

Lecture 9 — 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.

2 Phase transitions as a result of symmetry breaking

2.1 A phase transition on an Escher picture

In this section, we will exploit the concepts introduced in the previous sections to describe in detail a structural phase transition in 2 dimensions. Here, we outline only the main aspects of this phase transition — further details are provided in the extended version of the notes.

For our purposes, we will consider a slightly modified version of the Escher drawing in fig. 32, Lecture 1, which, as we had establish, has symmetry $p3m1$ (No. 14). The new drawing is shown

in Fig. 1, and differs from the original one by the fact that all fishes and turtles pointing in the "SSE" direction have been lightened in color.

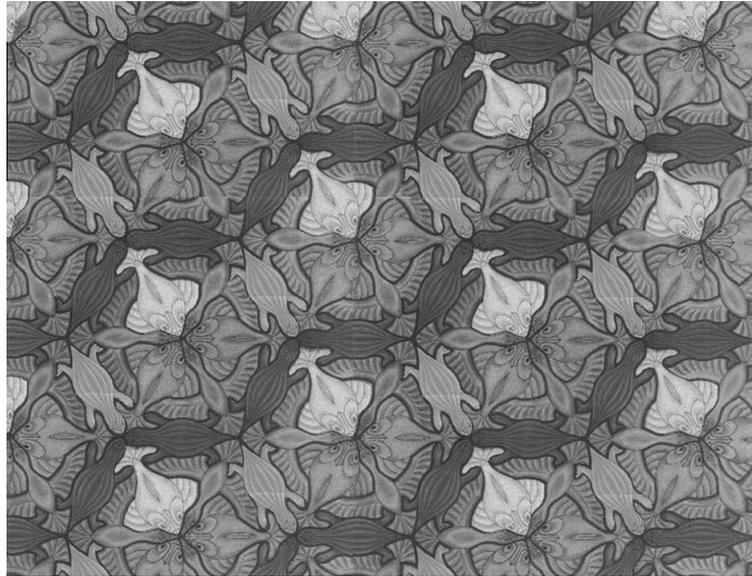


Figure 1: A modified version of the Escher drawing of fishes, birds and turtles. The original is in fig. 32, Lecture 1.

2.1.1 Low-symmetry group

The following observations can be made by inspecting the new pattern with the old symmetry superimposed (Fig. 2):

1. All the 3-fold axes are now lost, since they relate creatures of different color.
2. The mirror planes running parallel to the SSE direction are retained. All the other mirror planes are lost.
3. The glide planes running parallel to the SSE direction are retained. All the other glide planes are lost.
4. The size of the unit cell is unchanged.

By combining these observation, one can readily determine the symmetry of the modified pattern to be cm (No. 5), which is *rectangular* with a (conventional) centered cell of *twice* the size of the original hexagonal cell. The primitive cells of the two systems can be made identical. It is noteworthy that this determination did not require introducing a coordinate system for either symmetry.

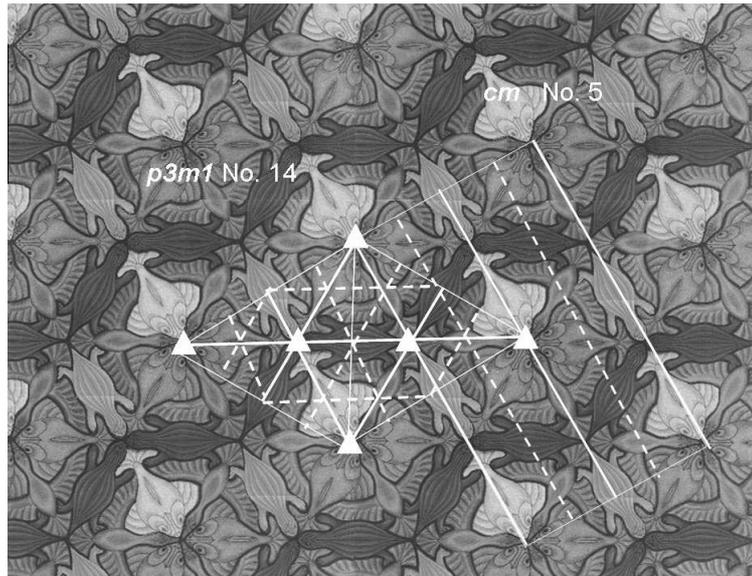


Figure 2: The pattern in Fig. 1 with the old $p3m1$ (No. 14) and the new cm (No. 5) symmetries superimposed.

2.2 Macroscopic quantities and the Neumann principle

One important observation is that in this phase transition **the point group has changed**, from $3m1$ to m . Changes in point group 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 physical property of a crystal must include the symmetry elements of the point group of the crystal**”. For example, the symmetry group $3m1$ is non-polar, whereas the new symmetry m could support an **electrical polarisation parallel** to the mirror plane.

3 Phase transitions and modes

In the previous section we have seen that a phase transition in a crystal results in a loss of some of the symmetry elements (generalised rotations and/or translations), so that a new, lower symmetry describes the crystal “below” the phase transition. In Lecture 7, we have learned that symmetries can be lowered in a systematic way by means of **lattice modes**. Here, therefore, we want to apply lattice mode analysis on our Escher picture and determine which modes give rise to the phase transition we just described.

3.1 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. The phase transition we just described involves a change of **colour** of parts of the figure, and colour is a **scalar variable**, so we expect we will need **scalar modes**.

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 7. **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). Other phase transitions require yet more exotic modes, e.g., pseudoscalars (chiral order transitions) and higher order tensors.

3.2 A simplified description of the Escher phase transition using scalar modes

Having settled on scalar modes, we can now devise a simplified description of the phase transition. The simplest way to do this is to choose a representative point on a mirror line and “activate” a single scalar mode at that point. For example, we can choose the “heart” of a turtle as representative of the colour of the whole turtle, and “activate” a scalar mode at that point, which will enforce the colour change. This is shown schematically in fig. 3. Note that **there are only three such points per unit cell**, so we will have only 3 degrees of freedom per unit cell. Also, we will have to worry only about the pattern *within one unit cell*: in fact

The propagation of the mode pattern (say, \mathfrak{P}) to the other unit cells follows the Bloch theorem:

$$\mathfrak{P}(\mathbf{R}_i) = \mathfrak{P}(0)e^{i\mathbf{k}\cdot\mathbf{R}_i} \quad (1)$$

Where \mathbf{k} is defined within the first Brillouin zone.

In our case, the propagation vector \mathbf{k} is zero, since there is no change in the unit cell, but we can clearly see that eq. 1 sets out a scheme to obtain more complex patterns, with either **superstructures** (i.e., larger unit cells) or an **incommensurate modulation**. The first case occurs when \mathbf{k}

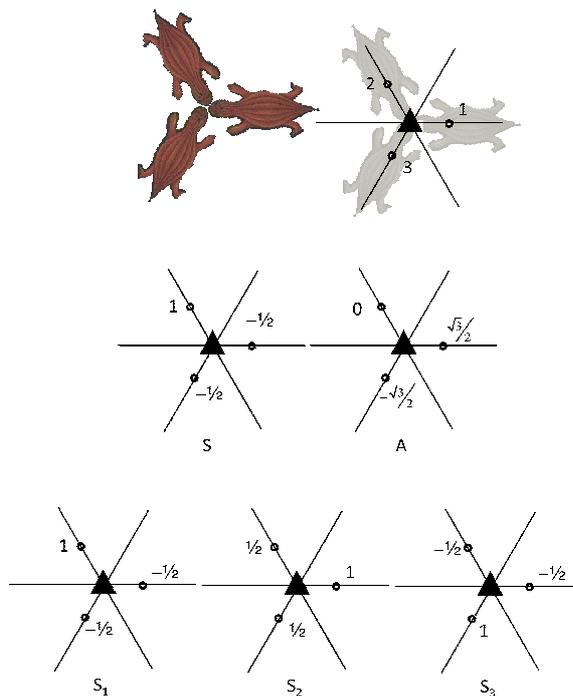


Figure 3: **Top:** simplified scheme to describe the color-change transition as a scalar field on 3 sites. **Middle:** The symmetric (S) and antisymmetric (A) scalar modes (see text). **Bottom:** the three S modes, obtained by applying a 3-fold rotation to the original S mode. These modes describe the three “domains” of the phase transition.

is *commensurate* with the lattice, i.e., when the components of \mathbf{k} are all rational fractions of 2π ; the second case when this is not so.

Our problem is further simplified by recognising that we only need to deal with proper and improper rotations (not roto-translations — glides and screw axes). Therefore, the symmetry-adapted patterns (i.e., the modes) within one unit cell are nothing other than **the scalar modes of a molecule with symmetry $3m1$ (or D_3 in Schoenflies notation)**. This symmetry is dealt with in depth in M. Dresselhaus’ book [2], and we refer to it for the details. Once again, however, the modes can be simply obtained in an intuitive way as follows.

We know we need 3 modes to account for the three degrees of freedom. One of the mode is the totally symmetric mode (similar to the case of the square molecule) — in this case, this corresponds to assigning the *same scalar* to the three sites. This mode is trivial, is 1-dimensional and, as for all totally symmetric modes, is not involved in the phase transition.

The two other modes **cannot be one-dimensional**, i.e., it is not possible to describe the effect of all symmetry operators as a simple multiplication of the mode by a real or complex number. These modes must therefore transform into linear combinations of each other by some of the operations, and in analogy with the case of the square molecule, **these two modes form a 2-**

dimensional invariant subspace. There is more than one way to choose the two modes, but the most convenient way is shown in fig. 3. One can immediately see that one of the two modes (S in the picture) is *symmetric* by one of the mirror plane, whereas the other one is *antisymmetric* by the same. It can also be seen with a bit more work that these modes have the same transformation properties of the functions x and y (with the y -axis along the mirror plane — this easy, since our “modes” are nothing other the value of those functions at the “heart” of the turtles) and of the unit vectors \hat{i} and \hat{j} (same axis conventions).

3.3 Order parameters

As we have seen in our simple example, **ordered (i.e., symmetry-breaking) states are described by linear combination of modes.** In our case, we only have two non-trivial modes belonging to the same invariant subspace; in general, there will be multiple modes with different subspace dimensions. A generic state within each subspace will be described as

$$c_1 \mathbf{m}_1 + c_2 \mathbf{m}_2 + \dots + c_n \mathbf{m}_n \quad (2)$$

where n is the dimension of the invariant subspace. Here there is an important distinction to be made between **linear** and **non-linear equations.**

Linear equations , e.g., the Schrodinger equations, the normal-mode secular equation etc. In this case, all the modes in the invariant subspace are **degenerate**, regardless of the coefficients.

Non-linear equations , e.g., the equations describing the stability of a phase. In this case, only symmetry-equivalent modes are degenerate, but arbitrary linear combinations of modes are not. For example, modes S and A in fig. 3 are *not* degenerate because they are *not* directly related by any symmetry, whereas modes S_1, S_2 and S_3 are degenerate and describe possible phase **domains.**

It is convenient to introduce the following:

The array of real or complex parameters:

$$\eta = \begin{bmatrix} c_1 \\ \vdots \\ c_n \end{bmatrix} \quad (3)$$

defining the mode within each invariant subspace is known as the *order parameter*, since it completely defines the ordered state for a particular mode.

Different modes within the same subspace — we say “different *directions* of the order parameter”— do not necessarily define the same low symmetry and are not always degenerate (A and S are not in this case).

The **amplitude** of the order parameter $|\eta|$ determines how much the colour has changed, i.e., how much the phase transition has “progressed”. $|\eta| = 0$ corresponds to the original, high-symmetry phase.

3.3.1 One important theorem about order parameters (given without proof)

The following theorem, here given without proof (for this see [2] again or the classic book by Landau and Lifshitz [1]), is at the very core of the theory of phase transitions.

1. The *square* of the amplitude of the order parameter for each invariant subspace i — a real quantity given by

$$|\eta^i|^2 = [c_1^i \dots c_n^i]^* \begin{bmatrix} c_1^i \\ \vdots \\ c_n^i \end{bmatrix} \quad (4)$$

is totally invariant by all symmetry operators of the high-symmetry group.

2. If two order parameters transform in the same way, then the following real quantity is also invariant:

$$\mathcal{R}e(\eta^i \cdot \eta^j) = \frac{1}{2} [c_1^i \dots c_n^i]^* \begin{bmatrix} c_1^j \\ \vdots \\ c_n^j \end{bmatrix} + c.c. \quad (5)$$

3. *If two order parameters transform in the different ways, then the only real quadratic invariant involving both parameters is*

$$\kappa^i |\eta^i|^2 + \kappa^j |\eta^j|^2 \quad (6)$$

where κ_i κ_j and are arbitrary real constants. In other words, we are not allowed to mix components from different order parameters to produce quadratic invariants, unless they transform with the same symmetry. On the other hand, it is possible to construct higher-order (cubic, quartic, etc.) invariants by mixing differently-transforming order parameters.

The first and second parts of the theorem are actually very easy to prove, since group operators act on order parameters as unitary matrices and therefore preserve amplitudes and dot products.

4 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 Ginsburg-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.

4.1 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:

$$\mathcal{F} = \mathcal{F}_0 + \Delta\mathcal{F}(\eta^i) \quad (7)$$

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.

4.2 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.

4.3 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:

$$\Delta\mathcal{F} = -\eta H + \frac{a}{2}\eta^2 + \frac{c}{3}\eta^3 + \frac{b}{4}\eta^4 + o(\eta^5) \quad (8)$$

The odd-power terms are strongly restricted by symmetry, and are never present, for instance, if there is a transformation $\eta \rightarrow -\eta$. 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. 8, 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.

4.3.1 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, there 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 known as **ferroic**. *Ferromagnetic, Ferroelectric and Ferroelastic transitions* are classic examples of ferroic transitions. In these case, we can write:

$$\mathcal{P} = -\frac{\partial\mathcal{F}}{\partial H} = \eta \quad (9)$$

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.)

4.3.2 The quadratic term in η

This term is always allowed and has the very simple structure explained in eq. 4-6. Because of this simple structure, where only terms with the same symmetry are coupled, one can easily show that **near the phase transition, all the order parameters with the same symmetry are proportional to each other**. Therefore, without loss of generality, one can consider an expansion of the type:

$$\sum_i \kappa^i |\eta^i|^2 \quad (10)$$

where all the η^i 's have different symmetries. 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 of two or more coefficient in the expansion in eq. 10 *can only be accidental*.

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.

4.3.3 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. 8, the cubic term (or any other odd-order term) would not be allowed if a transformation $\eta \rightarrow -\eta$ 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.

Example: In the Escher phase transition described above, the cubic term $\eta_1^3 + \eta_2^3$ is invariant. This can be easily seen from the fact that the modes transform under 3-fold rotation by ω or ω^2 multiplication (both cubic roots of 1), and under mirror operation by exchanging the two modes. Therefore **the Escher phase transition cannot be strictly second-order**. It can, however, be weakly first-order if the cubic term is small.

4.3.4 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 $\rightarrow +\infty$ as $|\eta| \rightarrow \infty$. In the simple, one-dimensional case, this is satisfied if $b > 0$. If higher-order terms are present (for instance, the 6^{th} 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.

4.4 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. 8 without the odd-order terms.

$$\Delta\mathcal{F} = -\eta H + \frac{a}{2}\eta^2 + \frac{b}{4}\eta^4 + o(\eta^4) \quad (11)$$

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.

4.4.1 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:

$$-H + a'(T - T_c)\eta + b\eta^3 = 0 \quad (12)$$

In zero field, $\mathcal{P}(H = 0) = \eta(H = 0)$ is known as the **spontaneous generalised polarisation**. Eq. 12 has the simple solutions:

$$\begin{aligned} \eta &= 0 \\ \eta &= \pm \sqrt{\frac{a'}{b}}(T_c - T)^{\frac{1}{2}} \end{aligned} \quad (13)$$

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. 4

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**.

4.4.2 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

$$\chi = \frac{\partial \mathcal{P}}{\partial H} = \frac{\partial \eta}{\partial H} \quad (14)$$

By differentiating eq. 8 with respect to H , one finds the general formula:

$$\chi^{-1} = \frac{\partial^2 \Delta\mathcal{F}}{\partial \eta^2} \quad (15)$$

which, in the specific case of eq. 11 yields:

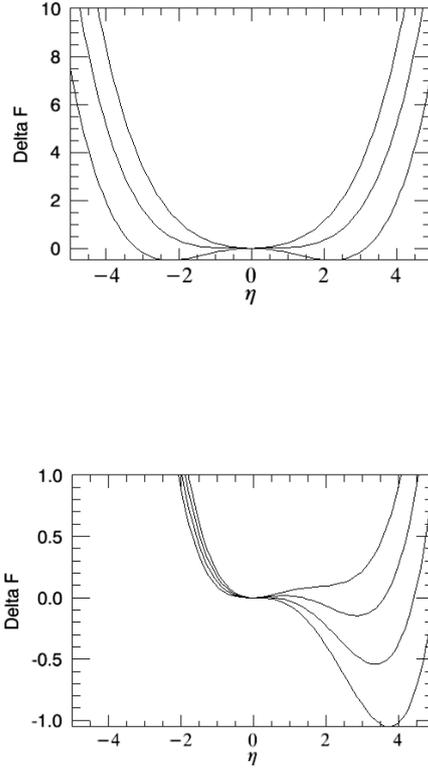


Figure 4: Two examples of the temperature dependence of the Landau free energy. **Top:** the simple form with quadratic and quartic terms produces a 2^{nd} -order phase transition. **Bottom:** adding a cubic term produces a 1^{st} -order phase transition.

$$\chi^{-1} = a'(T - T_c) + 3\eta^2 b \quad (16)$$

Eq. 16 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 :

$$\begin{aligned} \chi^{-1}(H = 0) &= a'(T - T_c) \quad \text{for } T > T_c \\ \chi^{-1}(H = 0) &= 2a'(T_c - T) \quad \text{for } T < T_c \end{aligned} \quad (17)$$

Note that **the zero-field susceptibility diverges at the critical temperature**. In fact, above T_c , eq. 17 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**.

4.4.3 The specific heat

It is easy to see that, within Landau theory, the specific heat:

$$c_v = -T \left. \frac{\partial^2 \mathcal{F}}{\partial T^2} \right|_V \quad (18)$$

has a simple discontinuity given by $\Delta c_v = 2T_c a'^2/b$. 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.

5 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 on 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:

$$\omega^2 \propto \chi^{-1} \quad (19)$$

Eq. 19, combined with eq. 17, gives the temperature dependence of the soft phonon frequency.

5.1 PbTiO₃: a classic example of a displacive soft-mode transition

PbTiO₃ 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. 5, 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. 11, 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.

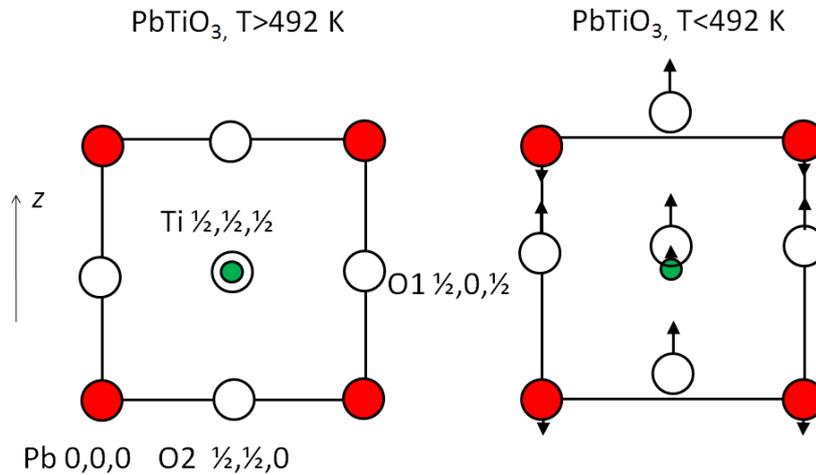


Figure 5: Crystal structures of PbTiO_3 above (**left**, space group $Pm\bar{3}m$) and below (**right**, space group $P4mm$) the ferroelectric Curie temperature. The displacements are exaggerated for clarity (in reality, they are about 0.1 fractional units for oxygen and 0.02 fractional units for Ti 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. 6. 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. 7. The left panel shows the “soft” LO 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 LO phonon frequency is linear with temperature. Also, the intercept is very close to T_0 — the zero intercept of the inverse susceptibility. This indicates that the Cochran relation is obeyed very well in this material.

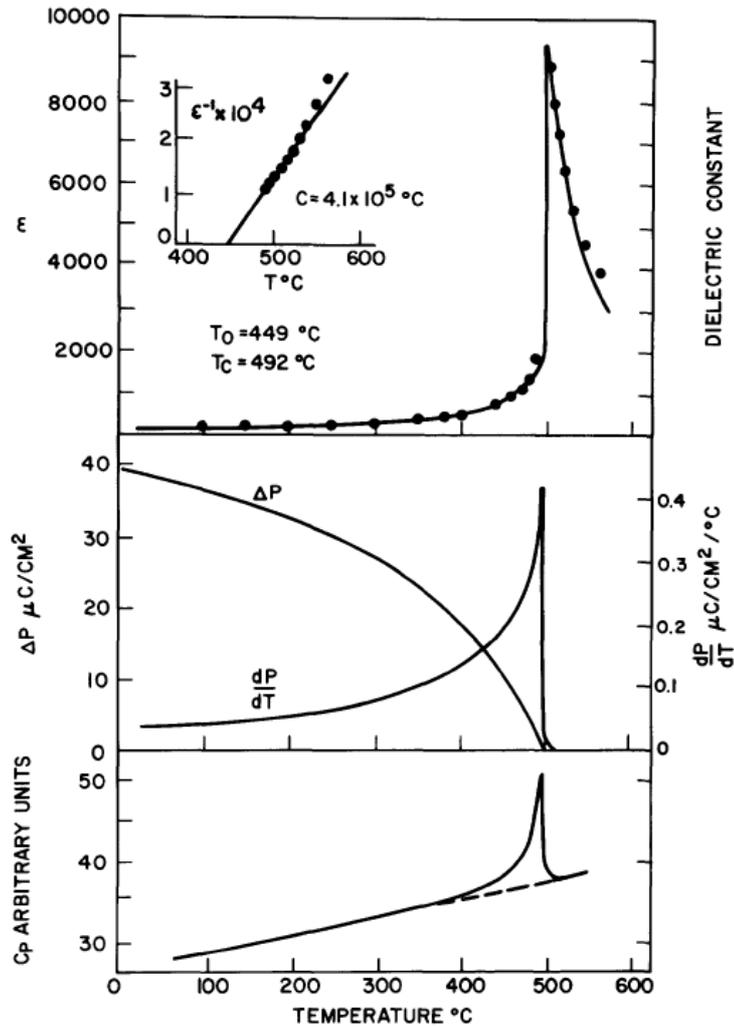


Figure 6: Dielectric properties of PbTiO_3 , as measured by .P. Remeika and A.P. Glass, *Mat. Res. Bull.* **5**, 37, (1970). **Top**: the dielectric constant and (**inset**) its inverse. **Middle**: the spontaneous polarisation and its temperature derivative (proportional to the measured pyroelectric currents); **Bottom**: the specific heat, showing a clear λ -type anomaly at the phase transition.

6 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, Melbourne, New Delhi, Singapore, 1980.

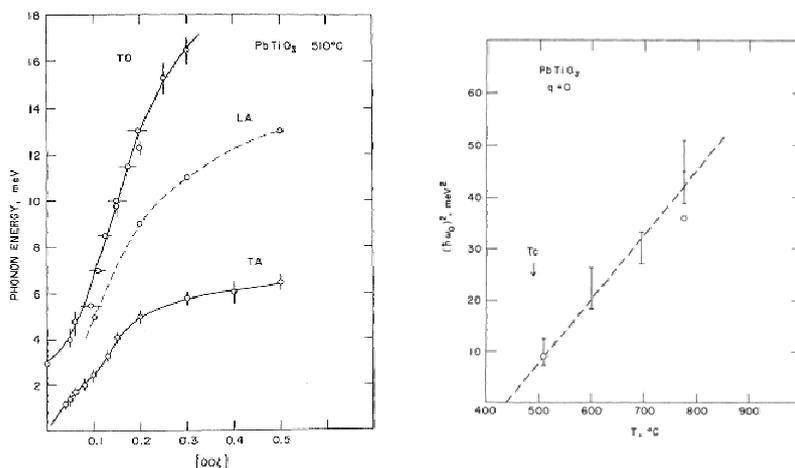


Figure 7: Phonon dispersion in PbTiO_3 , as measured by G. Shirane et al., *Phys. Rev B* **2**, 155 (1970). **Left** Phonon dispersion curves along the $[100]$ direction. The “soft” phonon is the TO mode at the zone centre (Γ point). **Right**: The *square* of the phonon energy (in meV^2) versus temperature. 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/crystallography-teaching/mt-2009/all_walpapers.pdf

7 Appendix I: further aspects of the Escher phase transition

7.1 Wyckoff positions

We shall now examine, with the help of the ITC, how the symmetry of individual sites is modified by the phase transition. The relevant pages of the ITC can be found on [3]. In the high-symmetry “phase”, there are 3 distinct Wyckoff sites with symmetry $3m.$, labeled $1a$, $1b$ and $1c$, all with multiplicity 1. They correspond to the heads of the fishes and birds (site $1a$ with our choice of origin), the tails of the turtles and birds (site $1b$) and the heads of the turtles/tails of fishes (site $1c$). All these sites are at the intersection of 3 mirror planes, of which one (parallel to the SSW

direction) survives. We conclude that the symmetry of those sites below the phase transition will be $.m..$ The other special position in $p3m1$ is $3d$, with a local symmetry of $.m..$ Sites with this symmetry are located along the spines of the creatures. Moreover, one can see that each mirror plane defines the spines of all 3 creatures in the same succession, so there is only one type of $.m.$ site. In cm , there is only one special Wyckoff site ($2a$) with multiplicity 2 and symmetry $.m..$ However, we note that the size of the unit cell has been doubled, so the multiplicity in the primitive cell would be 1. These sites corresponds to the spines of the creatures running in the SSW direction. The head/tail positions are no longer special, and have the same symmetry of the mirror they lie on. In the high-symmetry phase, general positions had multiplicity 6 (symbol $6e$). As an example, we can see that there are 6 identical front paws of the turtles arranged around their heads. In cm , the general position has multiplicity 4 (symbol $4b$, i.e., primitive multiplicity 2). This is because the darker turtles are no longer left-right-symmetric so that identical paws only come in pairs across the mirrors.

7.2 Basis transformation

Fig. 8 shows a set of basis vectors for the high-symmetry ($p3m1$) and low-symmetry (cm) groups, both chosen according to standard crystallographic conventions. The a -axes of the two cells have been chosen to coincide, whereas the b -axis in the rectangular cell is the shortest translation orthogonal to the a -axis. We have therefore

$$\begin{aligned}
 \mathbf{a}_r &= \mathbf{a}_h & (20) \\
 |\mathbf{a}_r| &= |\mathbf{a}_h| = a \\
 \mathbf{b}_r &= \mathbf{a}_h + 2\mathbf{b}_h \\
 |\mathbf{a}_r| &= a\sqrt{3}
 \end{aligned}$$

The covariant transformation is therefore:

$$[\mathbf{a}_r \ \mathbf{b}_r] = [\mathbf{a}_h \ \mathbf{b}_h] \begin{bmatrix} 1 & 1 \\ 0 & 2 \end{bmatrix} = [\mathbf{a}_h \ \mathbf{b}_h] \mathbf{P} \quad (21)$$

and the corresponding contravariant transformation is

$$\mathbf{Q} = \mathbf{P}^{-1} = \begin{bmatrix} 1 & -\frac{1}{2} \\ 0 & \frac{1}{2} \end{bmatrix} \quad (22)$$

We can use this, for example, to determine the rectangular coordinates for the 3-fold-axes positions in the original pattern, $1a = 0, 0$, $1b = \frac{1}{3}, \frac{2}{3}$ and $1c = \frac{2}{3}, \frac{1}{3}$. We find:

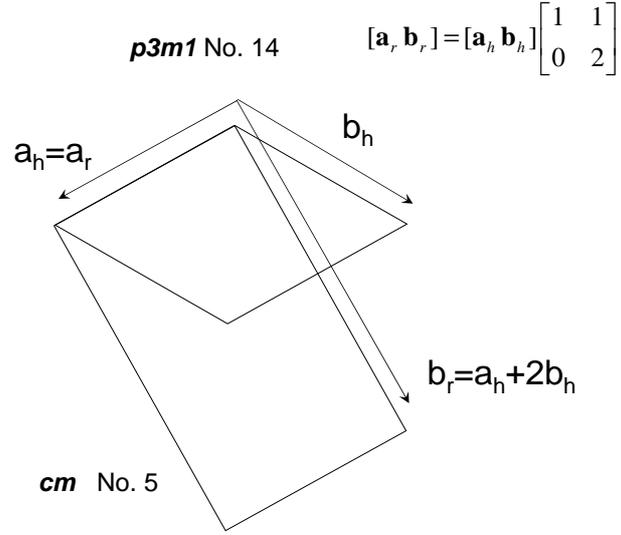


Figure 8: Basis vectors for the $p3m1$ and cm wallpaper groups, set as in Fig. 2.

$$\begin{aligned} \begin{bmatrix} 1 & -\frac{1}{2} \\ 0 & \frac{1}{2} \end{bmatrix} \begin{bmatrix} 0 \\ 0 \end{bmatrix} &= \begin{bmatrix} 0 \\ 0 \end{bmatrix} \\ \begin{bmatrix} 1 & -\frac{1}{2} \\ 0 & \frac{1}{2} \end{bmatrix} \begin{bmatrix} \frac{1}{3} \\ \frac{2}{3} \end{bmatrix} &= \begin{bmatrix} 0 \\ \frac{1}{3} \end{bmatrix} \\ \begin{bmatrix} 1 & -\frac{1}{2} \\ 0 & \frac{1}{2} \end{bmatrix} \begin{bmatrix} \frac{2}{3} \\ \frac{1}{3} \end{bmatrix} &= \begin{bmatrix} \frac{1}{2} \\ \frac{1}{6} \end{bmatrix} \end{aligned} \quad (23)$$

As we can see from the ITC, all three set of rectangular coordinates correspond to Wyckoff positions $2a$.

7.3 Metric tensor

The wallpaper group cm has an orthogonal coordinate system, and it is therefore easy to determine its metric tensor:

$$\mathbf{G}_r = a^2 \begin{bmatrix} 1 & 0 \\ 0 & 3 \end{bmatrix} \quad (24)$$

We can exploit the covariant properties of \mathbf{G} to determine the corresponding metric tensor in hexagonal coordinates:

$$(\mathbf{G}_r)_{ij} = (\mathbf{G}_h)_{kl} \mathbf{P}_i^k \mathbf{P}_j^l = \mathbf{P}^T \mathbf{G}_h \mathbf{P} \quad (25)$$

whence

$$\mathbf{G}_h = \mathbf{Q}^T \mathbf{G}_r \mathbf{Q} = a^2 \begin{bmatrix} 1 & -\frac{1}{2} \\ -\frac{1}{2} & 1 \end{bmatrix} \quad (26)$$

Let us verify the correctness of Eq. 26. The distance between Wyckoff positions $1c$ and $1a$ is the length of the vector $[\frac{2}{3} \frac{1}{3}]$, the square of which is

$$d^2 = \begin{bmatrix} \frac{2}{3} & \frac{1}{3} \\ \frac{1}{3} & \frac{2}{3} \end{bmatrix} a^2 \begin{bmatrix} 1 & -\frac{1}{2} \\ -\frac{1}{2} & 1 \end{bmatrix} \begin{bmatrix} \frac{2}{3} \\ \frac{1}{3} \end{bmatrix} = \frac{1}{3} a^2 \quad (27)$$

In rectangular coordinates, we can do the calculation by hand:

$$d^2 = \left(\frac{1}{2}\right)^2 a^2 + \left(\frac{1}{6}\right)^2 3a^2 = \frac{1}{3} a^2 \quad (28)$$