Lecture 10 — Phase transitions.

1 Introduction

The study of phase transitions is at the very core of structural condensed-matter physics, to the point that one might consider all we have learned in the previous lectures as a mere preparation for the last one. The reason why the structural physicist has so much to offer here is that, in a large class of phase transitions, **the system undergoes a symmetry change**. Here is a reminder of a few generic facts about phase transitions

- A phase transition can be driven by many parameters — temperature, pressure, chemical composition, magnetic or electric field etc. **If the driving parameter is temperature, the high-temperature phase is almost always more *disordered*, i.e., has a *higher symmetry* than the low-temperature phase**.

- As for the point here above, **phase transitions entail a change in the entropy of the system**. The change can be:

  Discontinuous. In this case, the phase transition is accompanied by release of **heat** (*latent heat*), and all the other thermodynamic quantities (internal energy, entropy, enthalpy, volume etc.) are **discontinuous as well**. Such a phase transition is known as **first-order transition**.

  Continuous. In this case, the phase transition is continuous across the transition temperature (or other transition parameter). The thermodynamic quantities are continuous, but **their first derivatives are discontinuous**. In particular, the **specific heat** has a pronounced anomaly (see below) and the thermal expansion coefficient has a step at the transition.

- Some important phase transitions do not entail a change in symmetry — e.g., the liquid-to-gas transition. Such phase transitions can only be first-order. We will not be concerned with them in this lecture.

2 Phase transitions as a result of symmetry breaking

In the previous lectures, we have learned that in 2D and 3D symmetry is broken at the level of the individual excitation. Therefore, at any temperature higher than $T = 0$, the fully symmetry is retrieved only because the population of each excitation (e.g., phonon mode, but we can include

electronic and magnetic excitations as well) is identical to that of its symmetry-equivalent modes. We can then ask ourselves what happens if the *frequency* of a particular mode becomes *zero* at a particular temperature. The answer is that this temperature is a *phase transition temperature* (T_c): the mode will become "frozen" and the pattern (e.g. of displacements) becoming *static*. What happens to the symmetry then? For a wide variety of phase transitions, both first- and second-order, one can show that:

- At T_c, a *single* mode becomes frozen in a given macroscopic part of the crystal (**domain**)—neither its symmetry-equivalent not any symmetry-inequivalent modes freeze in that domain. The symmetry within that domain will be therefore *lowered* by that frozen mode. Symmetry classification of modes and symmetry-lowering at phase transitions are therefore closely related topics.

- Overall symmetry is restored because symmetry-equivalent modes freeze in different domains.

- A phase transition of this kind is described by *amplitude parameter* of the relevant mode, which then describe the degree of "departure" from the high symmetry. This parameter is therefore called **order parameter**.

- Disorder = high symmetry. Order=low symmetry.

2.1 The nature of the modes: "order-disorder", "displacive" and other phase transitions.

The first thing to observe is the *nature* of the modes we require and their symmetry properties. In real crystal structures, there is a wide class of phase transitions, known as **order-disorder phase transitions**, which are described in terms of *scalar modes*. One example is when atoms in a previously **random alloy** become ordered on specific crystallographic sites, yielding (usually) a larger unit cell. Here, the scalar quantity in question is the **degree of ordering** on each site, i.e., the positive or negative deviation from a random occupancy of each site by a certain species.

Another very common class of phase transition is that of **displacive phase transition**. These are usually described in terms of **polar vector modes**, very similar to those we used to describe the distortion of our 4-fold molecule in Lecture 8. **Magnetic phase transitions** are also usually described using vectors — in this case **axial vectors** (as already mentioned, the **time reversal operator** is important in describing magnetic modes — see here below). Other phase transitions require yet more exotic modes, e.g., pseudoscalars (chiral order transitions) and higher order tensors.

2.2 Macroscopic quantities: the Neumann principle

When a phase transition occurs, the symmetry of the ordered phase is usually a **subgroup** of that of the disordered phase. Symmetry may be lowered because of loss of translational and/or rotational invariance. Changes in point group symmetry (i.e., loss of rotation/mirror symmetries) are extremely important, since they allow new macroscopic physical phenomena. This is expressed in the famous Neumann Principle (from Franz Ernst Neumann 1798-1895): "**The symmetry elements of any [macroscopic] physical property of a crystal must include the symmetry elements of the point group of the crystal**". For example, the point group $4/mmm$ is non-polar (see here below), whereas the point group 4 is polar. Therefore, a phase transition between *space* groups $I4/amd$ (crystal class = point group = $4/mmm$) and $I4$ (crystal class 4) can (and in general *will*) result in the development of a *macroscopic* electrical polarisation (ferroelectricity). When a phase transition results in the development of a new *macroscopic* property that couples to an external field, it is said to be a **ferroic transition**. It follows that all ferroic transitions reduce the point-group symmetry. Here below, we describe the two most famous examples of ferroic transitions: **ferroelectricity** and **ferromagnetism**.

2.2.1 Polarisation and ferroelectricity

Macroscopic polarisation describes the overall electrical dipole moment of a crystal, resulting form the sum of microscopic electrical dipole moments. It is measured in C/m^2. In real ferroelectric crystals, the macroscopic dipole moment is compensated by free surface charges, and there is no electric field outside the crystal. However, ferroelectrics insulators can be "switched" by the application of an external electric field, resulting in a current pulse between the two surfaces of the crystal. Since the polarisation $\boldsymbol{P}$ is a polar (conventional) vector, there must not be any symmetry operator in the point groups of a ferroelectric crystal that changes the direction of $\boldsymbol{P}$. At the very least, the point group of the crystal **must not contain the inversion**. It turns out that there are only 10 crystal classes that allow a macroscopic polarisation: $1, 2, m, mm2, 4, 4mm, 3, 3m, 6, 6mm$. A phase transition to one of these crystal classes will result in the development of ferroelectricity.

2.2.2 Magnetisation and ferromagnetism

The magnetisation $\mathbf{M}$ is an *axial* (or pseudo-) vector, which explains why ferromagnetic materials are not (usually) ferroelectric at the same time and why centrosymmetric ferromagnets can exist (pseudo-vectors are parity-even). However, there are much fewer restrictions on the crystal classes of ferromagnets. Ferromagnets cannot be truly cubic, since the direction of $\mathbf{M}$ in itself breaks the cubic symmetry. For example, iron is ferromagnetic with $\mathbf{M}$ in the $< 111 >$ direction,

and in the magnetic state one can measure a very slight rhombohedral distortion away from cubic — an effect known as **magnetostriction**. However, ferromagnets with point group $4/mmm$ can exist provided that $\mathbf{M}$ is along the c-axis, a classic example being magnetite (Fe_3O_4, SG $I4/amd$), the oldest known ferromagnetic material. The key to this apparent contradiction lies in the already-mentioned property of **time reversal**. $\mathbf{M}$ is the resultant of microscopic circulating currents. Therefore, its direction is reversed if one "runs the film backwards"— an operation that clearly leaves the crystal structure unchanged. Therefore, $\mathbf{M}$ can break the symmetry in a way that leaves the crystal structure invariant. In the aforementioned case of $I4/amd$, the true point-group symmetry in the magnetic state for $\mathbf{M} \parallel \mathbf{c}$ is $4/mm'm'$, where the symmetry operation m' involves taking a mirror image and reversing the arrow of time simultaneously. For all intents and purposes, $4/mm'm'$ looks like $4/mmm$ as far as the crystal structure is concerned.

2.3   Order parameters

Let us consider for the sake of discussion a phase transition driven by a $\Gamma = 0$ optical phonon(i.e., all unit cells in phase) in a crystal containing an array of square molecules yielding the displacement patterns described in Lecture 8 (Figs 1 and 5). Excluding mode Γ_4, which has zero energy, it is apparent that any of the modes in Fig 1 can be described by a single displacement parameter, so that a phase transition driven by any of these modes requires a *single* order parameter η. The situation in Fig 5 is more complex since each row contains two symmetry equivalent modes. Based on what we said here above, we expect each of these two modes to "freeze" in a separate domain. Furthermore, in Lecture 8, we simply *stated* without proof that these were the normal modes of the molecule, but the only thing we know for sure is that the normal modes are linear combination of these (since mixing modes with different transformation properties is not allowed). Note that this is not an issue for quantum excitations, because of the superposition principle (the modes are clearly degenerate), but it clearly becomes an issue as soon as the modes freeze and become classical displacements. We here briefly mention the solution to this problem: one needs to introduce an *array* of order parameters $[\eta_j]$, of length equal to the dimension of the linear space spanned by the symmetry-equivalent modes. In some cases, it will be necessary to consider *complex* order parameters. In the remainder, we will only be concerned with the first case.

3   The Landau theory of phase transitions

One of the most significant contributions of Lev Davidovich Landau (1908-1968) — one of the great physicists of the 20th century — has been the theory of phase transitions bearing his name. Landau theory is of central importance in many fields of condensed matter physics, including

structural phase transitions, magnetism and superconductivity (the latter through a modification of the original theory known as Ginsgburg-Landau theory — see a later part of the C3 course).

The essential feature of Landau theory is that it is a **phenomenological theory**. This means that, unlike a **microscopic theory**, it is *not* concerned with the details of the interactions at the atomic level that ultimately should govern the behaviour of any system. For a structural phase transitions, microscopic interactions would be ionic and covalent bonding, Coulomb interactions, Van der Waals interactions etc.; for a magnetic system, exchange and dipole interactions; for a superconductor, pairing interactions, etc. Instead, Landau theory is chiefly concerned with **symmetry** — in fact, it only applies to phase transitions entailing a change in symmetry. One of the upshots of this is that systems with similar symmetries — even very different systems, which we might expect to have very different microscopic theories — would look very similar within Landau theory. This connection between very distant branches of physics might be thought of as the origin of the idea of **universality**, which was to play a fundamental role in further developments of Landau theory.

3.1 The Landau free energy

The central idea of Landau theory is the construction of a quantity, known as Landau free energy or $\mathcal{F}$, which describes the energetics of the system in the vicinity of a phase transition. $\mathcal{F}$, which can be usually thought of as an approximation to the Helmholtz or Gibbs free energy per unit volume, is of course a real quantity, and depends on temperature, pressure and any other relevant *external* parameter (e.g., electric or magnetic field, stress, etc.). Crucially, **the Landau free energy also depends on the *order parameters* of all the relevant modes of the system**.

> **For a given set of external parameters, the stable state of the system is the one for which the Landau free energy is *minimal* as a function of all internal degrees of freedom.**

As we just mentioned, $\mathcal{F}$ depends on the internal variables of the system through the order parameters of the various modes. It should be clear from our discussion that **the modes describe the systematic lowering of the symmetry of the system from a "high-symmetry" state, which is almost always the high-temperature state**. In the Landau construction, one thus implicitly assumes the existence of a **high-symmetry phase** somewhere in the phase diagram, most likely at high temperatures. In this state, all the order parameters are zero. One can therefore naturally decompose $\mathcal{F}$ as:

$$\mathcal{F} = \mathcal{F}_0 + \Delta\mathcal{F}(\eta^i) \tag{1}$$

where $\mathcal{F}_0$ does not depend on the order parameter (and therefore has no influence on the phase

transition), while $\Delta\mathcal{F}(\eta^i)$ is **small** in the vicinity of the phase transition. As we stated before, we will only consider simple real modes, so the η^i here are distinct order parameters of symmetry-inequivalent modes that are candidate to drive the phase transition. In eq. 1, we are therefore testing how each mode affects the free energy.

3.2 The symmetry of the Landau free energy

The following statement is the point of departure for the Landau analysis:

> **For any value of the order parameters, $\Delta\mathcal{F}$ is *invariant* by any element g of the high-symmetry group G_0. In addition $\Delta\mathcal{F}$ may possess the additional symmetries of free space (most notably, parity and time reversal), provided that the external fields are transformed as well.**

We will not give here a full justification for this rather intuitive statements, which is connected to the crystal symmetries and the overall rotational invariance of the "complete" system, including the sources of the fields.

3.3 The Taylor expansion

Having recognised that $\Delta\mathcal{F}$ is "small" near the phase transition (i.e., where all the order parameters are zero), the next natural step is to perform a **Taylor expansion** of $\Delta\mathcal{F}(\eta^i)$ in powers of η^i. For example, in the case of a simple real, one dimensional order parameter, the expansion will look like this:

$$\Delta\mathcal{F} = -\eta H + \frac{a}{2}\eta^2 + \frac{c}{3}\eta^3 + \frac{b}{4}\eta^4 + o(\eta^5) \tag{2}$$

The odd-power terms are strongly restricted by symmetry, and are never present, for instance, if there is a transformation $\eta \to -\eta$. Finding the stable states will in any case entail minimising the free energy $\Delta\mathcal{F}$ as a function of the order parameter(s). From now on, we will continue with this simple free energy example, all but ignoring all the issues related to the dimensionality of the order parameter and the vector nature of the external fields. These issues introduce some complications, but do not change the essence of the discussion.

In eq. 2, we have used the arbitrariness in the definition of the order parameter η in such a way that the coefficient of the coupling term $-\eta H$ to the 'generalised' external field H is -1. Here below, we shall examine some of the terms in the expansion.

3.3.1 The linear term in η

In the Landau free energy there is never any linear term in the order parameters that does not couple to the external fields. (as we have seen, ther can be *bilinear* terms involving order parameters with the *same symmetry*). The reason for this is simple: $\Delta\mathcal{F}$ must be *invariant* by all elements of the high-symmetry group, and so must be each term of the expansion. However, if η were to be invariant by all symmetry operator, then the corresponding mode could not break any symmetry and could not be involved in a symmetry-breaking transition. Linear terms in a totally-symmetric mode parameter can therefore be incorporated in $\mathcal{F}_0$.

The term $-\eta H$ is not always present. For example, **the linear coupling term to an external field is permitted only if η is translationally invariant**. Finally, η must transform by rotation in such a way that $-\eta H$ is an invariant. If these conditions are met, the phase transition is **ferroic**. *Ferromagnetic, Ferroelectric and Ferroelastic transitions* are classic examples of ferroic transitions. In these case, we can write:

$$\mathcal{P} = -\frac{\partial \mathcal{F}}{\partial H} = \eta \tag{3}$$

where $\mathcal{P}$ is a **generalised polarisation**. In other words, **for a ferroic transition, the order parameter is the generalised polarisation** (electrical polarisation, magnetisation, strain etc.)

3.3.2 The quadratic term in η

This term is always allowed and has the following structure:

$$\sum_i \kappa^i (\eta^i)^2 \tag{4}$$

where all the η^i's have different symmetries (we *do not* have bilinear terms like $\eta^i \eta^j$). To ensure that the high-symmetry phase is the stable phase at high temperature, one must have $\kappa^i > 0$ for $T > T_c$ (so that all the second derivatives are positive for $\eta = 0$).

In the Landau theory, phase transitions occur when one of the coefficients of the quadratic term in the order parameter expansion *changes sign* (from positive to negative, e.g., as a function of temperature), whilst all the other coefficients remain *positive*. If the driving parameter is temperature, the sign-changing term is usually written $a'(T - T_c)\eta^2$, where T_c is the transition (or critical) temperature. Clearly, the simultaneous change or two or more coefficient in the expansion in eq. 4 *can only be accidental*. This is why only a *single* mode (or more precisely a single symmetry) drives each phase transition.

If there are no higher-order coupling terms between different order parameters **for** $T < T_c$**,** $\eta^i = 0$ **is still the stable state for all order parameters except for one order parameter (and the ones with the same symmetry)**. The startling conclusion is therefore that:

> Many Landau phase transitions involve only one order parameter, i.e., a group of coupled modes with the *same* symmetry.

This is clearly an extraordinary simplification, which is, however, very well obeyed in many phase transitions.

3.3.3   The cubic term in η

Landau free energies would be ill-conditioned if the Taylor expansion were to stop at an odd-order term, because it would be unbound from below. Nevertheless, the cubic terms are very important in the context of the Landau expansion, because if present, **they always force the transition to be first-order**. This is left as an exercise, and can be shown by analysing the point of extrema of the free energy and the signs of the second derivatives.

However, in many cases, cubic terms are not allowed by symmetry. For example, in an expansion as in eq. 2, the cubic term (or any other odd-order term) would not be allowed if a transformation $\eta \to -\eta$ existed.

> One of the conditions for a phase transition to be continuous is that the cubic term in the Taylor expansion is not allowed by symmetry — this is called the Landau condition for continuity.

3.3.4   The quartic term and higher-order terms in η

In the absence of higher-order terms, the quartic term is essential in producing a well-conditioned free energy, the requirement being that $\to +\infty$ as $|\eta| \to \infty$. In the simple, one-dimensional case, this is satisfied if $b > 0$. If higher-order terms are present (for instance, the 6th order term is always allowed by symmetry), the quartic term can be *negative*. One can see that, for appropriate values of the parameters, **a Landau free energy with a negative quartic term can produce a first-order phase transition**. In fact, a change in sign of the quartic term is the easiest mechanism to produce a change in character (from second to first order) of the phase transition.

3.4 Analysis of a simple Landau free energy

In this section, we will analyse the simple, "classic" form of the Landau free energy, i.e., eq. 2 without the odd-order terms.

$$\Delta\mathcal{F} = -\eta H + \frac{a}{2}\eta^2 + \frac{b}{4}\eta^4 + o(\eta^4) \tag{5}$$

This form of Landau free energy describes a continuous phase transition. Our purpose is to extract a few relevant thermodynamic parameters both above and below the phase transition.

3.4.1 The order parameter (generalised polarisation)

As we have seen, the order parameter is identical to the generalised polarisation in the case of a ferroic transitions. By minimising $\Delta\mathcal{F}$ with respect to η we obtain:

$$-H + a'(T - T_c)\eta + b\eta^3 = 0 \tag{6}$$

In zero field, $\mathcal{P}(H = 0) = \eta(H = 0)$ is known as the **spontaneous generalised polarisation**. Eq. 6 has the simple solutions:

$$
\begin{aligned}
\eta &= 0 \\
\eta &= \pm\sqrt{\frac{a'}{b}}(T_c - T)^{\frac{1}{2}} \quad (7)
\end{aligned}
$$

where the solutions on the second line are present only *below T_c*. It is easy to show that, for $T > T_c$, $\eta = 0$ is a *global minimum*, while for $T < T_c$ is a *local maximum*. The situation is depicted schematically in fig. 1

The case $H \neq 0$ is analysed in details in [1]); here it will suffice to say that, if $H \neq 0$, $\eta \neq 0$ both *above* and *below T_c*. In other words, **the external field breaks the symmetry and there is no longer a "true" phase transition**.
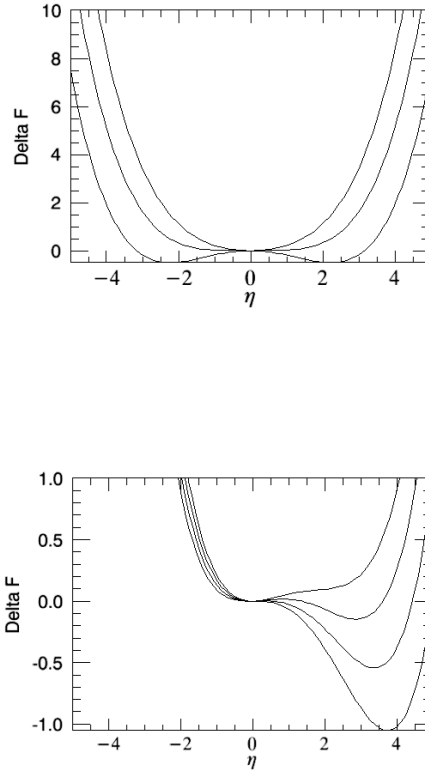
Figure 1: Two examples of the temperature dependence of the Landau free energy. **Top**: the simple form with quadratic and quartic terms produces a 2nd-order phase transition. **Bottom**: adding a cubic term produces a 1st-order phase transition.

3.4.2 The generalised susceptibility

The generalised susceptibility (magnetic susceptibility for a ferromagnetic transition, dielectric constant for a ferroelectric transition, etc) can also be calculated from the Landau free energy as

$$\chi = \frac{\partial \mathcal{P}}{\partial H} = \frac{\partial \eta}{\partial H} \tag{8}$$

Writing $\mathcal{F} = -\eta H + \Delta \mathcal{F}'(\eta)$, the quantity

$$\frac{\partial \mathcal{F}}{\partial \eta} = -H + \frac{\partial \Delta \mathcal{F}'}{\partial \eta} = 0 \tag{9}$$

is zero for all values of the field. By taking the *total* derivative of eq. 9 with respect to H, one

finds

$$-1 + \frac{\partial^2 \Delta \mathcal{F}'}{\partial \eta^2} \frac{\partial \eta}{\partial H} = 0 \tag{10}$$

whence the general formula:

$$\chi^{-1} = \frac{\partial^2 \Delta \mathcal{F}'}{\partial \eta^2} \tag{11}$$

which, in the specific case of eq. 5 yields:

$$\chi^{-1} = a'(T - T_c) + 3\eta^2 b \tag{12}$$

Eq. 12 is can be evaluated for all values of the field, but it is particularly easy to calculate at $H = 0$ (low-field susceptibility), where it produces different temperature dependences above and below T_c:

$$
\begin{aligned}
\chi^{-1}(H = 0) &= a'(T - T_c) \quad \text{for T} > \text{T}_\text{c} \\
\chi^{-1}(H = 0) &= 2a'(T_c - T) \quad \text{for T} < \text{T}_\text{c}
\end{aligned}
\tag{13}
$$

Note that **the zero-field susceptibility diverges at the critical temperature**. In fact, above T_c, eq. 13 gives the **Curie-Weiss** law for the susceptibility.

The negative-power-law behaviour of the generalised polarisation and the divergence of the susceptibility near the transition are essentially universal properties of all continuous phase transitions. However, the **critical exponents** (β for the generalised polarisation, γ and γ' for the susceptibility above and below T_c), are very often **quite different** from the Landau predictions of $\beta = 1/2$ and $\gamma = \gamma' = 1$. The exact critical exponents can be recovered in the framework of a more complex theory that takes into account the effect of **fluctuations**.

3.4.3 The specific heat

It is easy to see that, within Landau theory, the zero-field entropy for a given value of η is:

$$\Delta S = S - S_0 = -\left.\frac{\partial \mathcal{F}}{\partial T}\right|_V = -\frac{\partial \mathcal{F}}{\partial \eta}\frac{\partial \eta}{\partial T} \tag{14}$$

where

$$\frac{\partial \mathcal{F}}{\partial \eta} = a'(T - T_c)\eta + b\eta^3 \tag{15}$$

and S_0 is the component of the entropy not related to the phase transition. By employing eq. 7, one finds that $\Delta S = 0$ and $\Delta c_v = 0$ *above* T_c, whereas below T_c

$$\Delta S = -a'(T - T_c)\left(\sqrt{\frac{a'}{b}}(T_c - T)^{1/2}\right)\left(-\frac{1}{2}\sqrt{\frac{a'}{b}}(T_c - T)^{-1/2}\right) = -\frac{a'^2}{2b}(T_c - T) \tag{16}$$

The specific heat *below* T_c is:

$$\Delta c_v|_{T < T_c} = -T\left.\frac{\partial^2 \mathcal{F}}{\partial T^2}\right|_V = \frac{a'^2}{2b}T \tag{17}$$

Therefore, at T_c, c_v has a simple discontinuity given by $\Delta c_v = T_c a'^2/2b$. In reality, in most phase transition c_v has a divergent behaviour (known as a "λ" anomaly) — again a clear indication that Landau theory needs to be supplemented by fluctuation to obtain the correct quantitative behaviour of the thermodynamic quantities.

4 Displacive transitions and soft modes

Up to this point, we have discussed the Landau theory of phase transitions in a completely general way, without any concern about what happens to the crystal structure at the microscopic level. Our 2-dimensional example on the Escher drawing suggest that some phase transitions (order-disorder) can be driven by scalar fields, such as changes in occupancy of certain crystallographic sites. However, as anticipated, a large class of phase transitions are **displacive**, i.e., are driven by displacements of atoms or ions. Naturally, the relevant modes will be displacive, i.e., **in displacive phase transitions, the modes that drive the transitions are the same phonon modes driving the lattice dynamics**. Note that this is not at all an obvious result, as we are discussing very different timescales: phase transitions typically occur in a matter of seconds, whereas typical phonon frequencies are in the THz range. Nevertheless, this observation cannot be coincidental. Indeed

> **Most displacive phase transitions have a dynamical character, and are caused by *softening and "freezing" of a particular phonon*.**

What this means is that the **frequency** of a particular phonon — either an optical zone-centre phonon or an acoustic zone-boundary phonon, as we shall see briefly — starts to decrease as the phase transition is approached (the phonon "softens"), until the frequency reaches zero at the phase transition. At this point, the phonon is "frozen", i.e., it is no longer dynamical. It has, in fact, transformed into a **static displacement pattern** — exactly the mode we need to describe a symmetry lowering through the phase transition. Exactly at the phase transition, the phonons become highly anharmonic at the precise Brillouin zone point, but the crystal as a whole remains rather harmonic, and the thermal expansion anomalies are typically small. As we cool *below* the phase transition, something must happen to restore the quasi-harmonic character of all lattice vibrations, and this depends one the details of the phase transition:

- **Zone-centre phonons**: in this case, the optical zone-centre phonon *softens* completely at the phase transition, and then hardens again below it, as the system finds a new dynamical equilibrium around the distorted structure. The periodicity of the structure is unchanged through the phase transition.

- **Zone-boundary phonons**: When the distortion is driven by a zone-boundary phonon, the distorted structure will have a larger unit cell (the translational symmetry is broken). The zone boundary point will then "fold" to the new zone center, and the soft phonon will harden below the phase transition to become a **new zone center phonon**.

In 1960, W. Cochran (Advan. Phys. **9** 387 (1960)) proposed a simple relation between the soft phonon frequency and the Landau parameters:

$$\boxed{\omega^2 \propto \chi^{-1}} \tag{18}$$

Eq. 18, combined with eq. 13, gives the temperature dependence of the soft phonon frequency.

4.1   PbTiO$_3$: a classic example of a displacive soft-mode transition

PbTiO$_3$ has been considered for a long time a classic example of a displacive soft-mode transition at the Γ point (zone centre). Its crystal structure is that of the **perovskite** (see Lecture 3). In the high-temperature phase ($T > T_c$, with $T_c \approx 492$ K), it is **cubic** with space group $Pm\bar{3}m$. Below the phase transition, it becomes **tetragonal**, with space group $P4mm$ (same unit cell), and acquires a **spontaneous ferroelectric polarisation**. The phase transition is driven by a single zone-centre mode, shown in fig. 2, whereby both Ti and O displace along the c axis in

one direction and Pb displaces in the opposite direction. Although the symmetry analysis of this mode is quite complex, The Landau free energy can be reduced to the simple form of eq. 5, with the order parameter being the **amplitude of the mode**, or, more precisely, its **dipole moment**, so that the electrical polarization P is indeed proportional to the order parameter.
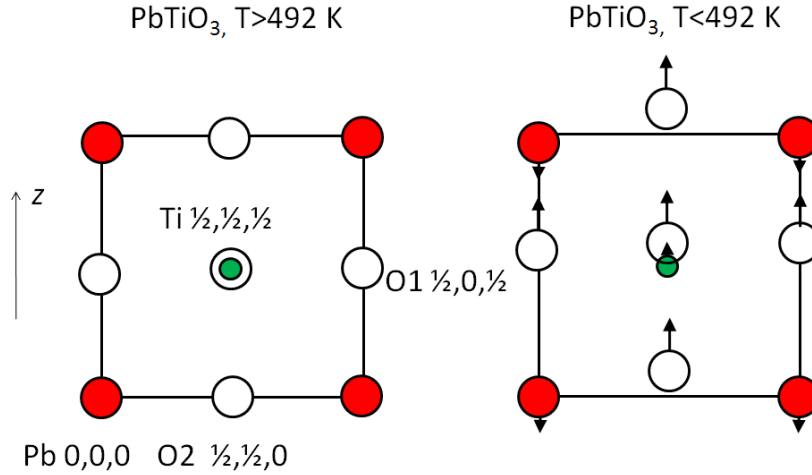

Figure 2: Crystal structures of PbTiO$_3$ above (**left**, space group $Pm\bar{3}m$) and below (**right**, space group $P4mm$) the ferroelectric Curie temperature. The displacements are exaggerated for clarity (in reality, they are about 0.1 fractional units for oxygen and 0.02 fractional units for Ti and Pb). The relevant mode is dipole active and, upon freezing, is responsible for the spontaneous polarisation.

The polarisation and dielectric constant, together with the specific heat, were measured by J.P. Remeika and A.P. Glass, Mat. Res. Bull. **5**, 37, (1970), and are reproduced in fig. 3. One can notice the divergence of the dielectric constant at the transition and the onset of **spontaneous polarisation** below the ferroelectric Curie temperature T$_C$. Note the discrepancy between the Curie temperature (492 K) and the zero intercept of the inverse susceptibility ($T_0 = 450$ K), indicating that the Curie law is not exactly obeyed and (possible) a slight first-order nature of the transition.

The phonon dispersion of PbTiO$_3$ was measured by G. Shirane et al., Phys. Rev B **2**, 155 (1970) and reproduced in fig. 4. The left panel shows the "soft" TO phonon branch above the transition (510 K). The right panel shows the temperature dependence of the phonon energy at the Γ point. One can clearly see that the *square* of the TO phonon frequency is linear with temperature. Also, the intercept is very close to T_0 — the zero intercept of the inverse susceptibility. This indicates
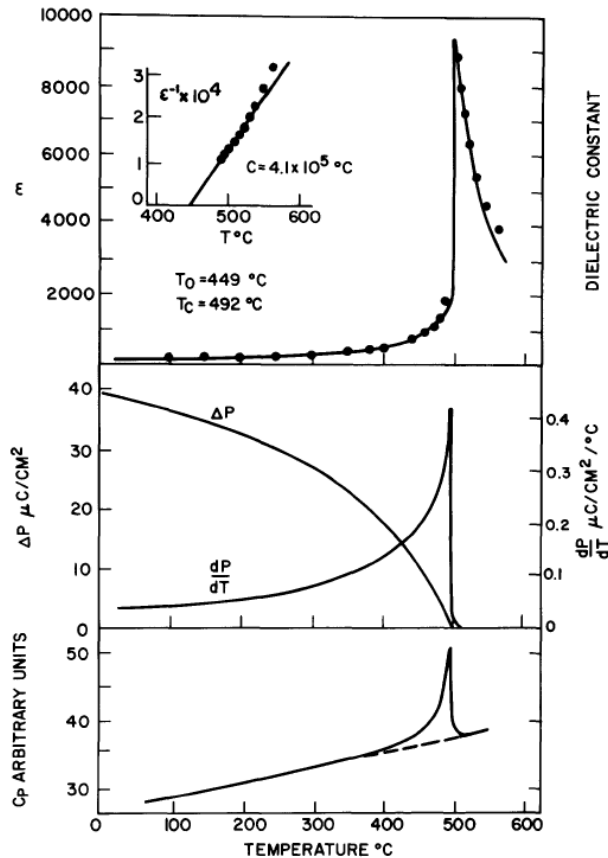
Figure 3: Dielectric properties of $PbTiO_3$, as measured by .P. Remeika and A.P. Glass, Mat. Res. Bull. **5**, 37, (1970). **Top**: the dielectric constant and (**inset**) its inverse. **Middle**: the spontaneous polarisation and its temperature derivative (proportional to the measured pyroelectric currents); **Bottom**: the specific heat, showing a clear λ-type anomaly at the phase transition.

that the Cochran relation is obeyed very well in this material.

5   Bibliography

Landau & Lifshitz - Statistical Physics [1] is part of the classic series on theoretical physics. Definitely worth learning from the old masters.

References

[1] L.D. Landau, E.M. Lifshitz, *et al. Statistical Physics: Volume 5 (Course of Theoretical Physics)*, 3rd edition, Butterworth-Heinemann, Oxford, Boston, Johannesburg, Melbourn, New Delhi, Singapore, 1980.
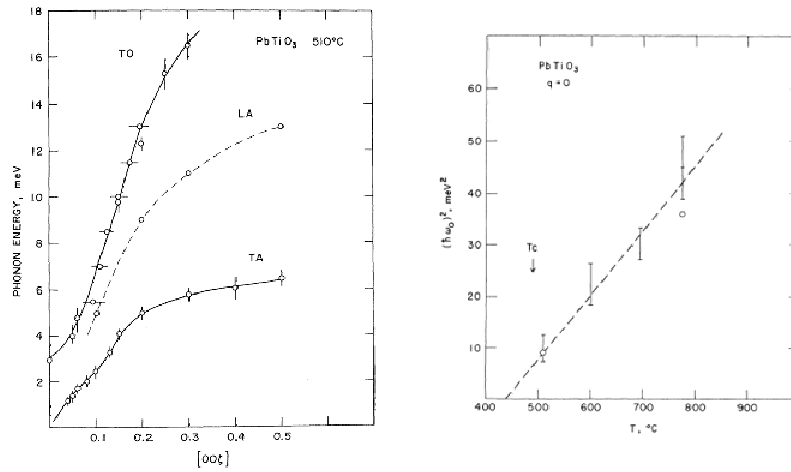
Figure 4: Phonon dispersion in PbTiO$_3$, as measured by G. Shirane et al., Phys. Rev B **2**, 155 (1970). **Left** Phonon dispersion curves along the [100] direction. The "soft" phonon is the TO mode at the zone centre (Γ point). **Right**: The *square* of the phonon energy (in meV^2) versus temperature. The linear Cochran relation is obeyed within the (rather large) error bars.

[2] M.S. Dresselhaus, G. Dresselhaus and A. Jorio, *Group Theory - Application to the Physics of Condensed Matter*, Springer-Verlag Berlin Heidelberg (2008).

[3] http://radaelli.physics.ox.ac.uk/documents/teaching/mt-2010/all_walpapers.pdf