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A pre-martensitic elastic anomaly in nanomaterials: elasticity of surface and interface layers

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Abstract

A pre-martensitic elastic anomaly inside the stability field of the austenite phase is predicted. While relaxation patterns near surfaces and interfaces are relatively insensitive to changes of pressure, an anomaly occurs as a precursor to the ferroelastic transition. The exponential relaxation pattern maintains its characteristic length but changes amplitude, like in the elastic softening of bulk materials. This effect is not related to the movement of interfaces but represents an intrinsic feature of the surface and interface layers. This effect is expected to be observable in ceramics consisting of nanomaterials with 'soft' inter-granular interfaces. The general theory and an exactly solvable model are presented and analysed numerically.

1. Introduction

An elastic instability is predicted as a precursor to a martensitic or ferroelastic phase transition. It relates to interfacial softening in the paraelastic phase and is best visible in materials where the volume of the interfaces is optimized, such as in nanomaterials. The effect is not related to the movement of domain walls as expected in the ferroelastic or martensitic phase but represents an intrinsic feature of the surface relaxation. The effect is similar to that of the softening of acoustic phonons (Carpenter and Salje 1998) while the response is now static and localized next to surfaces.

The existence of soft interface layers has often been postulated with consequences for enhanced diffusivity and structural relaxations (Green and Zerna 1954, Page *et al* 2004, Sennour *et al* 2008, Divinski and Herzig 2008, Aird and Salje 1998, 2000, Kuo 2008, Benveniste and Miloh 2007, Baumberger and Caroli 2006, Shenoy and Sharma 2003, Lee *et al* 2006, 2003a, 2003b, 1999, Salje *et al* 2005). Interfaces in super lattice structures are equally found to enhance, say, ferroelectricity related to interfacial relaxations (Shah *et al* 2008) while the strong temperature dependence of the wall thickness (Chrosch and Salje 1999) shows the intrinsic thermodynamic instability of wall profiles and may suggest that such features are also strongly pressure dependent. The elastic response of relaxational pattern is equally important for the propagation of seismic waves (Romanowicz and Durek 2000, Andrews *et al* 2006, Faul and Jackson 2007) while it

is unlikely that any such elastic softening has intrinsic origins besides in the vicinity of ferroelastic instabilities (Salje 2008).

It appears that the experimental evidence for intrinsic softening is relatively poor with most cases related to interfacial slip rather than elastic softening of the interface itself (Jackson *et al* 2000). It has been argued recently that if interfaces are not wetted (Faul and Jackson 2007) or related to movement of either the interface itself or atomic diffusion which would lead to such movements that interfaces contribute very little to the supposed softening of multigrain materials (Salje 2008). In particular the Hashin–Shtrikman limit of such materials including interfacial energies can lead to hardening rather than softening of nanomaterials (Salje 2007, Li *et al* 2005) which is very different from the case of voids which leads to a significant reduction of the elastic response of porous material (Milton 2002). Another example concerns interfaces in radiation damaged material which are denser than the bulk and the encapsulated amorphous regions and hence contribute greatly to the hardening of the material as compared with simple Voigt or Reuss interpolations (Salje 2007, Trachenko 2007). In the small grain Pertsev–Salje limit the elastic susceptibility of quartz, for example, is expected to display an almost second order phase transition at the alpha–beta transition point (Pertsev and Salje 2000). While this effect was observed by Rios *et al* (2001), more detailed measurements of the elastic behaviour by McKnight *et al* (2008) seem to be at variance with this result and display a classic behaviour albeit

with base line changes which seem to indicate grain boundary softening.

The fundamental question is whether elastic anomalies related to surfaces and twin boundaries (but not chemical interfaces such as seen in case of radiation damaged domains or glassy interfaces) can change the elastic moduli. More precisely, the question is whether a material, which relaxes structurally but remains topologically and chemically intact at the interface or surface, will show elastic softening related to this structural relaxation. Evidence for the equivalent effect in ferroelectric materials and vortex lattices was recently provided in the low temperature phase numerically by Lahoche *et al* (2007) and experimentally for the switching behaviour of vortex ferroelectric domains by Gruverman *et al* (2008). In either case the role of the surface relaxation is clearly seen for the arrangement of the polarization vectors. In the ferroelastic case, the relaxation of the surface layers of apatite showed that the relaxation extended for conditions unrelated to phase transitions to some five atomic layers (Lee *et al* 2000, Speer and Salje 1986).

In this paper the structural relaxation near surfaces and their elastic response is examined in the multilayer approach first introduced by Houchmanzadeh *et al* (1992). Interfacial layers can be understood in exactly the same manner provided that the model parameters are suitably adapted to this physical situation. This approach is a mechanical minimization problem and does not take into account higher order effects as one would encounter in Landau Ginzburg theory. Technically speaking we consider only the quadratic terms in any thermodynamic potential which is sufficient for states in the paraelastic phase. ‘Divergence’ will be seen when the transition points are approached. These divergences are physical reality although their amplitudes will be limited in higher order theory. Nevertheless, the physical character of the divergence remains the same as will be argued below. It will be shown that the decay function of the relaxation can change slightly (interfaces can become sharper or more diffuse) while the elastic response can be related to the bulk elastic constants via a suitable Gruneisen parameter. Intrinsic elastic softening occurs as a precursor to the ferroelastic or martensitic phase transition.

Finally, the relaxation is reduced in this paper to the simplest physical model, namely a chain of interacting springs, with no further internal degrees of freedom. In reality, materials with several atoms per unit cell will generally contain such additional degrees of freedom (Goncalves-Ferreira *et al* 2008, Salje 1985, Schmahl *et al* 1989) so that surface relaxations also become the obvious locus for secondary order parameters such as polarization, magnetic moments etc even though the relaxation is elastic in origin.

2. The layer model with second nearest neighbour interactions

The relaxation of any interface or surface layer can be written in a multilayer Hamiltonian in which the n th layer coordinate depends on the layers above and below the layer. In this paper the interactions are restricted to first and second

nearest neighbour interactions, the extension to higher order interactions was treated for the relaxation by Houchmanzadeh *et al* (1992) and can easily be adapted to the approach taking in this paper. The layer distance is $Z_{n+1} - Z_n$, the Hamiltonian is

$$H = \Sigma V(Z_{n+1} - Z_n) + V(Z_{n+2} - Z_n) \quad (1)$$

where V denotes an arbitrary interatomic or inter layer potential. The equilibrium condition for the stress-free scenario is

$$V'(b) + 2V'(2b) = 0 \quad (2)$$

where b is the equilibrium lattice parameter for the interlayer distance. $V'(b)$ and $V'(2b)$ are the first spatial derivatives of the potential at the distance b and $2b$, respectively.

The lattice parameter b changes to $b + \delta b$ when the stress σ is applied. Developing V into first order derivatives in b leads to

$$V'(b) + V''(b)\delta b + 2V'(2b) + 4V''(2b)\delta b = \delta\sigma. \quad (3)$$

The equilibrium condition for the stress-free case leads to $\delta\sigma = (V''(b) + 4V''(2b))\delta b$ and the effective elastic modulus becomes

$$C = (V''(b) + 4V''(2b))b = (\phi_1 + 4\phi_2)b. \quad (4)$$

The symbol ϕ is used for the classic force constants with the index 1 for nearest layer interactions and 2 for second nearest layer interactions. Elastic stability is obtained for $C > 0$ or $(\phi_1 + 4\phi_2) > 0$ in accordance with the criterion for the stability of zone centre phonons. We now consider the relaxation of the layers under stress around the new lattice parameter $b^* = b + \delta b$. The relaxational parameter is ε_n with $Z_{n+1} - Z_n = b^* + \varepsilon_n$ with $\varepsilon_n = 0$ in the bulk and finite values only near the surface or interface.

The equilibrium condition is $\delta H / \delta \varepsilon_n = 0$ with

$$\delta H / \delta \varepsilon_0 = V'(2b^*) + (\phi_1 + \phi_2)\varepsilon_0 + \phi_2\varepsilon_1 = 0 \quad (5)$$

for the first layer and

$$\delta H / \delta \varepsilon_n = \phi_2\varepsilon_{n-1} + (\phi_1 + 2\phi_2)\varepsilon_n + \phi_2\varepsilon_{n+1} = 0 \quad (6)$$

for the n th layer. For interfaces the parameter $V'(2b^*)$ defines the relaxation amplitude and, when appropriate, the boundary conditions. In case of surface relaxations with the vacuum as boundary condition outside the solid this parameter is simply the derivative of the interaction potential as taken at the second nearest neighbour position. This recursive expression has solutions which decay exponentially in the bulk of the material with

$$\varepsilon_n = \lambda^n \varepsilon_0 \quad (7)$$

where the characteristic length ($b \ln |\lambda|$) is determined by the ratio of the force constants ϕ_i

$$\lambda = -(1 + \phi_1/2\phi_2) \pm ((1 + \phi_1/2\phi_2)^2 - 1)^{1/2}. \quad (8)$$

The solution is a decaying wave with $|\lambda| < 1$. Its value depends only on the ratio $\phi_1/2\phi_2$ and hence the pressure effect can be written as

$$\begin{aligned} \phi_1/2\phi_2(\sigma) &= \phi_1/2\phi_2(\sigma = 0) \\ &+ (\phi_2\delta\phi_1/\delta\sigma - \phi_1\delta\phi_2/\delta\sigma)\sigma/2\phi_2^2. \end{aligned} \quad (9)$$

The frequency of the zone boundary phonon in the relaxed system is given by $\omega^2 = \phi_1 > 0$ which leads to the relation

$$\begin{aligned} \delta\phi_1/\delta\sigma &= 2\omega\delta\omega/\delta\sigma = 2\gamma_1\phi_1(\delta V/\delta\sigma)/V \\ &= 2\gamma_1\phi_1/b(\phi_1 + 4\phi_2) = 2\gamma_1\phi_1/C. \end{aligned} \quad (10)$$

The second equality represents the mode Gruneisen relationship and the last normalizes the stress by the elastic modulus. The second characteristic frequency relates to the zone boundary mode $\omega^2 = \phi_1 + 4\phi_2 > 0$. Using the same arguments as above one can show that

$$\delta\phi_2/\delta\sigma = (1/2(\gamma_2 - \gamma_1)\phi_1 + 2\gamma_2\phi_2)/C. \quad (11)$$

Two lattice instabilities occur for $\phi_1 = 0$ (anti-ferroelastic) and $\phi_1 = -4\phi_2$ (ferroelastic). At the instability points the characteristic length $b \ln |\lambda|$ vanishes which leads to a uniform sample. The thickness of the surface layer then scales as $b/\ln |\lambda|$ i.e. the surface layers spreads over the entire sample. The parameter λ becomes 1 for the ferroelastic phase transition and -1 for the anti-ferroelastic phase transition. The pressure derivatives disappear for $\phi_1 = 0$ because both terms in equation (9) disappear. In case of $\phi_1 = -4\phi_2$ it is easy to verify that the total stress derivative also disappears because the two terms in equation (9) cancel. This means that the characteristic length of the surface or interface relaxation does not change under stress at either transition conditions.

For conditions for very narrow interfaces far away from the transition points we have $\phi_1 \gg \phi_2$. Under these conditions the total derivative becomes

$$(\phi_2\delta\phi_1/\delta\sigma - \phi_1\delta\phi_2/\delta\sigma) = 1/2(\gamma_1 - \gamma_2)\phi_1^2/C \quad (12)$$

where C becomes $C = \phi_1 b$ so that equation (12) becomes simply $1/2(\gamma_1 - \gamma_2)\phi_1/b$

The variation of λ is then given by

$$\delta\lambda = (\gamma_2 - \gamma_1)/4\lambda^2(\delta\sigma/C) \quad (13)$$

with $\lambda = \phi_2/\phi_1$ in this limit. For long ranging relaxations, the variation is λ is small but for very short length scales the variation in λ can be significant.

3. Amplitude variations

We now turn to the pressure dependence of the amplitude of the structural relaxation. The relaxation amplitude is determined by ε_o in equation (5) with

$$\begin{aligned} \varepsilon_o &= -V'(2b)/[\phi_2(2 + \phi_1\phi_2 - 1 + \lambda)] \\ &= -V'(2b)/(\phi_1 + \phi_2 + \lambda\phi_2) \end{aligned} \quad (14)$$

$V'(2b)$ represents an interface or surface boundary condition which, say, for surface layers can include the role of absorbents, local fields etc. In the limit of $\phi_1 \gg \phi_2$ and hence small values of λ we find the trivial solution

$$\varepsilon_o = -V'(2b)/\phi_1 \quad (15)$$

which indicates that the first layer relaxes but that all further layers assume essentially the unrelaxed interatomic distances. The anti-ferroelastic phase transition occurs at $\phi_1 = 0$ and

$\lambda = -1$ so that in this case the first layer relaxation diverges because the unit cell doubles perpendicular to the surface or interface and the original interlayer distance is no longer defined in this model.

A ferroelastic transition occurs at $\phi_1 = -4\phi_2$ and $\lambda = 1$

$$\varepsilon_o = V'(2b)/2\phi_2 = -2V'(2b)/\phi_1. \quad (16)$$

If V' is given as a boundary condition the amplitude ε_o remains finite. We will show later that V' can depend explicitly on the second derivatives which will lead to a divergence of ε_o . We now focus, as an example, on the case that the relaxation is spread over a relatively small distance and investigate equation (15). The stress dependence of ε_o is

$$\begin{aligned} \delta\varepsilon_o/\delta\sigma &= -(\phi_1\delta V'(2b)/\delta\sigma - V'(2b)\delta\phi_1/\delta\sigma)/\phi_1^2 \\ &= -(\phi_1\delta V'(2b)/\delta b\delta b/\delta\sigma - V'(2b)\delta\phi_1/\delta\sigma)/\phi_1^2 \end{aligned} \quad (17)$$

where the second partial derivative is given by equation (10) while $\delta b/\delta\sigma$ is given by the elastic constants of the bulk in equation (4).

The elastic constant C^* for the first layer $\delta\varepsilon_o/\varepsilon_o/\delta\sigma$ is in this approximation

$$C^* = C/2\gamma_1. \quad (18)$$

Elastic softening occurs in the interfacial or surface layer when $\gamma_1 > 0.5$. For weakly anharmonic materials we find that the Gruneisen parameter is in the order between 0.1 and 1 so that the elastic response of the surface layer is in the same order of magnitude as the elastic modulus of the bulk.

4. A toy model: exact solutions and numerical results

We can now define a fully solvable model with interactions perpendicular to the surface. In figure 1 such a model with two generalized springs between nearest and next nearest layers is shown. The Hamiltonian is now

$$H = \Sigma(\phi_1/2(b + \varepsilon_i - a_1)^2 + \phi_2/2(2b + \varepsilon_i + \varepsilon_{i+1} - a_2)^2). \quad (19)$$

The surface condition is the vacuum with no additional boundary conditions attached. The generalized spring constants can assume positive and negative values and are defined as ϕ_1 and ϕ_2 . The equilibrium condition for the lattice parameter b follows from equation (2)

$$b = (\phi_1 a_1 + 2\phi_2 a_2)/(\phi_1 + 4\phi_2) \quad (20)$$

the denominator is C and the length parameter λ depends only on the ratio of the force constants $f = \phi_1/\phi_2$ as

$$\lambda = \pm 1/2(f^2 + 4f)^{1/2} - 1/2f - 1. \quad (21)$$

The sign is to be taken so that $\lambda \leq 1$. The amplitude function is

$$\varepsilon_o = 2(2a_1 - a_2)f/[(f + 4)(f^2 + 4f)^{1/2} + 4f + f^2]. \quad (22)$$

The misfit between the nearest layer lattice parameter a_1 and the next nearest layer lattice parameter a_2 is given by the pre-factor $2a_1 - a_2$. If both springs are individually in their energy minimum there is no lattice relaxation and

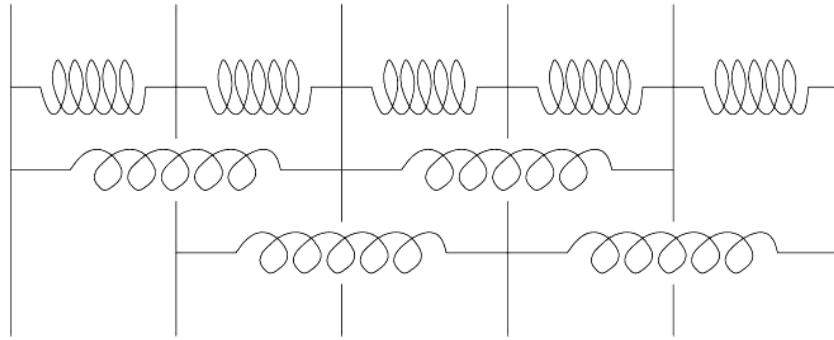


Figure 1. The two-spring model with free surfaces. Nearest neighbour layers are connected by a spring with force constant ϕ_1 , the second nearest neighbours are connected by springs with the force constant ϕ_2 . The equilibrium distances are a_1 and a_2 , the misfit parameter is $2a_1 - a_2$.

the amplitude becomes zero. The pressure dependence of the characteristic length and the amplitude depends only on the fraction f . Following the same arguments as above, the anharmonicity is expressed in terms of the Gruneisen parameters of the two characteristic modes at $k_1 = 0$ and $k_2 = \pi/b$

$$\delta f/\delta\sigma = (f + f^2/4)(\gamma_1 - \gamma_2)/C. \quad (23)$$

$\delta f/\delta\sigma$ plays the role of an ‘inverse elastic modulus of the relaxation’ with positive and negative admissible values. It is proportional to the difference of the Gruneisen parameters and inversely proportional to the elastic modulus of the bulk. Note that $\delta f/\delta\sigma = 0$ at both transition points as discussed above. External stress does not change f at these points. The stress dependence of λ can now be evaluated via

$$\delta\lambda/\delta\sigma = [(1 + f/2)/(f^2 + 4f)^{1/2} - 1/2]\delta f/\delta\sigma \quad (24)$$

and the amplitude function via

$$\begin{aligned} \delta\varepsilon_o/\delta\sigma = & 2(2a_1 - a_2)[(1 + 4/f)(2f + 4)/(f^2 + 4f)^{1/2} \\ & + 4/f^2(f^2 + 4f)^{1/2} + f]/[(1 + 4/f)(f^2 + 4f)^{1/2} \\ & + 4 + f]^2\delta f/\delta\sigma \end{aligned} \quad (25)$$

where each root-function has to be taken as its negative for $f < -4$. Numerical calculations were undertaken for the parameters $\lambda(f, \sigma)$ and $\varepsilon_o(f, \sigma)$ as functions of the ratio between the force constants f and the external pressure σ . The pressure is measured in units of C in order to allow a comparison with the elastic behaviour of the bulk. In the numerical analysis the difference of the Gruneisen parameters is put to 0.1 and the misfit strain to 5%. The calculations were done for the stability range $f > 0$ and $f < -4$. The results in figures 2–4 show that no singularities exist at the transition point $f = 0$. A singularity occurs near the ferroelastic transition point $f = -4$ for uniform stress fields. The details of the singularity are best seen in the derivative $\delta A/\delta f$ in figure 4(c). This effect is similar to the pre-wetting or pre-martensitic phenomenon as discussed by Houchmanzadeh *et al* (1992). At conditions far away from the instability points (0, -4) the absolute amplitudes and their derivatives are extremely small and surface layers are very thin with small values of λ . The total effect on the relaxation pattern is small under these conditions. The results in figure 4 show that the variation $\delta\lambda$ is small for all parameters of f .

5. Discussion

In a soft mode picture the square of the soft mode frequency is proportional to the force constants in the model. As an example, we can take ϕ_1 as related to the soft mode frequency and hence $f = f_0(T - T_c)/T_c$ in a high temperature approximation. Similarly, the frequency becomes explicitly pressure dependent so that we can take f as the thermodynamic control parameter. Approaching the phase transition point in a second order transition would generate the structural bulk instabilities. In case of proper ferroelastic transitions, the elastic constant becomes the order parameter susceptibility with a lowering of C in the paraelastic phase (Salje 1993). In case of the more common case of an improper ferroelastic transitions, no significant softening of C occurs in the paraelastic phase besides dynamical effects described by Carpenter and Salje (1998). All precursor effects described so far are uniform throughout the sample. The new feature, as described in this paper, consists of a heterogeneous precursor. The ferroelastic phase (martensite) nucleates at the surface of the sample as a relaxational deformation. The precursor regions decay exponentially towards the inside of the sample. The elastic response of the relaxation region is different from the bulk values but will be difficult to observe in a macroscopic sample unless local indentation or AFM methods are applied (Zhang *et al* 2006).

Two changes occur when the transition point is approached. First, the precursor regions expand with a length scale of $1/\ln(|\lambda|)$ thus invading the bulk. The value of λ approaches 1 and this correlation length diverges at the transition point. The second change is the amplitude of the relaxation which increases at the transition point. Accordingly, the surface elasticity will change as seen in figure 2(b). Experimentally, a very narrow precursor interval with diminished elastic moduli and a two-phase diffraction signal is expected. In figure 2(c) a log–log plot of the total precursor amplitude (local amplitude times the effective volume of the precursor region) versus $\log(T - T_c) = \log(f)$ shows a perfect power law behaviour with an effective exponent of 1.5. This has nothing to do with *critical* exponents which relate to the bulk parameters but relate exclusively to the precursor effect described in this paper. Note that in this paper we have not considered the anharmonic local potentials

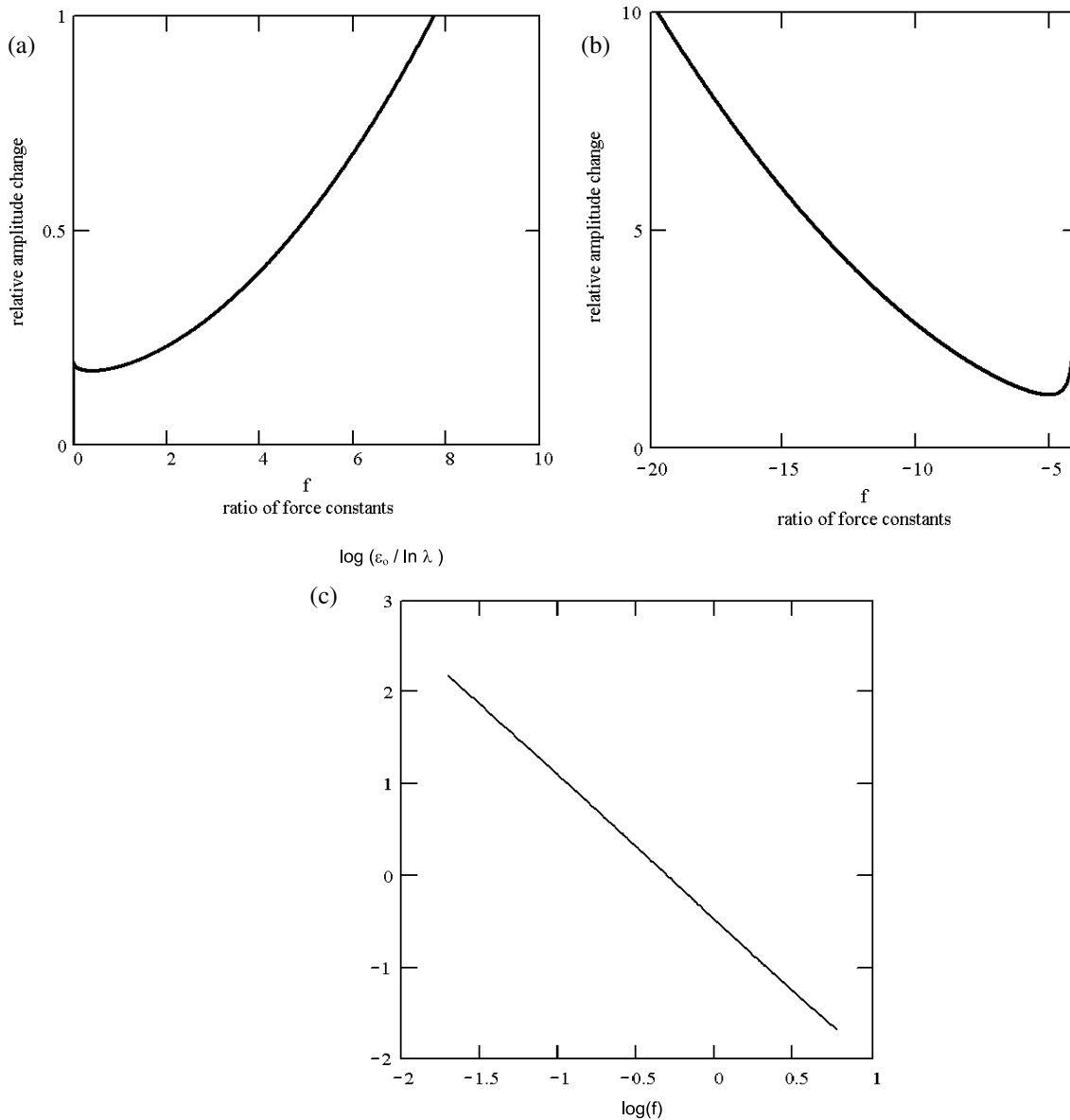


Figure 2. (a) Pressure dependence of the relative change of the relaxation amplitude in the ‘anti-ferroelastic’ regime ($\lambda > 0$). No singularity occurs for uniform stress fields. (b) Pressure dependence of the relative change of the relaxation amplitude in the ‘ferroelastic’ regime ($\lambda < 0$). Note the singularity at the $f = -4$ transition point. (c) Log/log plot of the precursor amplitude multiplied by the characteristic volume ($\log(\epsilon_0 / \ln \lambda)$) versus the ratio of the force constants. The latter stands for the temperature dependence within the P/T phase diagram. The linear plot implies power law behaviour characteristic for criticality while the model is purely mechanical and contains no critical fluctuations whatsoever. It demonstrates the dangers of ‘fitting’ precursor amplitudes to some power law and critical behaviour while the temperature evolution is clearly purely classic in reality.

and hence the details of the transition near the transition point are approximate. In fact, the treatment in this paper is purely mechanical with thermodynamic features represented only by the coupling of force constants and the soft mode via the mode Grüneisen parameter. The treatment is, thus, entirely within mean field theory, MFT, and has nothing to do with the scaling approaches taken by Binder (1983), Kretschme and Binder (1979), Binder and Landau (1976), Binder (1983) and, recently, Vink *et al* (2005). The scaling behaviour in this paper is a mechanical feature within MFT and could easily be misunderstood by experimentalists when measuring the relaxation volume in nanocrystals.

Finally, the two-phase behaviour should not be confused with the appearance of a hysteresis in first order transitions. The two-phase behaviour is an equilibrium feature and relates to the surface regions which are an intrinsic feature of the transition. They show no hysteresis behaviour.

In summary, while surface and interface layers show no big changes of the elastic behaviour compared with the bulk properties, and anomaly occurs when the ferroelastic (martensitic) transition is approached inside the paraelastic phase field. Firstly, the precursor regions near the grain surfaces increase in volume and amplitude. Secondly, the surface layers show an elastic softening or hardening. In

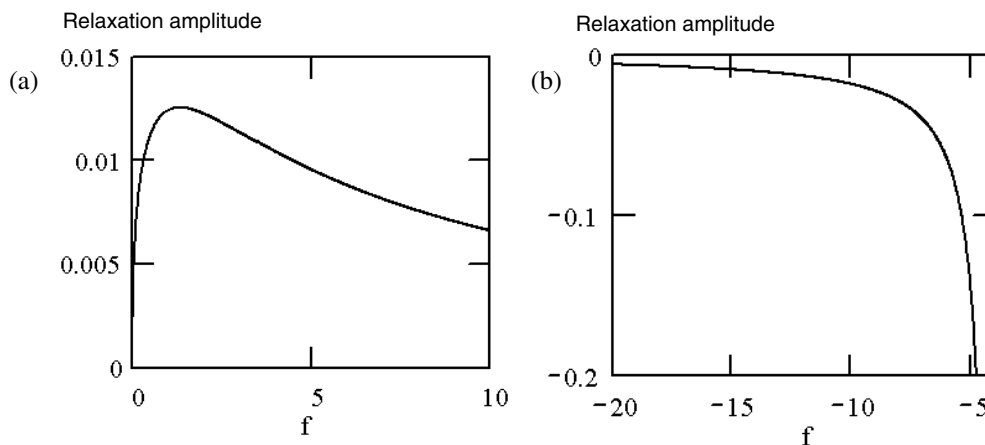


Figure 3. (a) Relaxation amplitude in the ‘anti-ferroelastic’ regime. The misfit parameter $2a_1 - a_2$ is set to 0.1, the lattice parameter is $b = 1$. (b) Relaxation amplitude in the ‘ferroelastic’ regime. The amplitude disappears for sharp interfaces and boundary layers while a pre-martensitic singularity occurs at the ferroelastic transition point $f = -4$. Conditions as in (a).

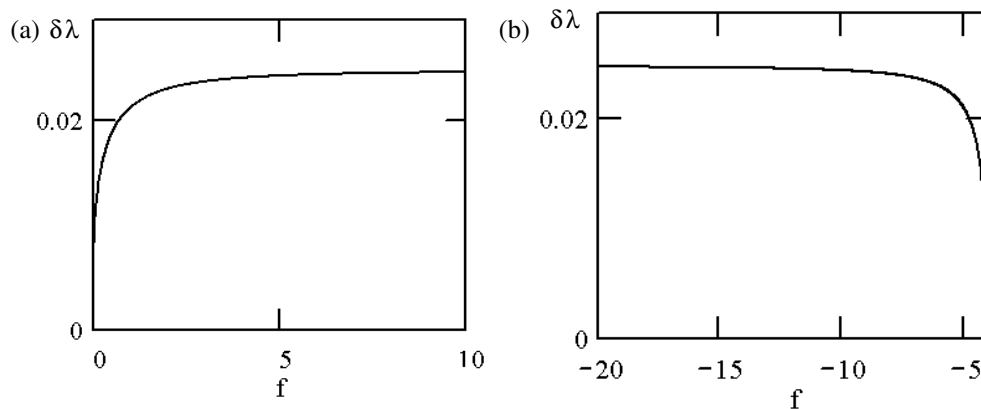


Figure 4. (a) Stress induced change of the relaxational length scale λ in the ‘anti-ferroelastic’ regime. (b) Stress induced change of the relaxational length scale λ in the ‘ferroelastic’ regime.

samples with large surface fractions, such as in nanoceramics, this effect should be easily measurable.

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