Physics of ferroelectrics

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1 Introduction and scope

These notes are designed to accompany those lectures of the course covering the physics of ferroelectrics. While there is a fair amount of algebra here and there, none of it is terribly taxing — moreover, the algebra is here largely to bolster arguments that can be made mostly in pictures, so if you are happy with the pictures, you have probably got the point.

The notes divide into two parts. In the first, we are concerned with the macroscopic description of ferroelectrics, namely the study of the electrical polarisation on length scales much longer than the separation between the atoms. On this scale the polarisation of a solid can be regarded as a continuous degree of freedom, just as one would look at the density of a fluid if one averaged over the short interatomic length scales. This view will enable us to understand the onset of ferroelectricity as a phase transition like any other, to discuss the types of phase transition, and to begin to address the issues of domains, switching, and hysteresis.

The second chapter introduces the study of ferroelectricity from the perspective of atomic scale physics. The reason that a particular material happens to be ferroelectric is of course that the chemistry and physics on an atomic scale favour a particular atomic rearrangement. As well as understanding the development of the macroscopic polarisation, we need also to understand how the microscopic degrees of freedom arrange themselves. In this chapter, we will particularly discuss how lattice vibrations (phonons) give a signature of the transition, and are affected by it. Because the lattice vibrations are directly observable by inelastic neutron scattering, and in certain cases also by infra-red absorption or Raman scattering, there are experimental probes that allow one access to details of the transition. Most of this chapter actually consists of an introduction to lattice dynamics (in a linear chain of atoms, which is all we shall need) for those who have not come across it before.

For further references on the physics (as opposed to the technology or the materials science) of ferroelectrics, one of the best books is an old one (F.Jona and G.Shirane, *Ferroelectric Crystals*, Dover 1993 (republication of Pergamon edition of 1962)). The first chapters of J.F.Scott , *Ferroelectric Memories*, AP, 2000 also cover most of the material on macroscopic properties of ferroelectrics that you will need for this course. Phonons and lattice dynamics are covered well in several solid state texts, for example C. Kittel, *Introduction to Solid State Physics*, 7th Edition, Wiley, 1996. If you can find it (not in print, but in some college libraries), I'd also recommend W.Cochran, *The Dynamics of Atoms in Crystals*, Edward Arnold, 1973.

2 Macroscopic properties

2.1 What is a ferroelectric?

A ferroelectric material has a permanent electric dipole, and is named in analogy to a ferromagnetic material (e.g. Fe) that has a permanent magnetic dipole.

One way to understand how ferroelectricity can arise is to start by looking at small molecules. A molecule that is symmetric, such as methane (CH_4) has no dipole, but many simple molecules are not symmetric (e.g. H_2O) and have a dipole moment.

The formal definition of a dipole moment is

$$\vec{p} = \int dV \rho(\vec{r})\vec{r} \tag{1}$$

where $\rho(\vec{r})$ is the charge density in the molecule - which consists of both the positive nuclear charge and the negative electronic charge density. Provided the molecule is overall neutral, this definition is conveniently independent of the choice of origin[1]

If the atoms can be treated as point charges Q_i at positions $\vec{R}_i$, then this just becomes

$$\vec{p} = \sum_i Q_i \vec{R}_i \tag{2}$$

It is clear from thinking about examples that ferroelectricity is prohibited if there is a centre of symmetry. If a centre of symmetry is not present, the remaining crystal classes[2] have one or more polar axes. Those that have a unique polar axis are *ferroelectric* and have a spontaneous electrical polarisation. The others show the *piezoelectric* effect, wherein an electrical polarisation is induced by application of an elastic stress; extension or compression will induce electrical polarisation of opposite signs.

A ferroelectric solid can be made up by adding together large numbers of molecules with their dipoles aligned, so that the total dipole moment is then

$$\vec{p} = \sum_{molecules} \vec{p}_{molecule} \tag{3}$$

but now it is more convenient to define the polarisation $\vec{P}$ as the dipole moment per unit volume

$$\begin{aligned} \vec{P} &= \frac{\vec{p}}{Total\ volume} \\ &= \frac{\vec{p}_{molecule}}{Volume\ per\ molecule} \\ &= \frac{Dipole\ moment\ per\ unit\ cell}{Volume\ of\ unit\ cell} \end{aligned} \tag{4}$$

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[1] There are some technical problems about extending this definition to an infinite solid, that I won't go into.

[2] Actually with one exception

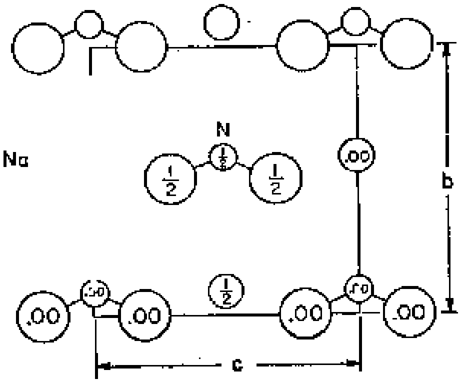

Figure 1: Crystal structure of $NaN0_2$. Atoms of the bent nitrite group are joined by lines; the coordinates in the figure are the heights of the atoms along the axis perpendicular to the page

2.1.1 Examples of ferroelectrics

One of the simplest examples of a ferroelectric is $NaNO_2$ (Fig. 1), which (in one of its several structures) can be viewed just as the prescription above as an array of aligned dipoles.

Unlike in a molecule, where the dipole moment can be oriented in any direction by rotating the molecule in free space, here the dipole moment points along a special axis or axes, aligned with the crystal. This is called the polar axis.

Usually there is more than one polar axis, and this is what makes ferroelectrics useful for devices, because on application of an electric field, the polarisation can be switched from one direction into another. We will come back to this in a moment.

The properties of ferroelectrics can be understood by reference to a (fictitious) one-dimensional crystal made up of two atoms of opposite charge shown in Fig. 2. In this crystal, it is clear that we can orient the dipoles to point all to the right, or all to the left. The two structures are completely equivalent, except that they have an opposite sign to the dipole moment. They must therefore have exactly the same energy.

We could transform one into the other by dragging one type of atom toward the other. As we do this, the bulk polarisation will reduce in magnitude, and change sign at the point where the atoms are equally spaced and finally switch to the opposite direction. Given that we know the crystal is stable in either of the two polarised states, there must be an energy barrier between the two states, and we can sketch a curve (Fig. 3) for the energy as a function of the polarisation.

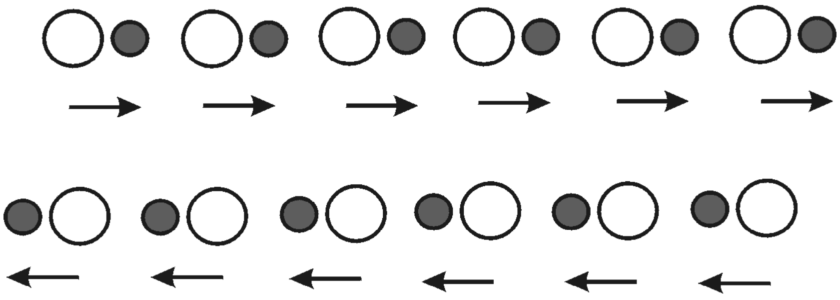

Figure 2: Model (fictitous) crystal

How can we switch between the two states? In an electric field $\vec{E}$ the two stable states no longer have the same energy because of the electric polarisation energy $-\vec{P}\cdot\vec{E}$. The wells are tilted by the electric field. It is also clear from this figure that a small field will not necessarily immediately switch the polarisation from one direction to the other because there is a barrier to be overcome. In an ideal (and fictitious) case where all the dipoles have to be overturned together — as in the figure — there will now be hysteresis, schematically demonstrated in Fig. 4. While this figure demonstrates the origins of the hysteresis phenomenon seen in real ferroelectrics, it is much too simple a description, because in a real material not all the microscopic dipoles will uniformly switch together.

2.1.2 Ferroelectric phase transitions

The description above is limited to low temperatures. It is common to observe that as the temperature is raised, the bulk polarisation decreases and vanishes abruptly at a temperature T_c. This is a phase transition, just as in

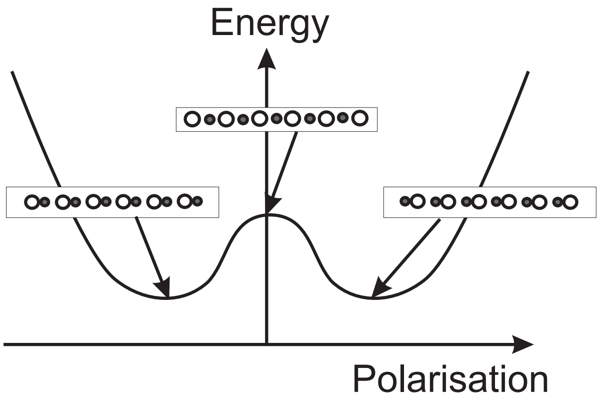

Figure 3: Schematic potential well

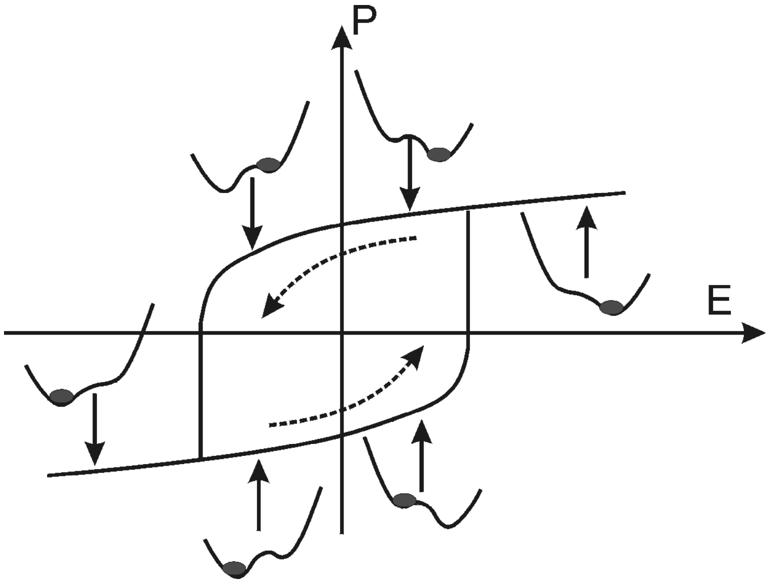

Figure 4: Schematic picture of hysteresis in an idealised ferroelectric

a ferromagnet raised above its Curie temperature, or a solid raised above its melting point.

It arises microscopically because as temperature is raised the thermal vibrations of the atoms in the solid cause fluctuations which overcome the potential barrier between the two (or more) wells. It is most easily understood in a molecular crystal such as $NaNO_2$, where one can imagine that each molecule can fluctuate between two configurations. each of which has a double potential well as in Fig. 3, and some interactions between the dipoles that tend to align them. The detailed microscopic theory of how this happens will be different from material to material, but the macroscopic properties of the phase transition will be similar across many different classes of materials. We will not discuss details of the chemistry and interactions, but instead present a macroscopic theory that provides a very useful description of many different ferroelectrics. This is the Landau theory of phase transitions.

2.2 Landau theory

Any crystal is in a thermodynamic equilibrium state that can be completely specified by the values of a number of variables, for example temperature T, entropy S, electric field E, polarisation P, stress σ and strain s.

Usually we are in a situation where we are applying externally electric fields E and elastic stresses σ, so we can regard the polarisation and strain

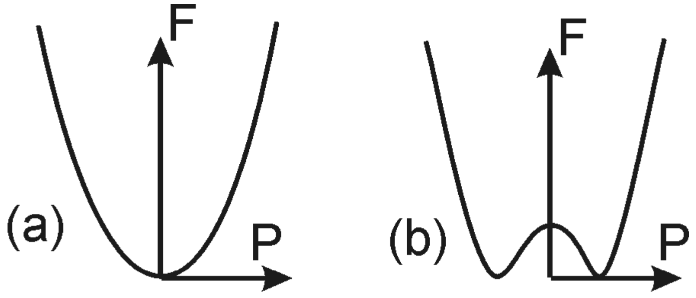

Figure 5: Free energy as a function of polarisation for (a) a para-electric material, and for (b) a ferroelectric material

as "internal" or dependent variables. A fundamental postulate of thermodynamics is that the free energy F can be expressed as a function of the ten variables (three components of polarisation, six components of the stress tensor, and temperature), and our goal here is to write down an *ansatz* for the free energy. The second important thermodynamic principle is that the values of the dependent variables in thermal equilibrium are obtained at the minimum of the free energy.

The approximation we make is just to expand the free energy in powers of the dependent variables, with unknown coefficients (which can be fit to experiment). If we are lucky, we may be able to truncate thus series with only a few terms. To be specific, let us take a simple example where we expand the free energy in terms of a single component of the polarisation, and ignore the strain field. This might be appropriate for a uniaxial ferroelectric. We shall choose the origin of energy for the free unpolarised, unstrained crystal to be zero, and hence write

$$\mathcal{F}_P = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + ... - EP \quad . \tag{5}$$

Here E is the electric field, and the unknown coefficients a, b, c, etc. are in general temperature-dependent, and may have any sign. The equilibrium configuration is determined by finding the minima of $\mathcal{F}$, where we shall have

$$\frac{\partial \mathcal{F}}{\partial P} = 0 \quad . \tag{6}$$

If a, b, c are all positive, the free energy (for $E = 0$) has a minimum at the origin (Fig. 5)

In this case we can ignore the higher order terms than quadratic to estimate the polarisation induced by an electric field from

$$\frac{\partial \mathcal{F}}{\partial P} = aP - E = 0 \quad , \tag{7}$$

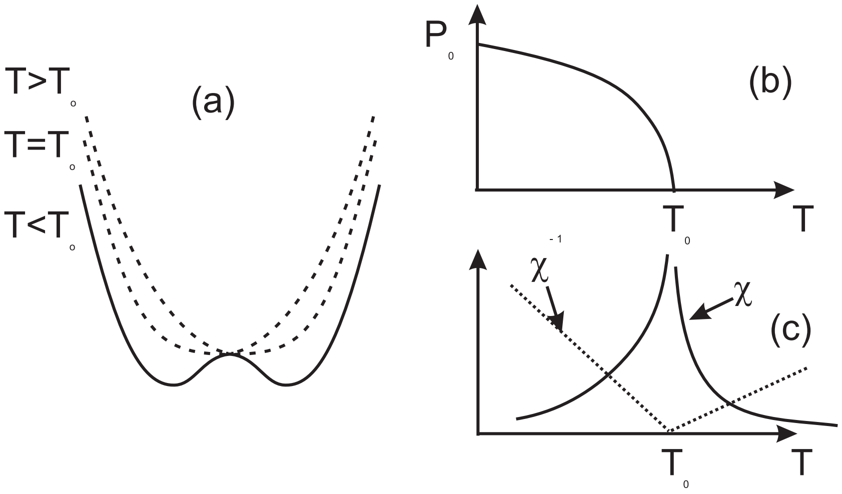

Figure 6: Second order phase transition. (a) Free energy as a function of the polarisation at $T > T_o$, $T = T_o$, and $T < T_o$; (b) Spontaneous polarisation $P_o(T)$ as a function of temperature (c) Inverse of the susceptibility χ, where $\chi = \partial P/\partial E|_{P_o}$ is evaluated at the equilibrium polarisation $P_o(T)$

and so we have a relationship between the polarisability and the field (in linear response, for small electric field) which defines the dielectric susceptibility

$$\chi = \frac{P}{E} = \frac{1}{a} \tag{8}$$

The dielectric susceptibility is proportional to the capacitance you would measure by putting the (insulating) ferroelectric in an electrical circuit.

On the other hand, if the parameters are such that $a < 0$, while $b, c > 0$, then the free energy will look like the second figure in Fig. 5, which has a minimum at a finite polarisation P. Here, the ground state has a spontaneous polarisation and is thus a ferroelectric.

The demarcation between these two curves comes if a changes continuously with temperature, and changes sign at a temperature T_o. This suggests a simple description of the ferroelectric transition might be obtained by assuming that $a(T)$ varies linearly with temperature, say of the form $a' \times (T - T_o)$.

A little bit of thought (see also the question sheet) will then show that this phenomenological description will predict the behaviour of the free energy, polarisation, and susceptibility shown in Fig. 6

This is an example of a second-order, or continuous, phase transition where the order parameter (here the spontaneous polarisation) vanishes continuously at the transition temperature $T_c = T_o$.

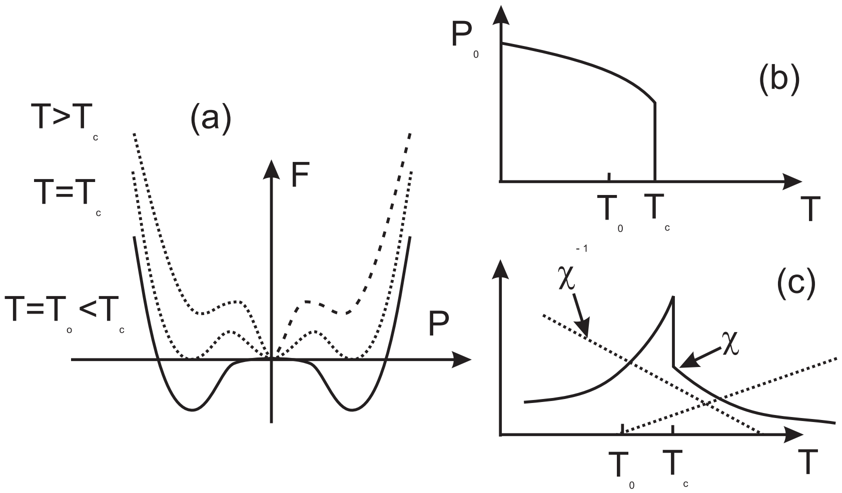

Figure 7: First order phase transition. a) Free energy as a function of the polarisation at $T > T_c$, $T = T_c$, and $T = T_o < T_c$; (b) Spontaneous polarisation $P_o(T)$ as a function of temperature (c) Susceptibility χ.

Logically (and practically as it turns out), we should consider the case of $b < 0$ (while c remains positive). This is sketched in Fig. 7. With the quartic coefficient negative it should be clear that even if $T > T_o$ (so the quadratic coefficent is positive) the free energy may have a subsidiary minimum at non-zero P. As a is reduced (the temperature lowered), this minimum will drop in energy to below that of the unpolarised state, and so will be the thermodynamically favoured configuration. The temperature at which this happens is the Curie temperature T_c (by definition), which however now exceeds T_o. At any temperature between T_c and T_o the unpolarised phase exists as a local minimum of the free energy. The most important feature of this phase transition is that the order parameter jumps discontinuously to zero at T_c. This type of phase transition is usually called a first-order or discontinuous transition. Other common examples of this type of transition are solid- liquid transitions.

2.2.1 Coupling to strain

An important feature of ferroelectric materials is often their great sensitivity to elastic stress. To understand why this happens we can again take recourse to Landau theory, by adding in strain dependent terms to Eq. (5). For a uniaxial ferroelectric, the leading order terms will be of the following form

$$\mathcal{F}_s = \frac{1}{2}Ks^2 + dsP^2 + ... - s\sigma \quad , \tag{9}$$

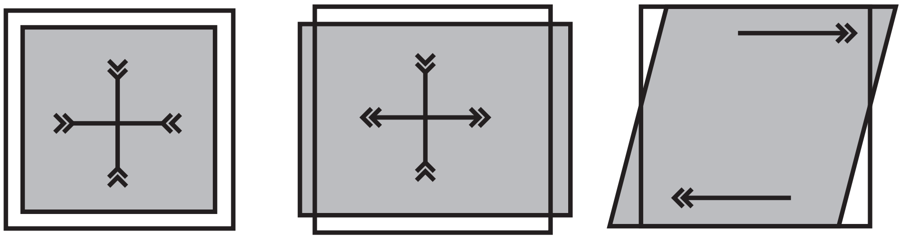

Figure 8: Sketch of a volume strain, and two types of shear strain – that are volume preserving

Here s is (a component of) the strain field, and the first term represents Hooke's law – that the elastic energy stored in a solid is quadratically dependent on the distortion, so K is (one of) the elastic constant(s). The second term is a coupling between the elastic strain and the polarisation; the fact that this is linear in the strain and quadratic in the polarisation depends on the special symmetry of the transition (see more below) [3].

I have chosen not to complicate things by introducing umpteen components of the stress and strain tensors, but for completeness (though not for examination) I will expand a bit on strain fields.

The strain in a solid is measured by how the displacement $\vec{u}$ of a point in the solid varies with position $\vec{r}$, and since this is the dependence of a vector upon a vector, the answer is a tensor: the strain is usually defined as

$$s_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i}\right) \quad . \tag{10}$$

here i, j mean the x, y, z components of the vectors. s is therefore a 3x3 symmetric matrix, with six independent components. In materials that are cubic, or nearly so, there will be three independent components to the strain — the volume strain (uniform in all three directions, and two kinds of shear). Rather than do the mathematics, these are best understood in pictures (Fig. 8)

In general, the polarisation will couple to one or more types of strain, and which types can generally be seen by inspection. Consider a cubic crystal (e.g.$BaTiO_3$) that undergoes a ferroelectric phase transition to a state where the polarisation can point along one of the six orthogonal cubic directions. Now it is clear that there is a special axis (one of the six directions after

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[3] While this is the leading term in pseudocubic materials, there are other materials (e.g. KH_2PO_4) where the symmetry is lower, and the coupling can be of the form sP – linear in both strain and polarisation. Materials with a linear relation between stress and polarisation are called piezoelectric

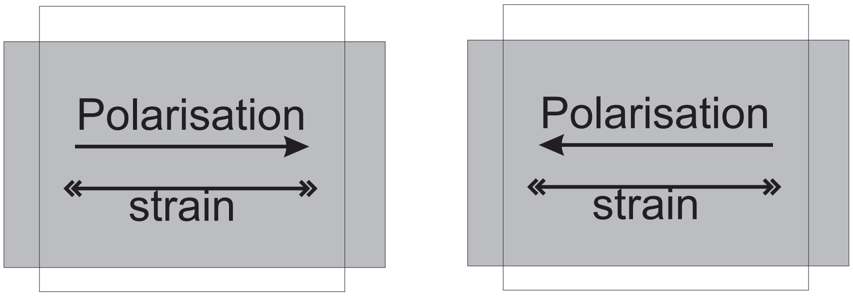

Figure 9: Strain in a polarised crystal: the spontaneous polarisation chooses an axis, and distorts the crystal from cubic to tetragonal. By symmetry, if the polarisation is reversed, the strain stays the same, so the allowed coupling term must be quadratic in the polarisation

the symmetry has been broken) and so it would no longer be expected that the crystal as a whole will remain cubic — one expects a distortion into a tetragonal crystal, which can be described by a tetragonal strain s_t. The fact that the lowest order coupling allowed in this case is of the form sP^2 (and not, for example, sP or s^2P) can be seen by a thought experiment based on Fig. 9.

Returning to the free energy, which now consists of the terms in Eq. (5) and Eq. (9), $\mathcal{F} = \mathcal{F}_P + \mathcal{F}_s$. we should now determine the properties in equilibrium by minimising with respect to both P and s, viz

$$\frac{\partial \mathcal{F}(P,s)}{\partial P} = \frac{\partial \mathcal{F}(P,s)}{\partial s} = 0 \tag{11}$$

Let us take the second of these equations first:

$$\frac{\partial \mathcal{F}(P,s)}{\partial s} = Ks + dP^2 - \sigma \tag{12}$$

There are a few different limits to look at. Firstly, note that if the polarisation is zero, we get Hooke's law $s = \sigma/K$.

The second – apparently trivial case – is when a stress is applied to force the strain to be exactly zero at all times. This is not as absurd as it seems, because often crystals can be considered to be clamped by their surroundings so that no strain is allowed at all. One common situation is of a thin epitaxial film which is forced to have the lattice constants matched to the substrate, and is free to relax only in the third direction. In the case of perfect "clamping" $s = 0$, and the free energy is just as before.

The third case to consider is when no external stresses are applied ($\sigma = 0$), and we then have

$$s = -dP^2/K \tag{13}$$

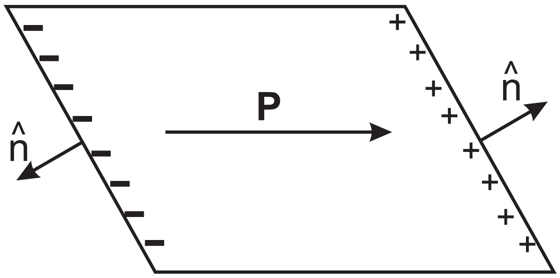

Figure 10: Surface charge density generated by a bulk polarisation at an interface

so that a spontaneous (tetragonal strain) occurs proportional to the square of the polarisation. Notice now that we can substitute for the strain as a function of polarisation, and we have a free energy

$$\mathcal{F}(P, s(P)) = \frac{1}{2}aP^2 + \frac{1}{4}(b - 2d^2/K)P^4 + \frac{1}{6}cP^6 + ... - EP \quad . \tag{14}$$

In comparison with the clamped system, the only change is to reduce the quartic coefficient (notice that the result is independent of the sign of d). This means that in the case of an already first-order transition ($b < 0$) the transition is driven even more strongly first order, and T_c is raised. It is also possible to have $2d^2/K > b > 0$, in which case a second-order transition in a clamped system becomes first-order when the strain is allowed to relax.

2.3 Domains

So far we have pretended that the polarisation in a ferroelectric can be treated as entirely uniform, and this is far from the case. There are many reasons for the existence of domains, including non-uniform strain, microscopic defects, and the thermal and electrical history of the sample. But even in an ideal crystal, domains are to be expected for energetic reasons.

The macroscopic bulk polarisation is produced by a displacement of positive charge relative to negative charge; at the surface of the sample there must then be a net charge density of opposite signs on the opposite sides of the crystal (Fig. 10). With a little geometry, the surface charge density (per unit area) can be seen to be

$$\sigma = \vec{P} \cdot \hat{n} \tag{15}$$

where $\hat{n}$ is the vector normal to the boundary. These surface charges themselves now generate electric fields, both internal, and external to the sample, and the fields themselves store energy - just as in a capacitor.

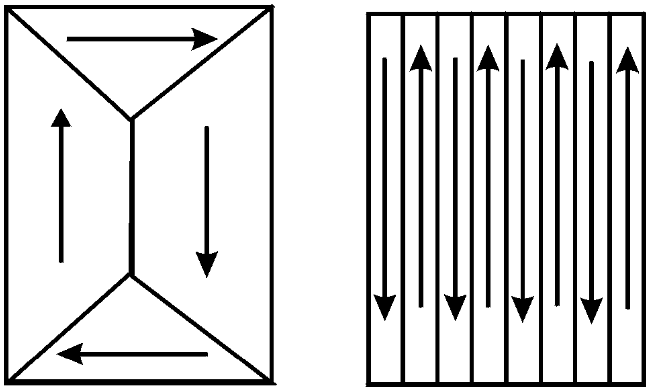

Figure 11: Ideal domain configuration in a single crystal of cubic ferroelectric material, where the coupling to strain is negligible. On the right is the configuration adopted when strain effects are important.

The system will minimise its energy by abolishing – as far as is possible – the surface charges, and in a thin film for example this makes clear that the preferred orientation of the polarisation will be "lying down" in the plane of the film, rather than pointing perpendicular to the film. If one has crystal that is thick in all dimensions, another situation is preferable – to introduce domains where the polarisation is oriented to be always parallel to the crystal surface. Such a situation can of course only be achieved by introducing domain walls into the bulk, and this will produce polarisation charges unless the walls are appropriately oriented.

The interface charge density between two neighbouring domains is, by extension of the formula at a free surface

$$\sigma = (\vec{P}_1 - \vec{P}_2) \cdot \hat{n} \tag{16}$$

where $\vec{P}_1$, $\vec{P}_2$ are the polarisations of the two domains, and $\hat{n}$ is a unit vector normal to the interface. The two cases when the surface charge will exactly vanish are when the polarisations are antiparallel to each other, and parallel to the domain wall (called a 180° domain wall), or when the domain wall bisects the angle between two domains pointing "head to tail". Because we are often dealing with nearly cubic crystals where the possible polarisations are at 90° to each other, the latter is often termed a 90° domain wall. Both these types of wall are illustrated in the sketch Fig. 11, which is the ideal configuration of the polarisation in a " bar" of ferroelectric single crystal — and which bears obvious comparison to the ideal magnetic configuration in a single crystal bar magnet, that may be familiar to some.

The presence of domain walls involves other energy costs. Firstly, the domain wall is microscopically different from the bulk, and the energy gain of forming the polarised ground state has been lost. Secondly, the polarisation is coupled to elastic strain – as we saw above – and we must also make sure that the strain fields are compatible. There is no difficulty with a 180° domain wall, but a 90° domain wall produces problems, and the "ideal" configuration of Fig. 11 is by no means ideal in terms of the strain fields. The existence of domains in a sample automatically generates inhomogeneities in the strain which interact in complex ways.

There is another feature of ferroelectric domain walls which is not shared by magnetic domains. As far as we are aware, magnetic monopoles do not exist, and therefore the (fictitious) magnetic charges that are generated on magnetic boundaries cannot be screened. In ferroelectrics, the surface polarisation charges can be, and are, screened by real electrical charges – from impurities, defects, and migrating ions for example. The motion of charged species (on a fairly slow time scale) to domain walls then provides a mechanism for memory, "imprinting", and "fatigue" – topics which will recur in later lectures.

Domains, their motion, pinning and switching are fascinating phenomena in their own right, and the complexities of domain motion in practical materials are at the heart of understanding device performance. The brief and idealised discussion above is only the most superficial of introductions to the topic.

3 Microscopic properties

3.1 Phonons

This section is an introduction to lattice vibrations — phonons — from a simple microscopic point of view. The basic principles can be set out within a model of a one-dimensional crystal.

3.1.1 One-dimensional monatomic chain

Our model consists of identical atoms connected by springs, shown in Fig. 12

In equilibrium, the atoms are uniformly spaced at a distance a, and we now look for oscillations about the equilibrium position. We assume the crystal is harmonic, so that the spring restoring force is linearly dependent upon the extension. Then if we take the displacement of the n^{th} atom (which is at the point $r_n = na$) to be u_n, its equation of motion is

$$m\frac{\partial^2 u_n}{\partial t^2} = K(u_{n+1} - u_n) + K(u_{n-1} - u_n) \tag{17}$$

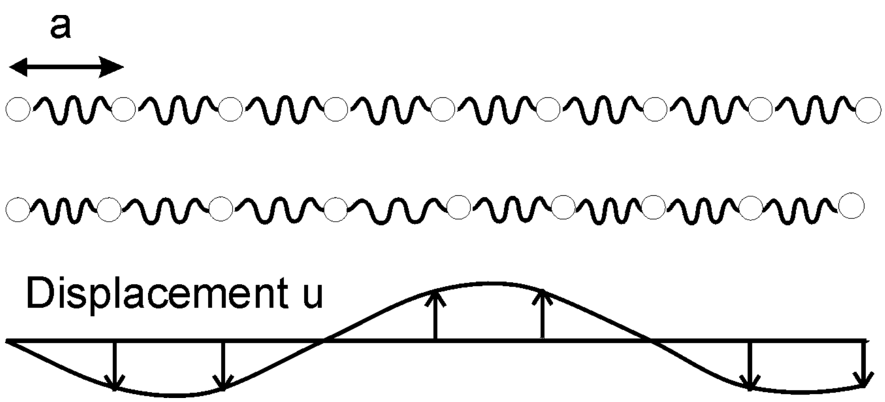

Figure 12: A one-dimensional linear chain. The atoms are shown in their equally spaced equilibrium conditions in the top row, and with a periodic distortion below. The bottom figure plots the displacments u_n as arrows, and the curve shows how this is a sine-wave of period $6a$, in this case.

We guess that the solution is a wave, of the form

$$u_n(t) = u_o cos(qr_n - \omega(q)t) \tag{18}$$

Here the wavelength of the wave is $\lambda = 2\pi/q$, and the period is $T = 2\pi/\omega(q)$; to check that this is a solution, and to determine the frequency we substitute in the equation of motion. To do this is left as an exercise, and a few lines of algebra will show that the solution Eq. (18) exists provided that

$$m\omega^2(q) = 2K(1 - \cos(qa)) = 4K\sin^2(\frac{qa}{2}) \tag{19}$$

so that

$$\omega(q) = 2(K/m)^{1/2}\sin(\frac{qa}{2}) \tag{20}$$

Eq. (19) is called a dispersion relation — the relation between the frequency of the mode and its wavevector, or equivalently the relationship between the wavelength and the period.

The wavevector q is inversely related to the wavelength; note that for long wavelength modes (i.e. $q \to 0$), the relationship is linear, viz

$$\omega(q) = (K/m)^{1/2}(qa) \tag{21}$$

which is the same as for a wire with tension Ka and density m/a. In the long wavelength limit, we have compressive sound waves that travel with a velocity $v = a(K/m)^{1/2}$. Because this kind of wave behaves like a sound wave, it is generally called an acoustic mode.

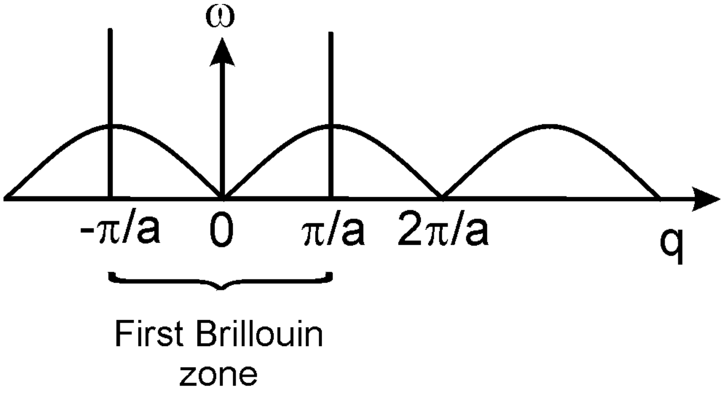

Figure 13: Dispersion relation between frequency and wavevector for a one-dimensional monatomic chain

The dispersion is not linear for larger values of q, and is in fact periodic (Fig. 13). The periodicity can easily be understood by reference to Eq. (18). Suppose we choose $q = 2\pi/a$. Note then that

$$qr_n = \frac{2\pi}{a} \times na = 2\pi n \tag{22}$$

so that all the atoms displace together, just as if $q = 0$. In general it is straightforward to show that if one replaces q by $q +$ integer $\times\, 2\pi a$, then the displacements are unchanged – so we may simplify our discussion by using only q vectors in the range

$$-\frac{\pi}{a} \leq q \leq \frac{\pi}{a} \quad . \tag{23}$$

This is called the first Brillouin zone.

3.1.2 One-dimensional diatomic chain

A one dimensional chain establishes the basic principles of the dispersion of lattice vibrations in solids, but of course a monatomic chain cannot be turned into a ferroelectric. To explain the microscopic physics behind ferroelectricity we need at least two atoms in a unit cell, and we will briefly sketch the general principloes of the diatomic chain.

For simplicity, we use again a phenomenological model of balls and springs, but now with two different atoms in the unit cell, two different masses and two different spring constants (notice that for the latter to be true we would need to have the atoms unequally spaced)(see Fig. 14). We can now write

Figure 14: Diatomic chain

down two equations of motion, one for each type of atom:

$$\begin{aligned} m_A \frac{\partial^2 u_{nA}}{\partial t^2} &= K(u_{nB} - u_{nA}) + K'(u_{n-1,B} - u_{nA}) \\ m_B \frac{\partial^2 u_{nB}}{\partial t^2} &= K'(u_{n+1A} - u_{nB}) + K(u_{n,A} - u_{nB}) \end{aligned} \tag{24}$$

The solution of this is a little more complicated than before (left as an optional problem on the question sheet), but we can now intuitively see that there ought to be a new type of phonon mode by considering a particular limit of the parameters. Suppose the two atoms are quite strongly bound together in pairs, as sketched in the figure above: then we might expect that $K \gg K'$, and to a first approximation the pairs can be treated as independent molecules. (We will also simplify the analysis by taking $m_A = m_B = m$.) Then every molecule will have a vibrational mode where the two atoms oscillate out of phase with each other with a frequency

$$\omega_o^2 = 2K/m \quad . \tag{25}$$

The corresponding coodinate which undergoes this oscillation is

$$u_{opt}(q = 0) = u_A - u_B \tag{26}$$

where I have explicitly remarked that this is at $q = 0$ if each molecule undergoes the oscillation in phase with the next.

We can of course make a wavelike solution by choosing the correct phase relationship from one unit cell to the next — as sketched in Fig. 15, but if $K' \ll K$ this will hardly change the restoring force at all, and so the frequency of this so-called optical phonon mode will be almost independent of q.

There are now two branches of the dispersion curve, along one of which the frequency vanishes linearly with wavevector, and where the other mode has a finite frequency as $q \to 0$(see Fig. 16). The name "optical" arises because at these long wavelengths the optical phonons can interact (either by absorption, or scattering) with light, and are therefore prominent features in the absorption and Raman spectra of solids in the infrared spectrum.

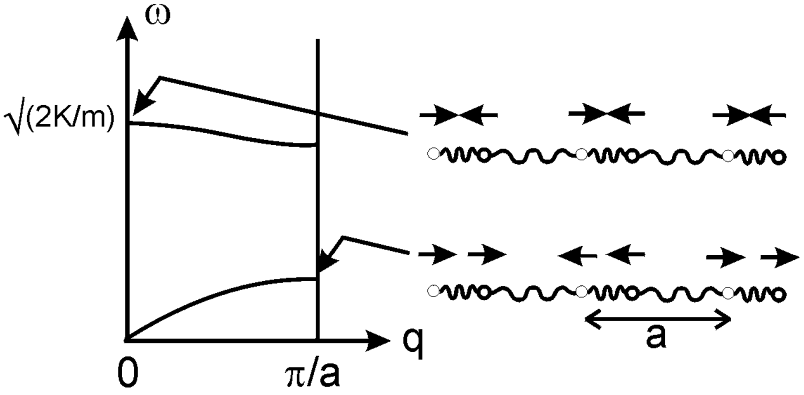

Figure 15: Dispersion of the optical and acoustic phonon branches in a diatomic chain, and a schematic picture of the atomic displacements in the optical mode at q=0

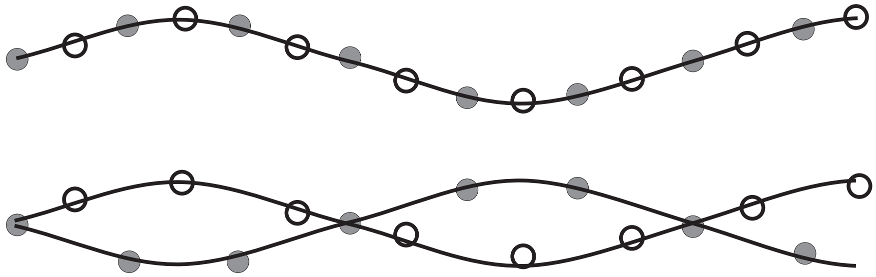

Figure 16: Pattern of atomic displacements for an acoustic and an optical phonon of the same wavevector.

3.1.3 Phonons in three-dimensional solids

The descriptions above are not too hard to generalise to three- dimensional solids, although the algebra gets overloaded with suffices.

Rather than a one-dimensional wavevector k corresponding to the direction of the 1D chain, there is now a three-dimensional dispersion relation $\omega(\vec{k})$, describing waves propagating in different directions.

Also, there are not just compressional waves, but also transverse, or shear waves, that will have different dispersion from the longitudinal (compressional) waves. (These exist in a crystal in any dimension, including our 1D chain, where they can be imagined to involve displacements perpendicular to the chain direction.) Quite generally, for each atom in the unit cell, one expects to find three branches of phonons (two transverse, and one longitudinal); always there are three acoustic branches, so a solid that has N atoms in its unit cell will have $3(N-1)$ optical modes. And again, each optical modes will be separated into two transverse branches and one longitudinal branch.[4]

3.2 Soft modes

After this lengthy introduction to the theory of lattice vibrations, we will get back to our simple description of the ferroelectric phase transition, by reference say to Fig. 3. We imagine that we are lowering the temperature through the point where the transition happens, and the free energy is developing a double minimum. What should happen to the phonons?

Remember that the phonon modes we calculated were in the harmonic approximation; i.e. we assume that the amplitude of the vibrations are always so small that we can expand the potential about the minimum of the energy. The spring constants K above come from the fact that one assumes that the elastic energy stored in a spring (bond) follows Hooke's law, viz

$$\mathcal{U}(x) = \frac{1}{2}Kx^2 \tag{27}$$

Suppose we can replace the internal energy of this formula by the free energy modelled in the Landau theory shown earlier, then the relevant stiffness constant for the $q = 0$ optic phonon *above* T_c is easily related to the coefficient $a(T)$ in the Landau theory.

It should be intuitively clear the the polarisation P must be related directly to the amplitude of the corresponding lattice displacement. Consequently, the free energy expansion of Eq. (5) could equally well have been written as a function of the lattice displacement u. For the diatomic chain, the relevant coordinate is exactly the coordinate of the optical phonon amplitude, viz

$$u_{opt} = u_A - u_B \tag{28}$$

and furthermore there is a relationship between the optical phonon amplitude and the polarisation

$$P = \frac{1}{V_{cell}}(e_T^* u_{opt} + O(u_{opt}^3)) \quad . \tag{29}$$

The quantity e_T^* is called the "transverse effective charge" [5]; its name reflects the fact that for rigid ions of charge $\pm Ze$, the dipole moment would just be

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[4] The distinction between longitudinal and transverse is only rigorous along lines of symmetry in $\vec{k}$-space.

[5] The 'transverse' in the name comes from the fact that e_T^* is responsible for the shift between the transverse and longitudinal optical phonons

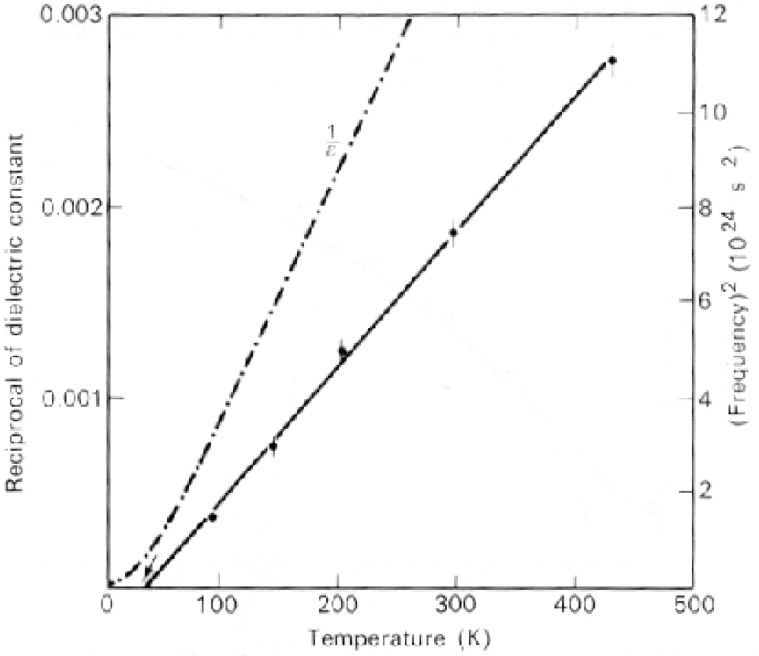

Figure 17: Comparison of the temperature-dependence of the square of an optic phonon frequency with the inverse of the dielectric susceptibility in $SrTiO_3$ (Cowley, Phys.Rev.Lett. **9** 159 [1962])

Zeu_{opt}. Now without rewriting the formulae, it is clear that in the harmonic approximation, the frequency of the $q = 0$ optical phonon must vanish as the transition is approached. This is because

$$m\frac{\partial^2 u_{opt}}{\partial t^2} = -\frac{\partial \mathcal{F}}{\partial u_{opt}} \propto -a(T)u_{opt} \tag{30}$$

and thus

$$\omega(q=0)^2 \propto \frac{1}{\chi} \quad . \tag{31}$$

The relationship of Eq. (31) holds quite well in many materials with an example given in Fig. 17

The Landau theory only discussed *uniform* components of the polarisation, and thus can only be a guide for $q = 0$. Of course if we wanted to model our ferroelectric material by a harmonic chain of balls and springs, we would have to infer that $K \rightarrow 0$ at the transition temperature — and so all the phonons (optical and acoustic) at all momenta would soften to zero frequency at the transition. This seems unreasonable, and it is of course not correct.

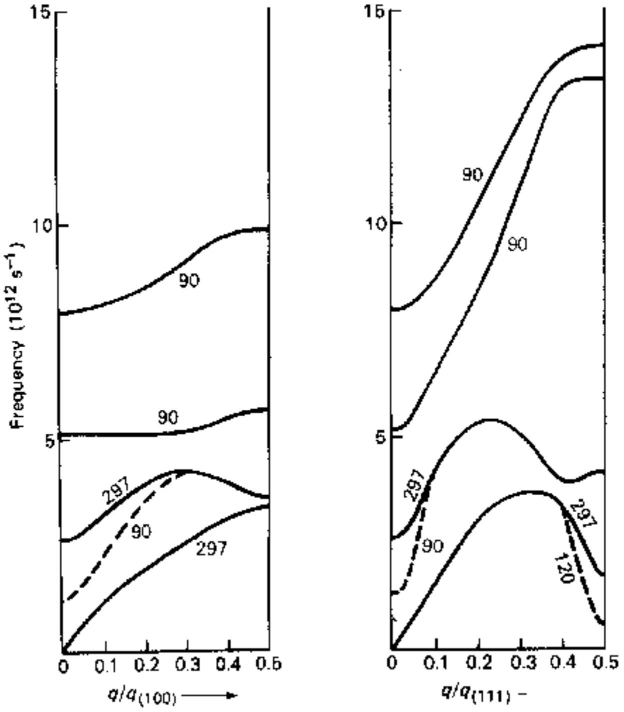

Figure 18: Phonon dispersion relations for $SrTiO_3$ measured at different temperatures for those modes where a considerable change with temperature is seen. Note that there is both softening of the optical phonon near $q = 0$ as well as a zone boundary phonon ($q = (\pi/a)(111)$).(Stirling, J.Phys.C **5**, 2711 [1972])

The typical situation is shown in Fig. 18 which shows the phonon spectra of $SrTiO_3$. Notice that the lowest optical phonon branch is soft near the origin, but rapidly stiffens as q increases. Only the long wavelength components of the optical phonon mode go soft, and only over a small part of the zone are the modes strongly temperature dependent. Note in Fig. 18 that there is a softening mode not just at the zone centre, but also an acoustic phonon mode softening at the zone edge. It is this latter mode that goes soft in $SrTiO_3$, which is not quite a ferroelectric — even though the dielectric constant becomes very large. Instead, the zone boundary mode — which has a periodicity of exactly two lattice constants in each of the x-,y-, and z- directions – corresponds to a soft mode where the articulated octahedra rotate alternately in opposite directions, just like an array of cog wheels.[6]

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[6] This kind of situation is often termed “anti-ferroelectricity”, as in the alternating spin order of an antiferromagnet.

3.3 A microscopic mean field theory

We close this overview of microscopics with a simple mean field theory of what is sometimes called the "polarisation catastrophe" for the onset of ferroelectricity. This theory plays the same role in ferroelectricity as the Weiss theory of ferromagnetism. The basic physical idea is that ions in solids are themselves polarisable in an electric field, so that on top of any polarisation generated by the rigid displacement of the ions from their lattice sites, there is an electronic polarisation generated by electric fields inside the solid.

Let's go back to our simple diatomic solid, which in the paraelectric phase has the ions equally spaced, and then make a small displacement of the ions relative to each other by an amount **u**, the same in each unit cell. If the ions have charges $\pm Ze$(Z is the ionic charge), the induced polarisation will be

$$\mathbf{P} = \frac{1}{\Omega_o}\left[Ze\mathbf{u} + \alpha\mathbf{E}_{loc}\right] \quad . \tag{32}$$

Here Ω_o is the unit cell volume, and α the ionic polarisability. E_{loc} is the *local electric field* – i.e. that electric field at the site of the atom that is produced by the dipoles throughout the rest of the solid.

The calculation of the local field is not a simple matter in general – we should sum up the contribution of all the dipolar fields generated by all the cells throughout the solid. But there is a simple way to estimate it, sometimes called the cavity method. The atomic dipoles far away from the site where we want to calculate the field are treated as a continuum with uniform polarisation **P** and we cut out a small sphere around the site. We learned earlier that when the bulk polarisation has a discontinuity (at a surface), the discontinuity is equivalent to a surface charge density $\sigma = \mathbf{P}\cdot\hat{n}$, where $\hat{n}$ is the surface normal. Hence we will have a (non-uniform) charge density on the surface of our imaginary sphere (see Fig. 19). This charge density produces a field - which by reference to the figure can be seen to be in the *same* direction of the polarisation.

By an elementary electrostatic calculation — which I will not do here, but can be found in any textbook on electromagnetism, the electric field inside the sphere can be calculated and it is found to be uniform, given by

$$\mathbf{E}_{loc} = \mathbf{P}/(3\epsilon_o) \tag{33}$$

($\epsilon_o \approx 9\times 10^{-12} Fm^{-1}$ is the permittivity of free space). Substituting in Eq. (32), and solving for **P**, we get

$$\mathbf{P} = \frac{Ze\mathbf{u}/\Omega_o}{[1-\alpha/(3\epsilon_o\Omega_o)]} = \frac{Z^*e\mathbf{u}}{\Omega_o} \quad . \tag{34}$$

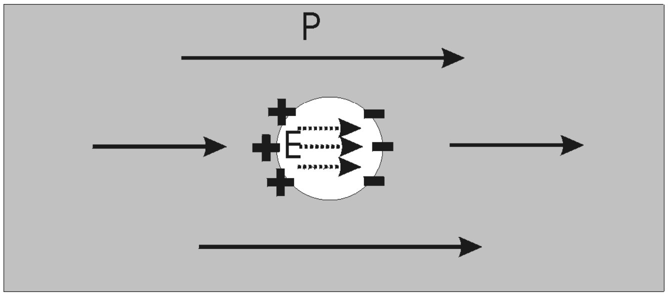

Figure 19: Local electric field in a cavity inside a ferroelectric.

Because of the polarisability of the ions, the *effective charge* Z^* is larger than the bare charge, and if α is large enough, the denominator may vanish, and the induced polarisation will diverge. Within this theory, this divergence marks the onset of the ferroelectric instability.

QUESTIONS[7]

1. Which of these molecules possesses a static electrical dipole moment: O_2, CH_4, H_2O, NO_2, N_2O_4,CO, CO_2 ?

2. Write notes comparing and contrasting the macroscopic aspects of ferromagnetism and ferroelectricity.

3. Use the following Landau theory for the Free energy density (per unit volume)

$$\mathcal{F} = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + ... \tag{35}$$

   where the coefficient $a = a' \times (T - T_c)$ is temperature dependent, and all the other coefficients are constant. Although the polarisation P is of course a vector, we assume that it can point only in a symmetry direction of the crystal, and so it is replaced by a scalar.

   (a) Assume that $b > 0$ and $c = 0$. Use Eq. (35) to determine the form for the equilibrium $P(T)$.

   (b) Including in $\mathcal{F}$ the energy of the polarisation coupled to an external electric field E, determine the dielectric susceptibility $\chi = \frac{\partial P}{\partial E}$ both above and below the critical temperature.

   (c) Sketch curves for $P(T)$, $\chi^{-1}(T)$, and $\chi(T)$.

   (d) The electric field E is increased slowly from zero to large positive values, reversed to large negative values, ind then increased back to zero again. Sketch the form of the hysteresis loop in the P, E plane for $T < T_o$.

   (e) In a different material, the free energy is described by a similar form to Eq. (35), but with $b < 0$ and $c > 0$. By sketching $\mathcal{F}$ at different temperatures, discuss the behaviour of the equilibrium polarisation and the linear susceptibility, contrasting the results with those found in (c).

   (f) Using the model in (e) sketch the P-E hysteresis curves in three cases: $T < T_o$, $T_c > T > T_o$, and $T > T_c$, where T_c is the equilibrium transition temperature at zero electric field.

4. In a piezoelectric crystal, an elastic strain is linearly coupled to the polarization — i.e. $P = \alpha s$. If such a piezoelectric material undergoes a phase transition to a ferroelectric state on cooling, suggest a

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[7] Questions with an asterisk go beyond the requirements of the course

form for the Landau free energy as an expansion in both the polarisation and strain (use a simple scalar theory with one component of the polarisation, and one component of the strain).

Compare the two situations of "clamping" (s=0) and equilibrium relaxation of the strain.

5. By substituting Eq. (18) in Eq. (17) derive the dispersion relation Eq. (19) for the one-dimensional monatomic chain.

6. Write brief notes explaining the concept of a "soft mode" near a ferroelectric phase transition.

7. ** This question involves somewhat messy algebra to derive the dispersion relation for the diatomic chain.

   In the diatomic chain, we take the unit cell to be of length a, and take x_A and x_B to be the coordinates of the A and B atoms within the unit cell. Hence, in the n^{th} cell,

$$r_{n,A} = na + x_A; \qquad r_{n,B} = na + x_B \quad . \tag{36}$$

   In the equations of motionEq. (24), look for solutions of the form

$$u_{n,\alpha} = e_\alpha(q) \exp i(qr_{n,\alpha} - \omega(q)t) + e^*_\alpha(q) \exp i(-qr_{n,\alpha} + \omega(q)t) \tag{37}$$

   where $\alpha = A$ or B, and e_α are complex numbers that give the amplitude and phase of the oscillation of the two atoms.

   Separating out the terms that have the same time dependence, show that (for equal masses, $m_A = m_B = m$)

$$\begin{aligned} m\omega^2(q)e_A(q) &= D_{AA}(q)e_A(q) + D_{AB}(q)e_B(q) \\ m\omega^2(q)e_B(q) &= D_{BA}(q)e_A(q) + D_{BB}(q)e_B(q) \end{aligned} \tag{38}$$

   where

$$D_{AA}(q) = D_{BB}(q) = K + K' \quad , \tag{39}$$

$$\begin{aligned} -D_{AB}(q) &= K \exp iq(r_{n,B} - r_{n,A}) + K' \exp iq(r_{n-1,B} - r_{n,A}) \\ -D_{BA}(q) &= K \exp iq(r_{n,A} - r_{n,B}) + K' \exp iq(r_{n+1,A} - r_{n,B}) \end{aligned} \tag{40}$$

   Check that $D_{AB} = D^*_{BA}$.

The 2x2 matrix equation can have a non-trivial solution if the determinant vanishes:

$$\left| \begin{array}{cc} D_{AA}(q) - m\omega^2(q) & D_{AB}(q) \\ D_{BA}(q) & D_{BB}(q) - m\omega^2(q) \end{array} \right| = 0 \tag{41}$$

Hence show that the frequencies of the modes are given by

$$m\omega^2(q) = K + K' \pm [(K+K')^2 - 2KK'\sin^2(\frac{qa}{2})]^{1/2} \quad . \tag{42}$$

Sketch the dispersion relations when $K/K' = 2$.

Discuss what happens if $K = K'$.