $\det(\mathbf{D}(z)) > 0$  if  $|z| = 1$ . Thus, the moduli of all the roots  $z_j$  and  $z_j^{-1}$  of the equation  $\det(\mathbf{D}(z)) = 0$  must be different from unity if the crystal is stable; otherwise at least one of the eigenvalues would vanish. It is now clear that out of each pair of the roots  $z_j$  and  $z_j^{-1}$  exactly one root has its modulus less than unity. Only for the sake of convenience have the roots of moduli less than one been denoted by  $z_j$  and not by  $z_j^{-1}$ . It is just these  $3(M-1)$  roots  $z_j, |z_j| < 1$ , of the equation  $\det(\mathbf{D}(z)) = 0$  that must be used to evaluate the response function  $G_{\alpha\beta}(l, l')$  in equation (5). It should be added here that the condition  $|z_j| < 1, j = 1, \dots, 3(M-1)$ , is only a necessary condition for the crystal to be stable. It only ensures that the eigenvalues of the energy matrix  $H_{\alpha\beta}(l, l')$  are different from zero, whereas stability requires that all the eigenvalues be positive.

From a physical point of view the static response function  $G_{\alpha\beta}(l, l')$  describes the distribution of the local strain  $\mathbf{x}(l)$  in the infinite crystal subject to a given distribution of the local stress  $s(l)$ . A local stress  $s(l)$  appears when two opposite forces are applied to neighbouring planes. Within the simplifications made, the forces are assumed to be homogeneously distributed in the direction parallel to the planes. The distribution of the local strain  $\mathbf{x}(l)$  in the crystal subject to a stress  $s(l)$  is then

$$\mathbf{x}(l) = \sum_{l'} \mathbf{G}(l, l') s(l'). \quad (6)$$

It is instructive to consider the distribution of the strain  $\mathbf{x}(l)$  under a stress  $s(l)$  localised, let us say, at  $l = 0$ , i.e.  $s(0) = s$  and  $s(l) = 0$  if  $l \neq 0$ . The resulting deformation  $\mathbf{x}(l) = \mathbf{G}(l, 0)s$  is then determined by a series of exponential functions  $z_j^{|l|}$  decreasing with distance  $|l|$  from the applied stress. The decrease is monotonic if the corresponding  $z_j$  is real positive and damped-oscillatory if  $z_j$  is complex or real negative. Equivalently, this can be expressed by saying that such a distortion is described by some wavefunctions  $z_j = e^{ik_j a l}$ , where the wavevectors  $k_j$  are generally complex,  $k_j = k_j' + ik_j''$ , the real part  $k_j'$  being responsible for the modulation and the imaginary part  $k_j''$  for the spatial damping. This statement generalises the asymptotic formula obtained by Allan and Lannoo (1988) to all conceivable combinations of damped-oscillatory functions.

When the effective force constants  $\beta_n$  change, for instance with temperature, the quantities  $z_j$  also change and one of them  $z_j$  may eventually acquire the modulus  $|z_j| = 1$ . This corresponds to an instability of the crystal. The response function (equation (5)) then becomes divergent because either  $z_j^2 = 1$  or there exists a root  $z_j$  complex conjugate to  $z_j$ ,  $z_l = z_j^* = e^{-ik_j' a}$ , so that  $z_l = z_l^{-1}$ , a property which is a consequence of the fact that the coefficients of the equation  $\det(\mathbf{D}(z)) = 0$  are real. The relative wavevector  $k_j$  becomes real and is the wavevector of the soft mode driving the phase transition (see Zieliński 1988).

In the presence of surfaces the response function has to be modified. For this purpose we define the potential energy of the semi-infinite series of planes labelled by  $l = 1, 2, 3, \dots$

$$E = \frac{1}{2} \sum_{l, l'=1}^{\infty} \mathbf{x}^{\dagger}(l) \mathbf{h}(l, l') \mathbf{x}(l') \quad (7)$$

where

$$\mathbf{h}(l, l') = \mathbf{H}(l, l') + \mathbf{V}_0(l, l') \quad l, l' \geq 1. \quad (8)$$

The cleavage operator  $\mathbf{V}_0(l, l')$  is defined to eliminate from the energy matrix  $\mathbf{H}(l, l')$  all the interactions of the lattice planes contained in the crystal (i.e. for  $l \geq 1$ ) with the non-existent planes labelled by  $l \leq 0$ . The explicit cleavage operator in the present model is

$$\mathbf{V}_0(l, l') = - \sum_{n=1}^{M-1} n \beta_{l+n} \quad \text{for } 1 \leq l' \leq l \leq M-1 \quad (9a)$$

and

$$\mathbf{V}_0(l, l') = \mathbf{V}_0(l', l) \quad \text{for } M-1 \geq l' \geq l \geq 1. \quad (9b)$$

To make use of the surface response theory (Dobrzynski 1986) it is convenient to define formally

$$\mathbf{V}_0(l, l') = -\mathbf{H}(l, l') \quad \text{for } l \geq 1 \text{ and } l' \leq 0 \quad (9c)$$

and

$$\mathbf{A}_0(l, l') = \sum_{l''=-M+2}^{M-1} \mathbf{V}_0(l, l'') \mathbf{G}(l'', l') \quad \text{for } l, l' \geq 1. \quad (10)$$

Thus, taking into account the indices  $l, l' = 1, \dots, M-1$  and the matrix indices  $\alpha, \beta = 1, 2, 3$ , the dimension of the non-zero block of the cleavage operator is  $3(M-1) \times 6(M-1)$  and the dimension of the non-zero part of the operator  $\mathbf{A}_0(l, l')$  is  $3(M-1) \times \infty$ . Then the response function  $g(l, l')$  defined so as to fulfil the relation

$$\sum_{l''=1}^{\infty} \mathbf{h}(l, l'') \mathbf{g}(l'', l') = \delta_{ll'} \mathbf{I}$$

reads (Dobrzynski 1986, Zieliński 1988)

$$\mathbf{g}(l, l') = \mathbf{G}(l, l') - \sum_{m, m'=1}^{M-1} \mathbf{G}(l, m) \mathbf{\Delta}^{-1}(m, m') \mathbf{A}_0(m', l') \quad (11)$$

where the sign 'inverse' refers to the  $3(M-1) \times 3(M-1)$  matrix  $\mathbf{\Delta}$  of the elements

$$\Delta_{\alpha\beta}(m, m') = \delta_{mm'} \delta_{\alpha\beta} + A_{0, \alpha\beta}(m, m') \quad m, m' = 1, \dots, M-1; \alpha, \beta = 1, 2, 3. \quad (12)$$

In fact, the surface described by the expression (11) is ideal in the sense that the cleavage operator (equations (9a) and (9b)) only eliminates some force constants whereas in the real material account should be taken of a possible difference between the remaining force constants near to the surface and the corresponding force constants in the bulk. Such a variation of the force constants only requires a modification of the cleavage operator (see Zieliński 1988) in the derivation of formula (11).

In a way completely analogous to that in which expression (11) has been derived one can obtain the response function for systems with several surfaces and/or interfaces (Dobrzynski 1986). As an example a model crystal with two parallel surfaces (a slab) will be treated in the next section.

### 3. Perpendicular relaxation in a crystal with two surfaces

The general formulae presented in the previous section become markedly simpler on the assumption that the displacements perpendicular to the surface are independent of parallel translations of the lattice planes. We shall adopt such an assumption and consider only perpendicular displacements in order to study the main features of the theory on a simple example. The resulting expressions are readily applicable to materials in which only a perpendicular relaxation occurs (Jona and Marcus 1988). Now the vector and matrix notation of  $\mathbf{u}(l)$ ,  $\mathbf{x}(l)$ ,  $\boldsymbol{\beta}_n$ ,  $\mathbf{H}(l, l')$ ,  $\mathbf{G}(l, l')$  and  $\mathbf{g}(l, l')$  can be dropped.

Putting  $M = 2$ , which is the simplest case exhibiting a spatial dispersion, one obtains the corresponding bulk response function

$$G(l, l') = \frac{1}{\beta_2} \frac{z_1^{|l-l'+1|}}{z_1^2 - 1} \quad (13)$$

where

$$z_1 = \begin{cases} -r + (r^2 - 1)^{1/2} & \text{if } r > 1 (\beta_2 > 0) \\ -r - (r^2 - 1)^{1/2} & \text{if } r < -1 (\beta_2 < 0) \end{cases} \quad (14)$$

while

$$r = (\beta_1 + 2\beta_2)/2\beta_2.$$

In the interval  $-1 \leq r \leq 1$  the crystal is unstable.

Admitting that the longitudinal force constants  $\beta_1$  and  $\beta_2$  depend on temperature, as is usually assumed in soft-mode theories of phase transitions (Cowley 1980), one finds that the limit  $r \rightarrow -1_-$  corresponds to an elastic phase transition whereas the limit  $r \rightarrow 1_+$  corresponds to an instability with the soft mode of wavevector  $k = \pi/a$  from the Brillouin zone boundary.

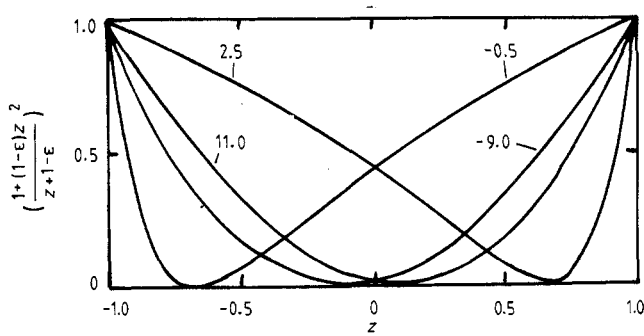
The expression for the response function in the crystal consisting of  $L + 1$  lattice planes and thus possessing two parallel surfaces is

$$\begin{aligned} g(l, l') &= \frac{1}{\beta_2} \frac{z_1^{|l-l'+1|}}{z_1^2 - 1} \left( \frac{z_1 + 1 - \varepsilon}{1 + (1 - \varepsilon)z_1} \right) \frac{z_1^{l+l'}}{\beta_2(z_1^2 - 1)} \\ &\quad \times \frac{(z_1 + 1 - \varepsilon)z_1^{2L+1}}{\beta_2(z_1^2 - 1)\{[1 + (1 - \varepsilon)z_1]^2 - z_1^{2L}(z_1 + 1 - \varepsilon)^2\}} \\ &\quad \times \left\{ [1 + (1 - \varepsilon)z_1] \left[ \left( \frac{z_1 + 1 - \varepsilon}{1 + (1 - \varepsilon)z_1} \right)^2 z_1^{l+l'-1} + z_1^{l-l'} \right] \right. \\ &\quad \left. - (z_1 + 1 - \varepsilon)(z_1^{l-l'} + z_1^{l'-l}) \right\} \quad (15) \end{aligned}$$

where the quantity  $\varepsilon$  defines the deviation of the surface force constant  $\beta_1^s$  from the corresponding bulk force constant:  $\varepsilon = (\beta_1^s - \beta_1)/\beta_2$ . Formula (15) allows for the determination of the relaxed structure under any distribution of applied stress. Putting a stress  $s(1)$  between two first planes  $l = 1$  and  $l = 2$  only and passing to the limit  $L \rightarrow \infty$  one recovers the asymptotic expression obtained by Allan and Lannoo (1988) for a semi-infinite sample with a stress localised on the surface. When  $0 < z_1 < 1$ , i.e.  $\beta_2 < 0$ , the local strain  $x(l) = g(l, 1)s(1)$  decays exponentially with distance from the surface, whereas for  $-1 < z_1 < 0$ , i.e.  $\beta_2 > 0$ , the relaxation has an alternating character most frequently observed in real materials. Different spatial modulations would appear for the range of interactions  $M$  larger than 2 (Zieliński 1988).

A thermal variation of the force constants towards the limits of stability, i.e. when  $z_1 \rightarrow 1$  or  $z_1 \rightarrow -1$  (see equation (14)), results in an increase in the amplitude and the spatial extent of the structural distortion. In crystals undergoing the corresponding bulk phase transitions, such behaviour manifests itself by the pretransitional appearance of the structure peculiar to the new phase.

An interesting property of a crystal with surfaces is that under some conditions an instability of the structure may occur even in the region of  $\beta_1$  and  $\beta_2$  where the bulk



**Figure 1.** Right-hand side of equation (16) versus  $z$  for some values of  $\varepsilon$  (indicated above the curves). Solutions of equation (16) correspond to the intersection of these curves with the  $z^{2L}$  curve.

structure is stable. Such an instability should be understood as a phase transition localised at the surface. Here the transition will consist of the loss of the equidistant structure by the system of identical lattice planes. The critical value  $z_1 = z_c$  corresponding to such an instability is defined by the divergence of the response function (15) and can be obtained from the equation

$$z_c^{2L} = \left( \frac{1 + (1 - \varepsilon)z_c}{z_c + 1 - \varepsilon} \right)^2 \quad (16)$$

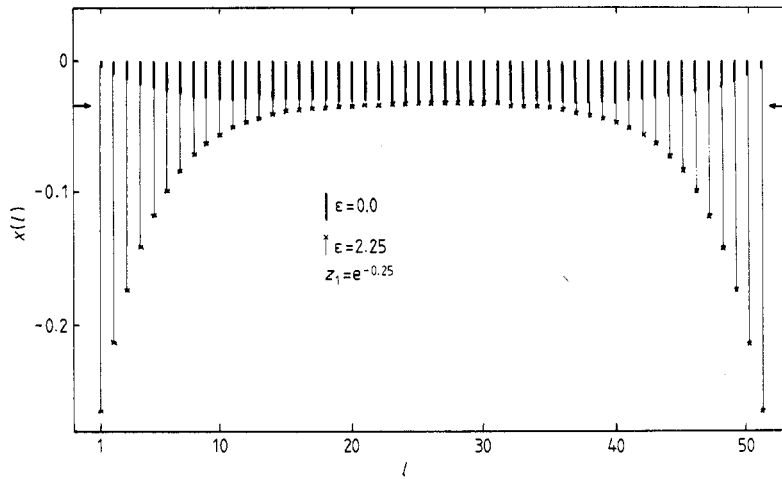
The plot of the right-hand side of equation (16) in figure 1 helps one to realise that the condition (16) can be fulfilled in the region of stability of the bulk, i.e. for  $|z_c| < 1$ , only when either  $\varepsilon < 0$  and  $-1 < z_c < 0$  or  $\varepsilon > 2$  and  $0 < z_c < 1$ . Indeed, the crystal is always stable for  $z_1 = 0$ ; then the closest to  $z_1 = 0$  point of intersection of the function  $z_1^{2L}$  with the corresponding line from figure 1 marks the instability. In any case the surface phase transition occurs at  $\beta_1^1 < \beta_1$ . It seems likely that such a surface relaxation phase transition is able to provoke a related surface reconstruction phase transition. The latter can also be described within the same kind of theory taking into account possible structural distortions within the planes (Wang *et al* 1988).

#### 4. Surface effects of homogeneous stress

The application of a macroscopic stress to a perfect infinite crystal always results in a homogeneous deformation of the material whose reaction to the stress is defined by macroscopic and inner elastic constants (Cousins 1978). However, in reality any stress can only be transmitted to the material through the boundaries of the sample. Some inhomogeneity of the deformation should, therefore, be expected near to the loaded surfaces and even in a neighbourhood of the surfaces free of stress in the case when the stress is uniaxial. Knowledge of the static response functions allows for the quantitative description of the structure in finite stressed crystals within the limits of elasticity.

As the simplest example we shall consider the effect of a uniaxial stress imposed perpendicular on the surface of the slab treated in the previous section. The distribution of the local stress  $s(l)$  produced by opposite external forces applied to the limiting planes





**Figure 2.** Deformation  $x(l) = u(l + 1) - u(l)$  of slab containing 52 atomic layers under homogeneous compressive stress in case  $\beta_2 < 0$ . Influence of the surface force constant is visible. Arrow indicates homogeneous deformation of infinite crystal.

of the slab  $l = 1$  and  $l = L + 1$  respectively is homogeneous:  $s(l) = s$ . Consequently, in the absence of other stresses, the deformation  $x(l)$  is

$$x(l) = s \sum_{l'=1}^L g(l, l'). \tag{17}$$

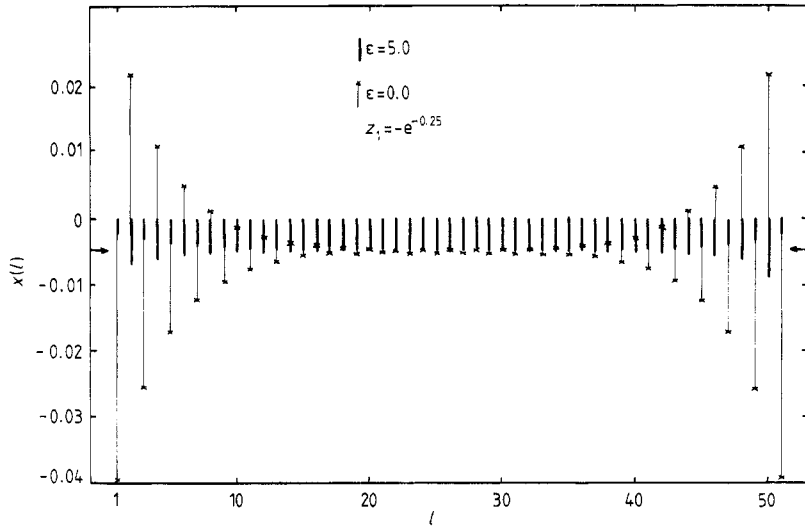
(One should notice that the number of local strain variables  $x(l) = u(l + 1) - u(l)$  is  $L$  in the slab of  $L + 1$  planes.)

In view of the analytical form of the response function (equation (15)) the summation in equation (17) reduces to some geometrical series and can be done explicitly:

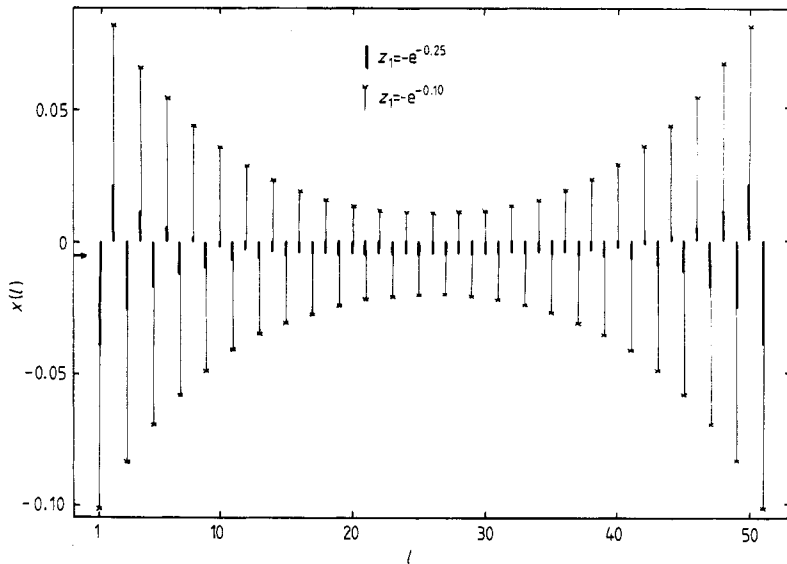
$$x(l) = \frac{sz_1}{\beta_2(z_1^2 - 1)(z_1 - 1)} \times \left( -(z_1 + 1) + (1 + \gamma) \frac{z_1^l + z_1^{l+1-l} - (z_1^{l-L} + z_1^{1-l})\gamma^{-1}}{z_1^l\gamma - z_1^{-L}\gamma^{-1}} \right) \tag{18}$$

where  $\gamma = (z_1 + 1 - \epsilon)/[1 + (1 - \epsilon)z_1]$ . The first term in the large parentheses of equation (18) describes the homogeneous response of the infinite material to the applied stress. The response of the crystal with surfaces can also be homogeneous provided that  $\epsilon = 2$  ( $\gamma = -1$ ). This is, however, only a special case. Normally, a finite crystal subject to a homogeneous stress shows a deformation that depends on the distance from the surface and only at a certain depth acquires the form peculiar to the bulk material. An example of such behaviour is depicted in figure 2 for  $z_1 > 0$ , i.e.  $\beta_2 < 0$ . The value  $\epsilon = 2.25$  is chosen rather close to the critical value  $\epsilon_c = 2.284$  corresponding to the surface instability (see the previous section). This explains the strong compression in the vicinity of the surfaces.

The influence of the surface force constant  $\beta_1^{\dagger}$  in the case  $z_1 < 0$ , i.e.  $\beta_2 > 0$ , is shown in figure 3. Here the uniaxial stress locally produces an alternating structure compatible with the mode of the wavevector  $k = \pi/a$ . If the surface force constant is sufficiently hard,  $\epsilon > 2$ , the first inter-layer distance is shorter than the second one, etc. For  $\epsilon < 2$



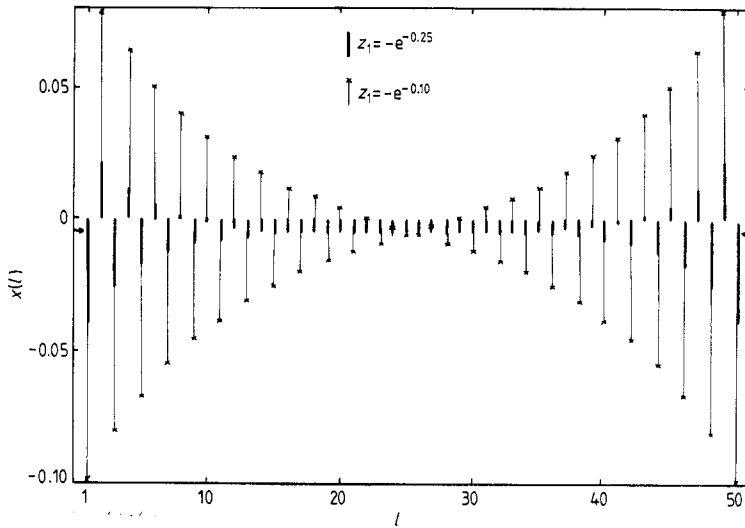
**Figure 3.** Alternating deformation of the slab under homogeneous compressive stress for  $\beta_2 > 0$ .



**Figure 4.** Slab of even number of layers under uniaxial compressive stress;  $\epsilon = 0$ .

the sequence is the reverse. This exemplifies the role of the surfaces in creating one of the two possible antiphase domains in the phase transition driven by the soft mode with  $k = \pi/a$ .

When the bulk instability is approached, i.e.  $z_1 \rightarrow -1$ , the deformation corresponding to the soft mode becomes stronger and more extended in space, as is shown in figures 4 and 5. The comparison of both figures reveals the dependence of the distorted



**Figure 5.** Slab of odd number of layers under uniaxial compressive stress;  $\epsilon = 0$ . Nucleus of antiphase domain wall is visible in the middle.

structure on the number of layers in the slab. Since both the slab itself and the stress have reflection symmetry with respect to the middle plane of the slab, the deformation of both surfaces is completely symmetrical. In the case of an odd number of layers this symmetry can only be achieved by creating a defect (antiphase domain wall) shown in figure 5.

Formula (18) applies to a compressive ( $s < 0$ ) as well as to an elongating ( $s > 0$ ) stress. However, the latter is much more difficult to obtain experimentally.

From the experimental point of view free surfaces of uniaxially stressed crystals are more interesting as they are easily accessible for structural studies. The behaviour of such surfaces can also be analysed with the use of the derived response functions. Denoting by  $x$  the direction normal to the slab and by  $y$  the direction of the axis of the stress  $s_{22}$  parallel to the slab, one can write the following equations of equilibrium:

$$\sum_{l'=1}^L h(l, l')x(l')/a + \eta(l)e_{22} = 0 \quad (19)$$

$$\sum_{l'=1}^L \eta(l')x(l')/a + c_{22}e_{22} = s_{22} \quad (20)$$

where  $h(l, l')$ ,  $l, l' = 1, \dots, L$ , is the matrix of potential energy analogous to equation (8) and  $c_{22}$  is the longitudinal elastic constant in the  $y$  direction. Far enough from the loaded surfaces the compressive strain in the material is sufficiently homogeneous and is denoted here by  $e_{22}$ . The coefficient  $\eta(l)$  is related to the force constants of the pairs of atoms linked by contacts oblique with respect to the  $x$  and  $y$  directions. In the bulk material the quantity  $\eta(l)$  becomes independent of  $l$  and amounts to the elastic constant

$c_{12}$ . Remembering that  $\sum_{l''=1}^L h(l, l'')g(l'', l') = \delta_{ll'}$ , one finds the deformation  $x(l)$  from equations (19) and (20):

$$x(l) = \frac{-s_{22}a}{c_{22}[1 - \sum_{l, l'=1}^L \eta(l)g(l, l')\eta(l')]} \sum_{l'=1}^L g(l, l')\eta(l'). \quad (21)$$

In the special case, where only interactions between the atoms of different  $y$  coordinates exist for nearest-neighbour planes, the quantity  $\eta(l)$  becomes  $l$ -independent and the deformation of the crystal is just proportional to that given by equation (18).

## 5. Discussion

The analytical results obtained in §§ 3 and 4 are directly applicable to centrosymmetric crystals with surfaces oriented so that the perpendicular motions of the lattice planes can be decoupled from their parallel displacements. Additionally, the site symmetry of all the atoms has to include inversion. Otherwise degrees of freedom should be taken into account corresponding to internal strains (Cousins 1978). This will increase the dimension of the generalised force constant matrices in equation (1), but the main scheme of the theory will remain the same. It seems that the surface effect in Ge and Si stressed crystals (Cousins *et al* 1987) mainly comes from the spatial dispersion of the materials and can be described with the use of this kind of theory.

The most interesting phenomena predicted by the present model seem to occur in free and stressed crystals undergoing structural phase transitions. Thanks to the spatial dispersion, the surfaces of such materials play the role of nuclei of the new phase within the matrix of the initial phase. In perfectly prepared thin layers of such crystals the surfaces can even control the appearance of domains and domain boundaries (see figures 4 and 5). For the moment experimental studies are limited to the role of surfaces in lock-in phase transitions of incommensurate modulated crystals (Garel and Moudden 1987) but further investigations in this direction are imminent in the near future.

A limitation of the present model comes from the harmonic approximation, which may well be insufficient if the deformation becomes too strong. It means that, very close to continuous phase transitions and under very high stress, anharmonic terms should be added to the expression (1). In such a case perturbation theory has to be used to obtain a realistic response function of the system.

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