

Crystal Structure and Dynamics

Paolo G. Radaelli, Michaelmas Term 2012

Part 3: Dynamics and phase transitions Lectures 8-10

Web Site:

<http://www2.physics.ox.ac.uk/students/course-materials/c3-condensed-matter-major-option>

Bibliography

- **M.S. Dresselhaus, G. Dresselhaus and A. Jorio**, *Group Theory - Application to the Physics of Condensed Matter*, Springer-Verlag Berlin Heidelberg (2008). A recent book on irreducible representation theory and its application to a variety of physical problems. It should also be available on line free of charge from Oxford accounts.
- **Volker Heine** *Group Theory in Quantum Mechanics*, Dover Publication Press, 1993. A very popular book on the applications of group theory to quantum mechanics.
- **Neil W. Ashcroft and N. David Mermin**, *Solid State Physics*, HRW International Editions, CBS Publishing Asia Ltd (1976). Among many other things, it contains an excellent description of thermal expansion in insulators.
- **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. Part of the classic series on theoretical physics. Definitely worth learning from the old masters.

Contents

| | | |
|----------|-----------------------------------------------------------------------------------|-----------|
| 1 | Lecture 8 — Lattice modes and their symmetry | 3 |
| 1.1 | Molecular vibrations — mode decomposition | 3 |
| 1.2 | Molecular vibrations — symmetry of the normal modes | 8 |
| 1.3 | Extended lattices: phonons and the Bloch theorem | 9 |
| 1.3.1 | Classical/Quantum analogy | 11 |
| 1.3.2 | Inversion and parity | 12 |
| 1.4 | Experimental techniques using light as a probe: “Infra-Red” and “Raman” | 12 |
| 1.4.1 | IR absorption and reflection | 13 |
| 1.5 | Raman scattering | 15 |
| 1.6 | Inelastic neutron scattering | 16 |
| 2 | Lecture 9 — Anharmonic effects in crystals | 18 |
| 2.1 | Thermal expansion | 18 |
| 2.1.1 | Thermal expansion in metals | 21 |
| 2.2 | Conservation of crystal momentum | 21 |
| 2.3 | Heat transport theory | 23 |
| 2.4 | Thermal conductivity due to phonons | 25 |
| 3 | Lecture 10 — Phase Transitions | 29 |
| 3.1 | Continuous and discontinuous phase transitions | 29 |
| 3.2 | Phase transitions as a result of symmetry breaking | 29 |
| 3.3 | Macroscopic quantities: the Neumann principle | 30 |
| 3.3.1 | Polarisation and ferroelectricity | 31 |
| 3.3.2 | Magnetisation and ferromagnetism | 31 |
| 3.4 | The Landau theory of phase transitions | 31 |
| 3.5 | Analysis of a simple Landau free energy | 34 |
| 3.5.1 | The order parameter (generalised polarisation) | 34 |
| 3.5.2 | The generalised susceptibility | 36 |
| 3.5.3 | The specific heat | 37 |
| 3.6 | Displacive transitions and soft modes | 37 |

1 Lecture 8 — Lattice modes and their symmetry

1.1 Molecular vibrations — mode decomposition

- We have seen in previous sections that dynamical effects can destroy the translational symmetry in a crystal, giving rise to scattering *outside* the RL nodes. In addition, other symmetries will be broken by individual excitations. Here, we want to illustrate **how symmetry breaking can be classified with the help of symmetry**.
- Normal modes of vibration can be fully classified based on the symmetry of the potential. This is an entirely classical derivation.
- In the quantum realm, the **eigenstates** of a Hamiltonian with a given symmetry will not possess the full symmetry of the Hamiltonian, but can also be classified on the basis of symmetry. This is one of the most powerful applications of symmetry to quantum mechanics: one can deduce the whole multiplet structure of a Hamiltonian from symmetry considerations alone.
- Since the presence of a lattice gives rise to additional complications, we will first illustrate the principle using *isolated molecules*. We will show that molecular vibrations can break the symmetry of the molecule in a systematic way.
- Isolated molecules possess a *point-group symmetry*, which is not restricted to be one of the 32 crystallographic point groups.
- In the remainder, we will call **modes** the *static* patterns of distortion of a molecule, which can be thought of as snapshots of the molecule as it vibrates (strictly speaking, displacements in a mode can have complex coefficients — see below). **Normal modes** will have the usual meaning of special patterns of distortions associated with a *single vibrational frequency* ω . An example of a **mode** is given in fig. 1 for a hypothetical square molecule.
- The mode in fig. 1 has no symmetry whatsoever. However, one can construct modes that retain some of the original symmetry. Modes in fig. 2, for example, are not completely arbitrary: they transform in a well-defined way by application of the symmetry transformations of the original molecule (which has point-group symmetry $4mm$ in 2D). Specifically, they are either *symmetric* or *antisymmetric* upon application of any of the 8 symmetry operators of $4mm$ (see Lecture 1):

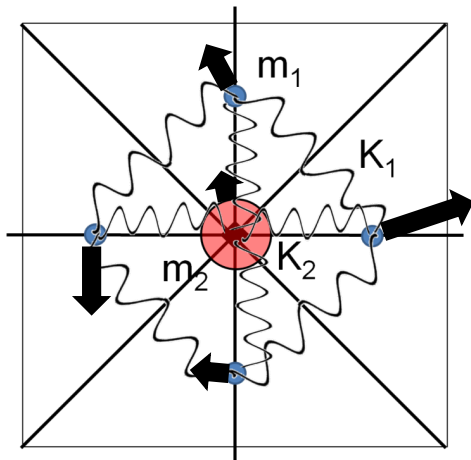


Figure 1: A snapshot of a vibrating square molecule.

- ◇ Mode Γ_1 is *symmetric* under *all* the symmetry operators of the group — we say that it transforms under the *totally symmetric mode*.
 - ◇ Mode Γ_2 is *symmetric* under 1, 2, m_{10} and m_{01} and *antisymmetric* under 4^+ , 4^- , m_{11} and $m_{1\bar{1}}$.
 - ◇ Mode Γ_3 is *symmetric* under 1, 2, m_{11} and $m_{1\bar{1}}$ and *antisymmetric* under 4^+ , 4^- , m_{10} and m_{01} .
 - ◇ Mode Γ_4 is *symmetric* under 1, 2, 4^+ and 4^- and *antisymmetric* under m_{10} , m_{01} , m_{11} and $m_{1\bar{1}}$.
- Once can also say that each “symmetric” operator is equivalent to multiplying all the displacements of a given mode by +1, whereas each “antisymmetric” operator by -1. This is the simplest example of a **irreducible representation** of a group — a central concept in group theory: the action of a symmetry operator on a mode has been “reduced” to multiplying that mode by a number. In a concise way, we could write, for example:

$$\begin{aligned}
 4^+ [\Gamma_2] &= -1 [\Gamma_2] \\
 2 [\Gamma_3] &= +1 [\Gamma_3] \\
 m_{11} [\Gamma_4] &= -1 [\Gamma_4]
 \end{aligned}
 \tag{1}$$

- Not all modes can be fully “reduced” in this way. An example is given in fig. 3 . We can see that:

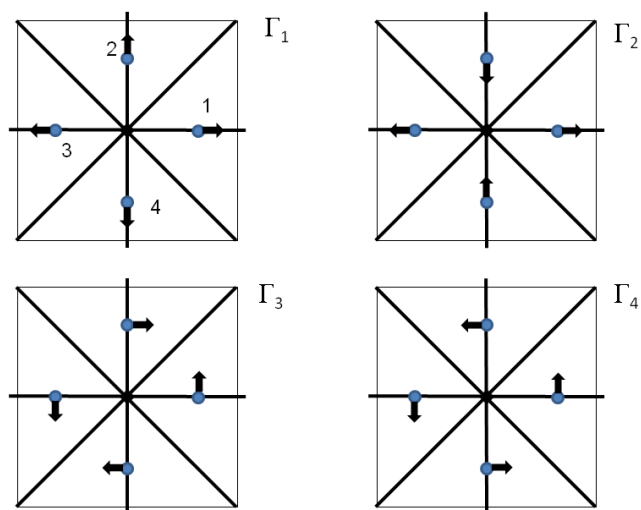


Figure 2: The four “1 dimensional modes” of the square molecule. These modes transform into either themselves (symmetric) or minus themselves (antisymmetric) upon all symmetries of the molecule.

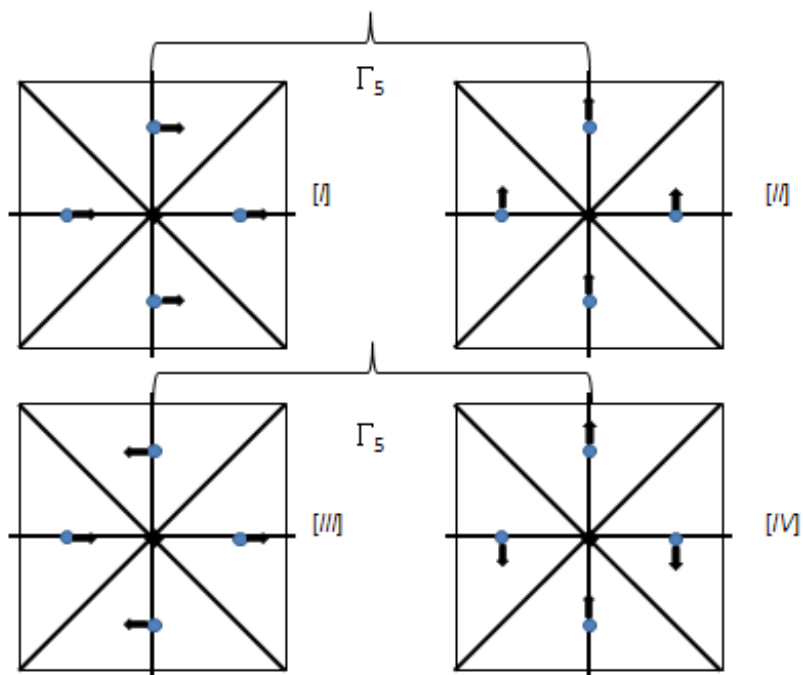


Figure 3: The four “2 dimensional modes” of the square molecule. These modes transform into either \pm themselves (symmetric/antisymmetric) or *into each other in pairs* upon all symmetries of the molecule. Note that all these modes are *antisymmetric* upon 2-fold rotation.

- ◇ Certain symmetry operators **interchange the modes**. For example, the operator 4^+ transforms mode $[I]$ into mode $[II]$ and $[III]$ into mode $[IV]$, etc.
 - ◇ One can prove that there is no way of decomposing these modes as a linear combination of "fully reduced" modes that transform as the previous group, i.e., as a multiplication by $+1$ or -1 .
 - ◇ $[I]$ is *never* transformed into $[III]$ (or vice versa) and $[III]$ is *never* transformed into $[IV]$ (or vice versa).
- Here, it is clearly impossible to transform these modes by multiplying each of them by a number. However, the symmetry operations on these modes can still be summarised in an extremely concise mathematical form. In order to achieve this, we can consider these modes as **basis vectors** of an abstract **mode space**. Linear combinations of these modes simply mean vector addition of the displacements of each atom.
 - Crucially, the symmetry transformations **preserve the linearity of mode space**, so that, if g is an operator, \mathbf{m}_1 and \mathbf{m}_2 are modes and a and b are constants. This is a key requirement of a **representation of the group**.

$$g[a\mathbf{m}_1 + b\mathbf{m}_2] = ag\mathbf{m}_1 + bg\mathbf{m}_2 \quad (2)$$

- Let us consider in particular the set of displacements that are **linear combinations** of modes $[I]$ and $[II]$ — in other words, all the displacements of the type

$$a[I] + b[II] \rightarrow \begin{pmatrix} a \\ b \end{pmatrix} \quad (3)$$

where the **array notation** in eq. 3 should be obvious. An alternative phrasing is that we are considering the **subspace** spanned by modes $[I]$ and $[II]$.

- The transformations can now be expressed in **matrix form**, as illustrated in tab. 1. Modes $[III]$ - $[IV]$ transform in the same way.
- As a second example, we analyse the displacements of the *central atom* of our hypothetical molecule, located on the fourfold axis. This atom has two degrees of freedom, as shown in fig 4. The two corresponding modes transform in the same way as modes $[I]$ and $[II]$ (or $[III]$ and $[IV]$). In the language of representation theory, we say that there transform according to **irreducible representation** Γ_5 .

Table 1: Matrix representation of the transformations of point group $4mm$ on the subspace spanned by modes $[I]$ and $[II]$

| 1 | 2 | 4^+ | 4^- |
|-------------------------------------------------|--------------------------------------------------|-------------------------------------------------|--------------------------------------------------|
| $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ | $\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$ | $\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$ |
| m_{10} | m_{01} | m_{11} | $m_{1\bar{1}}$ |
| $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ | $\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$ | $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$ |

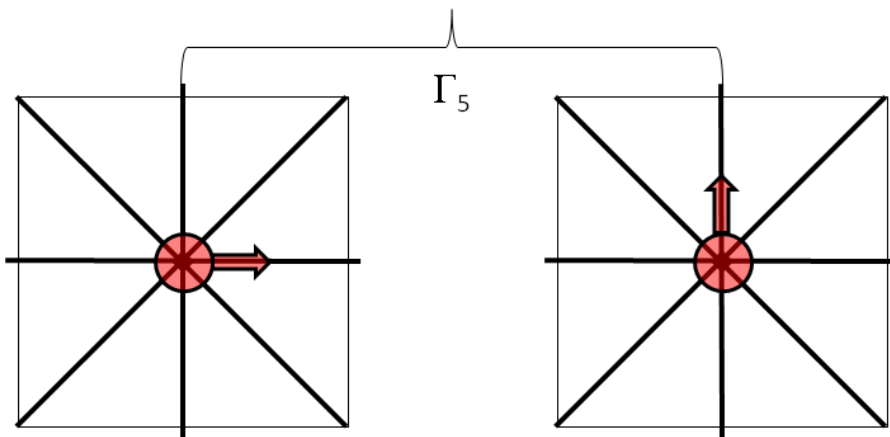


Figure 4: The two central-atom modes of the square molecule. One can verify that they transform as the "2-D" corner modes, i.e., with the representation Γ_5

- The 10 modes described here above exhaust all the 8 degrees of freedom of the 4 atoms at the corner of the molecule plus the atom at the centre. Therefore, any arbitrary displacement pattern can be written as a linear combination of the 10 modes, which represent a **complete basis** for the space of all possible distortions of the molecule.

The **theory of irreducible representations** teaches how to decompose arbitrary displacement patterns as linear combinations of special **basis modes**, transforming according to rules similar to the ones illustrated here above.

1.2 Molecular vibrations — symmetry of the normal modes

- We will now see how the analysis in the previous section helps us to identify **normal modes** *without knowing anything about the potential* (other than its symmetry). Let us consider a normal mode Q_i . We know that our basis modes q_j form a complete basis for any distortion, so it must be possible to write:

$$Q_i = \sum_j a_{ij} q_j \quad (4)$$

(in the general case, a_{ij} can be *complex*)

- Let us assume that Q_i is **non-degenerate**, so that it uniquely satisfies the secular equation with a frequency ω_i . We can simply use physical intuition to conclude that **all the modes related by symmetry to Q_i , such as ($g[Q_i]$) must also be eigenvectors with the same frequency**. However, we just assumed that Q_i is **non-degenerate**, so it must necessarily follow that

$$g[Q_i] = cQ_i \quad (5)$$

for every operator g in the symmetry group. Here c is a **constant** (in fact, a *unitary constant*). The only modes that transform in this way are the 4 modes $\Gamma_1 - \Gamma_4$. One can show that no other linear combination of the 10 modes will do. We reach therefore the following surprising conclusion:

The non-degenerate modes of our molecule must transform as one of the four modes $\Gamma_1 - \Gamma_4$. Since there are no other modes with these transformation properties, $\Gamma_1 - \Gamma_4$ must be normal modes!

- We reached this conclusion absolutely for free, without any knowledge of the potential. Moreover, once we know the pattern of distortions and the spring constants, it is very easy to find out the frequency of vibration of each of the modes. This is explained in some detail in the extended version of the notes, but basically what one does is to equate the **potential energy of the molecule at maximum mode amplitude (stretch)** with its **kinetic energy at zero stretch** (a bit of extra care is required if the modes have complex coefficients, i.e., complex phase factors the different atoms). The frequency of mode Γ_4 is zero by inspection (it is a pure rotation of the whole molecule).

- Normal modes with degeneracy *other than 1* are associated with irreducible mode multiplets, such as modes I-IV and the modes of the central atom. The symmetry analysis fully determines the mode degeneracy: here, only doublets are possible, since Γ_5 acts on a 2D mode space. The normal modes with non-zero energy for a spring potential (as shown in fig 1) are depicted in fig. 5 (more on the extend version of the handouts).

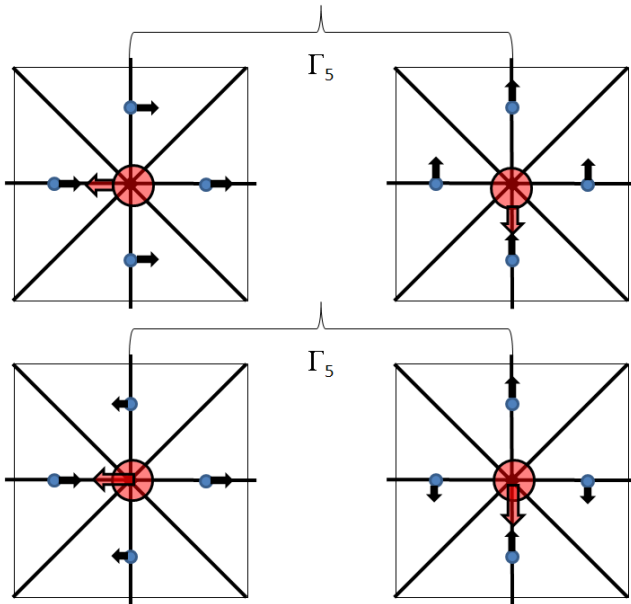


Figure 5: Examples of non-zero-frequency normal modes of Γ_5 symmetry involving two-atom displacements. The exact mixing coefficient depend on the mass and spring constant parameters.

1.3 Extended lattices: phonons and the Bloch theorem

- We now want to apply similar considerations in the presence of a **lattice**, i.e., of *translational symmetry*. As a simple case, we can think of the (previously isolated) molecules as being placed at the nodes of a primitive or centred lattice with the same symmetry as the molecule. Since the point group was $4mm$ (in 2D), we will obtain the plane (wallpaper) group $p4mm$. Likewise, in 3D, the point group is $4/mmm$ and the possible space groups $P4/mmm$ and $I4/mmm$.
- Starting from one of the previous modes, we can construct whole-lattice

(extended) **Bloch modes** as follows:

- ◇ Start from one of the previous modes applied to the molecule in unit cell 0, which we shall call $[u(0)]$.
- ◇ To all molecules located in unit cells at position lattice positions \mathbf{r}_i , we apply the following *complex* mode

$$[u(\mathbf{r}_i)] = [u(0)]e^{i\mathbf{k}\cdot\mathbf{r}_i} \quad (6)$$

- ◇ The vector \mathbf{k} is known as the **propagation vector** of the mode, and can be restricted to the *first Brillouin zone*. This is clear from the fact that an arbitrary propagation vector \mathbf{k} can be written as

$$\mathbf{k} = \boldsymbol{\tau} + \mathbf{k}' \quad (7)$$

Where $\boldsymbol{\tau}$ is a *RL* vector. However, $\boldsymbol{\tau}$ can always be omitted since $\mathbf{r}_i \cdot \boldsymbol{\tau} = 2\pi n$

- We can now show that the *translation operator* applied to one of the modes thus constructed is **equivalent to multiplying the mode by a constant** — this is completely analogous to one of the modes $\Gamma_1 - \Gamma_4$ described above for the isolated molecule. In fact, if one applies the lattice translation t (with translation vector \mathbf{t}) to the mode in eq. 6, one obtains

$$t[u(\mathbf{r}_i)] = e^{-i\mathbf{k}\cdot\mathbf{t}}[u(\mathbf{r}_i)] \quad (8)$$

This is shown graphically in fig. 6.

- These modes are *fully reduced* as far as the translations are concerned. Using the same reasoning as for the single molecule, one finds that **normal modes of a translationally invariant potential must have this Bloch form**. This is an elegant proof of the **Bloch theorem** (here, the classical analogue). Considerable effort is required to obtain fully reduced modes in the presence of rotations and translations.
- In the particular case we described:
 - ◇ The three zero-frequency modes of the single molecule will give rise to **acoustic modes**. All the other modes will be **optical**.
 - ◇ If no other spring constants are introduced, the energy of the modes will be unchanged. Springs *between* the “molecules” in different unit cells, will give rise to *dispersion*, i.e., the energy will depend on \mathbf{k} .

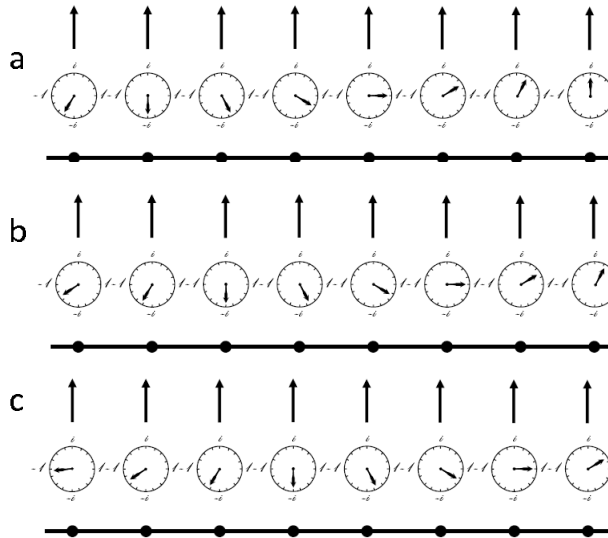


Figure 6: A simple example of a vector Bloch mode to illustrate the transformation properties of these modes upon translation. The arrows represent the *amplitude* of the mode (here a constant vector), while the clocks represent the *phases*. Mode (b) and (c) are the same as mode (a) translated by one or two unit cells to the *right*. However, they can also be obtained *multiplying* mode (a) by $\exp(ikR)$ where R is one or two lattice spacings for (b) and (c), respectively, and k is the **propagation or Bloch vector of the mode**.

1.3.1 Classical/Quantum analogy

- The examples above have been derived in a purely classical context. However, **there is complete analogy with the quantum mechanical case**, provided that the concept of “symmetry of the potential” is replaced with “symmetry of the Hamiltonian” and “symmetry of the modes” with “symmetry of the wave functions”.
- In complete analogy with the classical case one finds, for example, that **non-degenerate eigenstates must be fully reduced with respect to the symmetry group of the Hamiltonian** (i.e., a symmetry transformation must be equivalent to a multiplication by a complex scalar constant).
- Likewise, **the entire multiplet structure of a given Hamiltonian (how many multiplets of a given degeneracy) is entirely determined by symmetry, and is the same for Hamiltonians with the same symmetry**. The relative position of the multiplets, their energy levels and the wave functions are potential-dependent.

1.3.2 Inversion and parity

- **Inversion** is a special symmetry operation: it always commutes with all other rotations/reflections and forms a group of two elements with the identity.
- It is possible to show that in **centrosymmetric crystals** (i.e., those possessing the inversion as a symmetry element) **all solutions of the Schroedinger and normal-mode equations have a definite parity** — in other words, transform either into themselves (even-parity or “gerade” solutions) or into *minus* themselves (odd-parity or “ungerade” solutions) by inversion. As we shall see, this is important in determining the Infrared and Raman selection rules.

1.4 Experimental techniques using light as a probe: “Infra-Red” and “Raman”

- Optical techniques are extremely useful to determine vibration frequencies in molecules, as well as phonon frequencies in solids. Here, we will briefly introduce two techniques — **Infrared (IR) absorption/reflection** and **Raman scattering**.
- IR spectroscopy is performed by measuring the *absorption* or *reflection* of infra-red radiation (the latter exploiting the fact that reflectivity contains information about absorption). In the more “direct” absorption process, a photon is completely absorbed and a *phonon* is created instead (fig. 7 a).
- Raman scattering is a “photon-in-photon-out” technique, where one measures the *wavelength change of visible light* as a phonon is created or annihilated (fig. 7 b). Typical values of the incident energy and wave-vector are:

$$\begin{array}{ll} \text{IR} & \hbar\omega \sim 10 - 100 \text{ meV} \\ & \frac{1}{\lambda} \sim 10^3 \text{ cm}^{-1} \\ \text{Raman} & \hbar\omega \sim 1 - 10 \text{ eV} \\ & \frac{1}{\lambda} \sim 10^5 \text{ cm}^{-1} \end{array} \quad (9)$$

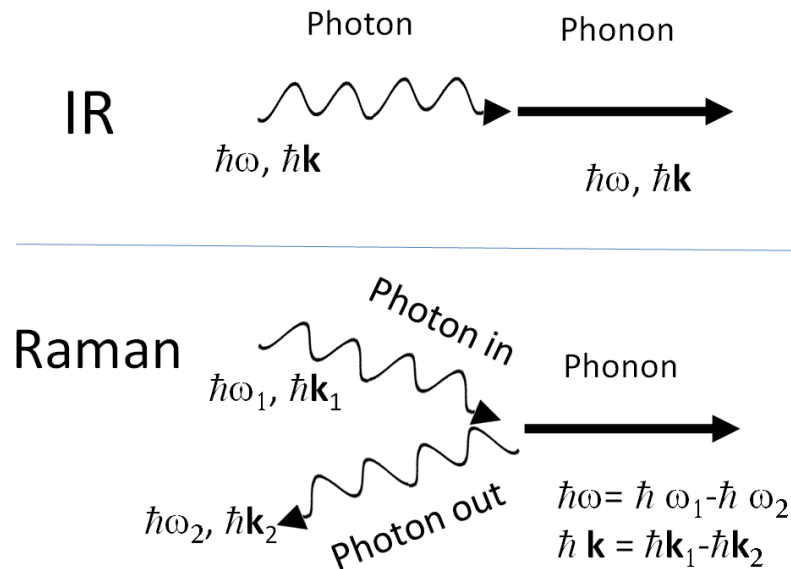


Figure 7: Diagrammatic representation of the IR and Raman scattering processes in a crystalline material, illustrating the energy and momentum conservation. For a molecule, the recoil of the molecule itself ensures conservation of momentum.

1.4.1 IR absorption and reflection

- The following results can be obtained by analysing the *Classical Dipole Oscillator Model* (see also Optical Properties part of C3 course):
 - ◊ The reflectivity R of a material contains information about both refractive index n and absorption coefficient α .
 - ◊ Near a resonance, both R and n become **anomalous**, and show a **peak** at the resonant energy.
 - ◊ The width of the peak is related to the width (sharpness) of the resonance (the “ γ ” damping coefficient, which you might have encountered already).
- An example of an absorption spectrum for a the Vanillin molecule is shown in fig 8.
- Typical vibration frequencies in molecules and *optical* phonon frequencies in solids (see here below) are of the order of several THz ($1000 \text{ cm}^{-1} = 30 \text{ THz}$), which falls in the IR region of the electromagnetic spectrum.
- It is the displacement of oscillating dipoles that causes the polarisation. In other words, in order for a resonance to cause a IR anomaly, the vibration of phonon modes *must generate oscillating electrical dipoles*.

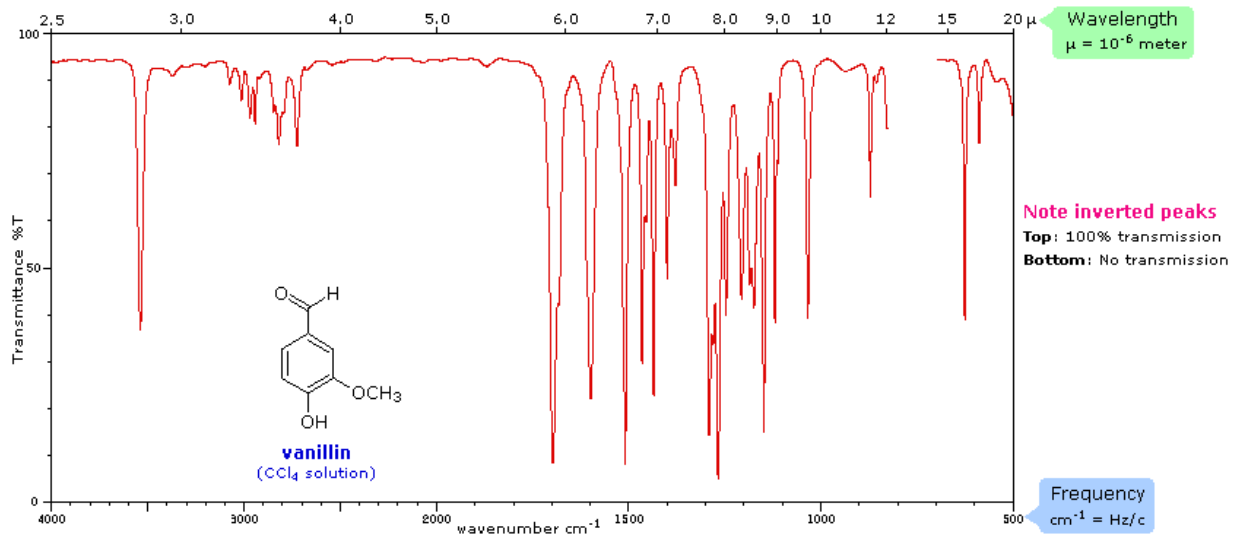


Figure 8: The IR transmission (1/absorption) spectrum of the vanillin molecule. Note the sharp peaks where the IR light is strongly absorbed by the molecular vibration modes.

- The momentum of the electromagnetic radiation, $h\nu/c$, is much smaller than that of typical phonons, except for phonons very near the zone centre. On the other hand, the frequency of near-zone-centre *acoustic* phonons is much too low to be accessed with this method. Therefore, in extended solids, IR spectroscopy *essentially probes zone-centre optical phonons*.
- IR absorption at low temperatures can be calculated using the **Fermi Golden Rule**, where the *initial state* ψ_i has zero phonons, while the *final state* ψ_f has one phonon.

$$T_{i \rightarrow f} = 2\pi/\hbar |\langle \psi_f | H' | \psi_i \rangle|^2 \rho = T_{i \rightarrow f} = 2\pi/\hbar |\mathbf{E} \cdot \langle \psi_f | \mathbf{u} | \psi_i \rangle|^2 \rho \quad (10)$$

since the perturbing Hamiltonian is $H' = -\mathbf{E} \cdot \mathbf{u}$ where \mathbf{u} is the **dipole operator** $\mathbf{u} = \sum_n q_n \mathbf{r}_n$, the summation running over all the atoms in the crystal.

- Since a dipole moment is parity-odd (i.e., it change sign upon inversion) only parity-odd modes (i.e., modes that are antisymmetric by inversion) can be “IR active”. This is true both for *centrosymmetric molecules* and for *centrosymmetric crystals*, since in both cases phonons can also be classified as parity-even and parity-odd.
- For *non-centrosymmetric molecules* and *non-centrosymmetric crystals*, phonons **cannot** also be classified as parity-even and parity-odd, and the matrix element in eq. 10 is in general non-zero (i.e., all modes are IR active).

1.5 Raman scattering

- In extended solids, **inelastic light scattering** techniques can be used to measure both *acoustic* and *optical* phonons. Inelastic light scattering via acoustic phonons is known as **Brillouin scattering** — a technique that is perhaps more often applied to liquids. Inelastic light scattering via molecular vibrations or optical phonons is known as **Raman scattering**. In both cases, the previous considerations apply and the phonons probed optically are those very near the zone centre.
- The mechanism giving rise to Raman scattering involves a **change in the polarisability** of the molecule or crystal as it vibrates, which generates alternative selection rules to the IR process. This can be seen classically as follows: the polarisation vector inside the material at a given position \mathbf{r} and time t can be written as:

$$\begin{aligned} \mathbf{P}(t, \mathbf{r}) &= \overline{\overline{\alpha}} \mathbf{E} e^{i(\mathbf{k}_0 \mathbf{r} - \omega_0 t)} + c.c. \\ \overline{\overline{\alpha}} &= \overline{\overline{\alpha}}_0 + \sum_i \overline{\overline{\alpha}}_i Q_i e^{i(\mathbf{k}_i \mathbf{r} - \omega_i t)} + \dots + c.c. \end{aligned} \quad (11)$$

- In eq. 11 \mathbf{k}_0 and ω_0 are the wavevector and frequency of the electric field and \mathbf{k}_i and ω_i are the values for normal mode i having amplitude Q_i . The quantities $\overline{\overline{\alpha}}_0$ and $\overline{\overline{\alpha}}_i$ are components of the **polarisability tensor**, since, in general, \mathbf{P} is not parallel to \mathbf{E} . Importantly, all the $\overline{\overline{\alpha}}$'s are **properties of the crystal, and must have the full symmetry of the crystal**.

By combining the two expressions in eq. 11 we obtain

$$\mathbf{P}(t, \mathbf{r}) = \overline{\overline{\alpha}}_0 \mathbf{E} e^{i(\mathbf{k}_0 \mathbf{r} - \omega_0 t)} + \sum_i \overline{\overline{\alpha}}_i Q_i \mathbf{E} e^{i[(\mathbf{k}_0 \pm \mathbf{k}_i) \mathbf{r} - (\omega_0 \pm \omega_i) t]} + \dots + c.c. \quad (12)$$

- From eq. 12 that the polarisation vibrates with three distinct frequencies: that of the original photon and those shifted upwards or downwards by the phonon frequency.
- Once again, we remind that the $\overline{\overline{\alpha}}$'s **must have the full symmetry of the molecule or crystal. In the case of a centrosymmetric molecule or crystal, they must be parity-even for a centrosymmetric system**. Both \mathbf{P} and \mathbf{E} are parity-odd, so **the phonon or vibration must be parity-even** (inversion-symmetric).

1.6 Inelastic neutron scattering

- Inelastic neutron scattering (INS) is another powerful technique to measure molecular and lattice vibrations. In this case, the probe is a thermal neutron, and one measures the change in energy and momentum of the scattered neutron. This process is illustrated in diagrammatic form in fig. 9 for a crystal. For a molecule, as in the case of IR and Raman scattering, conservation of momentum is ensured by the recoil motion of the molecule itself.

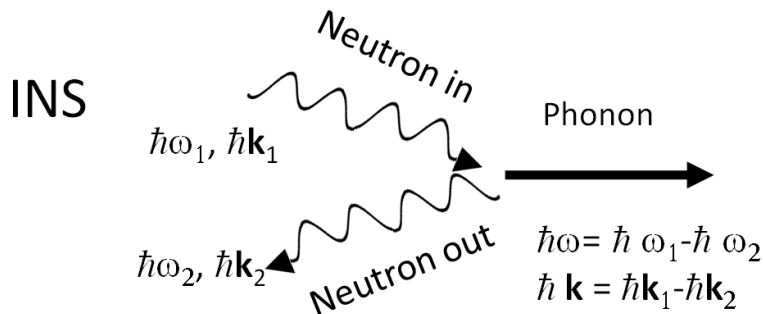


Figure 9: Diagrammatic representation of the inelastic neutron scattering process (INS) in a crystalline material, illustrating the energy and momentum conservation. For a molecule, the recoil of the molecule itself ensures conservation of momentum.

- Typical neutron parameters employed for INS are

$$\begin{aligned} \text{INS} \quad \hbar\omega &\sim 10 - 400 \text{ meV} \\ \frac{1}{\lambda} &\sim 10^7 - 10^9 \text{ cm}^{-1} \end{aligned} \tag{13}$$

- As we can see by comparing with eq. 9, the neutron and IR energies are comparable, but the **neutron wavenumber (momentum) is much larger**, enabling one to access several Brillouin zones. The main advantages of INS over IR and Raman are in fact
 - ◇ The range and momentum is much extended.
 - ◇ There are no selection rules, so all phonon modes can be accessed at the same time.

- The most popular neutron instrument used to measure phonons in crystal is known as a **triple-axis spectrometer** (fig. 10). By varying the monochromator, sample, analysed and detector angle one can explore a vast say of the energy-momentum space.

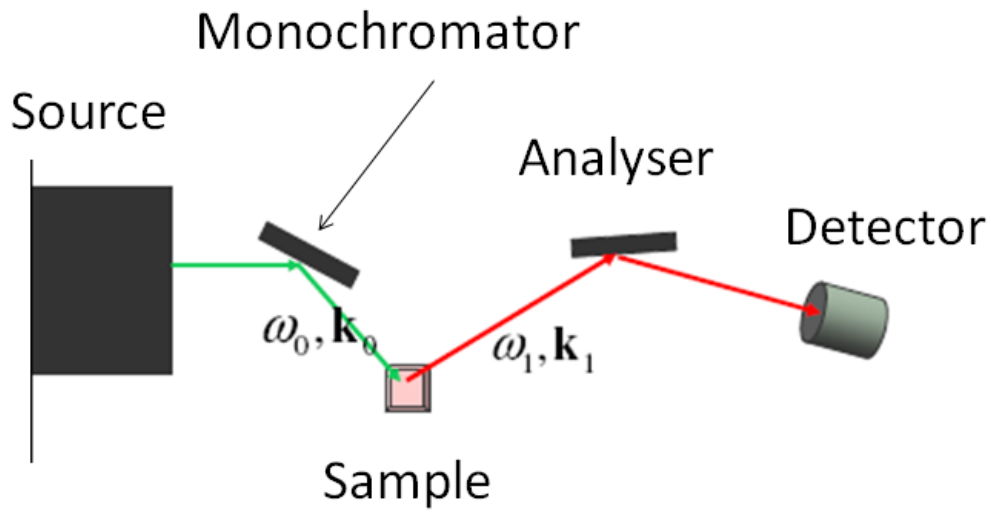


Figure 10: Schematic drawing of a “triple-axis” spectrometer.

2 Lecture 9 — Anharmonic effects in crystals

- Several important phenomena in crystals cannot be explained by assuming that atomic vibrations are harmonic. In particular, **thermal expansion is zero**, and **the temperature dependence of the phonon thermal conductivity is completely incorrect** in the harmonic approximation.
- The result on **thermal expansion** can be obtained by purely classical thermodynamic considerations. We will demonstrate this first to illustrate the general importance of anharmonicity.
- Explaining **phonon thermal conductivity** requires to introduce the principle of **conservation of crystal momentum**.

2.1 Thermal expansion

- The equilibrium state for a solid (e.g., at ambient pressure) is reached when the external pressure exactly balances the volume derivative of the free energy at a given temperature:

$$P = - \left(\frac{\partial F}{\partial V} \right)_T \quad (14)$$

where F is the Helmholtz free energy given by

$$F = U - TS \quad (15)$$

- The Helmholtz free energy of an insulator has two contributions:
 - ◇ The equilibrium energy U_0 of the crystal lattice, i.e., the energy of the “springs” in their equilibrium positions. By definition, $P_0 = \frac{\partial U_0}{\partial V}$ is *temperature independent*:

$$\frac{\partial P_0}{\partial T} = \frac{\partial^2 U_0}{\partial V \partial T} = 0 \quad (16)$$

- ◇ The energy and entropy term for the **phonon system**. The volume derivative of this part of the Helmholtz free energy can be considered to be the **pressure of the phonon gas** P_{ph} .
- The calculation of P_{ph} in the general case (including anharmonicity) is not difficult but is rather lengthy, and is reported in the extra material. Here, we will assume the result as given:

$$P_{ph} = -\frac{\partial}{\partial V} \left[\frac{1}{2} \sum_{\mathbf{k},s} \hbar\omega_s(\mathbf{k}) \right] + \sum_{\mathbf{k},s} \left(-\hbar \frac{\partial\omega_s(\mathbf{k})}{\partial V} \right) \frac{1}{e^{\beta\hbar\omega_s(\mathbf{k})} - 1} \quad (17)$$

- We can proceed with the derivation of the **linear thermal expansion coefficient** — by definition:

$$\alpha = \frac{1}{3V} \left(\frac{\partial V}{\partial T} \right)_P = -\frac{1}{3V} \frac{(\partial P/\partial T)_V}{(\partial P/\partial V)_T} \quad (18)$$

where the right side of eq. 18 is obtained by recognising that T , P and V are linked by the **equation of state**,

$$f(T, P, V) = 0 \quad (19)$$

taking the *total* derivatives with respect to each variable and solving the resulting determinant equation.

Using the definition of the **bulk modulus** (inverse compressibility):

$$B = -V (\partial P/\partial V)_T \quad (20)$$

eq. 18 becomes:

$$\alpha = \frac{1}{3B} \left(\frac{\partial P}{\partial T} \right)_V = \frac{1}{3B} \left(\frac{\partial P_{ph}}{\partial T} \right)_V \quad (21)$$

where we have used eq. 16.

- The first term is the volume derivative of the zero-point energy; it is **temperature independent** and can be ignored for the calculation of the thermal expansion coefficient.
- The second term depends on temperature through the phonon population $n_s(\mathbf{k}) = (\exp(\beta\hbar\omega_s(\mathbf{k})) - 1)^{-1}$, but **is non-zero only if at least some the phonon frequencies depend on volume**.
- In analogy with case of the single oscillator, we can conclude that:

If the lattice potential is harmonic, the phonon frequencies are volume-independent, and the thermal expansion coefficient is zero at all temperatures.

- it is therefore necessary to go beyond the harmonic approximation to explain why materials expand (or contract) when heated. We can write

$$\alpha = \frac{1}{3B} \sum_{\mathbf{k},s} \left(-\frac{\partial \hbar\omega_s(\mathbf{k})}{\partial V} \right) \frac{\partial}{\partial T} n_s(\mathbf{k}) \quad (22)$$

- Remembering the expression for the specific heat:

$$c_V = \sum_{\mathbf{k},s} \frac{\hbar\omega_s(\mathbf{k})}{V} \frac{\partial}{\partial T} n_s(\mathbf{k}) \quad (23)$$

- it is natural to define the **contribution to individual phonon modes to the specific heat**:

$$c_{vs}(\mathbf{k}) = \frac{\hbar\omega_s(\mathbf{k})}{V} \frac{\partial}{\partial T} n_s(\mathbf{k}) \quad (24)$$

the so-called **partial Grüneisen parameter** — related to the anharmonicity of individual phonons:

$$\gamma_{ks} = -\frac{V}{\omega_s(\mathbf{k})} \frac{\partial \omega_s(\mathbf{k})}{\partial V} = -\frac{\partial(\ln \omega_s(\mathbf{k}))}{\partial(\ln V)} \quad (25)$$

and the **overall Grüneisen parameter**

$$\gamma = \frac{\sum_{\mathbf{k},s} c_{vs}(\mathbf{k}) \gamma_{ks}}{\sum_{\mathbf{k},s} c_{vs}(\mathbf{k})} \quad (26)$$

With these definitions, the thermal expansion coefficient is written as

$$\alpha = \frac{\gamma c_v}{3B} \quad (27)$$

Note that γ is **dimensionless**, and for typical materials is **positive** (springs become stiffer as the volume is reduced) and is usually of the order of unity, although it can be much larger and sometimes *negative* in special cases.

2.1.1 Thermal expansion in metals

- The previous derivation of the thermal expansion coefficient only strictly applied to insulators, since it only took into account the pressure of the phonon gas. It is natural to extend this to metals by including the pressure of the electron gas. It is an elementary result of the Sommerfeld theory of metals that:

$$\begin{aligned} P_{el} &= \frac{2}{3} \frac{U_{el}}{V} \\ \left(\frac{\partial P_{el}}{\partial T} \right)_V &= \frac{2}{3} c_v^{el} \end{aligned} \quad (28)$$

- The complete expression of the linear thermal expansion coefficient is therefore

$$\alpha = \frac{1}{3B} \left(\gamma c_v^{ph} + \frac{2}{3} c_v^{el} \right) \quad (29)$$

- In assessing the relative importance of the two terms, it is important to remember that typically $\gamma \approx 1$ and that, in the Debye model:

$$\frac{c_v^{el}}{c_v^{ph}} = \frac{5}{24\pi^2} Z \frac{\Theta_D^3}{T^2 T_F} \quad (30)$$

where Z is the nominal valence of the metal.

- When evaluated numerically, eq. 30 leads to the conclusion that the pressure of the electron gas contributes significantly to the thermal expansion only below $\sim 10K$. The main difference in the thermal expansion of insulators and metals is therefore in the low-temperature behaviour: $\propto T^3$ for insulators, $\propto T$ for metals.

2.2 Conservation of crystal momentum

- In order to describe thermal conductivity, we need to employ the concept of *crystal momentum*. This is also necessary to understand scattering experiments. You will have seen this already in previous courses, but a reminder is included here, using a symmetry-based approach (see also extended version of the notes).

- The following are results that can be obtained from the applications of elementary quantum mechanics:
 - ◊ In quantum mechanics, a *symmetry operator* is a **unitary operator in Hilbert space** ($\hat{O}^\dagger \hat{O} = 1$).
 - ◊ If the Hamiltonian has a certain symmetry group, then it **commutes** with all the corresponding symmetry operators, and has a common set of basis vectors with them.
 - ◊ For all *unitary* operators \hat{O} , there exist a *Hermitian* operator \hat{A} ($\hat{A}^\dagger = \hat{A}$) so that $\hat{O} = e^{i\hat{A}}$.
 - ◊ If \hat{O} is an **infinitesimal symmetry**, then the corresponding Hermitian operator \hat{A} **commutes with the Hamiltonian** (it represent a **conserved quantity**). This is a statement of Noether Theorem.
- When applied to infinitesimal translations, Noether Theorem famously results in the **conservation of real momentum**. Once considering the system as composed by the crystal, its excitations and any external particles (in a scattering process), real momentum is always conserved.
- When considering the crystal as a **fixed potential**, translational symmetry is only **discrete** (by units of lattice translations). Therefore, Noether Theorem does not apply and **real momentum is not conserved**. This is clear, since excitations and external particles can exchange real momentum **with the crystal**, and their real momentum is not conserved overall.
- However, operators of the form

$$\hat{T}_{\mathbf{R}} = e^{i\frac{1}{\hbar}\hat{\mathcal{K}}\cdot\mathbf{R}} \quad (31)$$

where \mathbf{R} is a lattice translation **still commute with the Hamiltonian**. Moreover, this is true of all lattice translations. We will call $\hat{\mathcal{K}}$ the **crystal momentum operator**.

- The consequence of this is that

$$\hbar\mathbf{K}_i = \hbar\mathbf{K}_f + \hbar\boldsymbol{\tau} \quad (32)$$

where $\hbar\mathbf{K}_i$ and $\hbar\mathbf{K}_f$ are the initial and final values of the crystal momentum. In other words, **crystal momentum is conserved to within \hbar times a reciprocal lattice vector**.

- The crystal momentum of Bloch eigenfunctions of the form $[u(\mathbf{r})]e^{i\mathbf{k}\cdot\mathbf{r}}$ is $\hbar\mathbf{k}$, so that

$$\hat{\mathcal{K}}u(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} = \hbar\mathbf{k}u(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \quad (33)$$

- The crystal momentum of an ensemble of Bloch states (even of different types, e.g., phonons and electrons) that are **not interacting** is $\hbar\sum_i \mathbf{k}_i$
- The crystal momentum of a particle far away from the crystal (e.g., before or after the scattering process) is the same as its real momentum.
- Energy is **always conserved exactly** (the energy transferred to the crystal as a whole is always negligible).

Normal processes conserve real momentum exactly. In an *umklapp* process, the additive term $\hbar\tau$ corresponds to real momentum transferred to the center of mass of the crystal.

2.3 Heat transport theory

- All transport phenomena (mass transport, charge transport, spin transport, heat transport) are **non-equilibrium, steady state phenomena**, and they are characterised by a **quantity that is being transported**, say Q , and a **transport speed** v .
- One defines a **current** as $j = (Q/V)v$ where V is the volume. For example, for charge transport the transported quantity is electric charge, so $Q/V = -en_e$ and the transport speed is the drift velocity $v_d = -eE\tau/m^*$, so that $j_e = e^2n_e\tau/m^* E$.
- The conductivity (in this case, the electrical conductivity) is the ratio of the current and the “driving parameter” (E in this case).
- For thermal transport, the transported quantity is heat (or entropy) and the velocity is that of the particles that transport the entropy.
- Whereas an electron retains its charge after a collision, **a particle releases its entropy when it reaches thermal equilibrium through collisions** (not all collisions are capable of this).
- Let us look at the scheme shown in fig. 11 (typical phonon mean free paths at RT are a few tens of nm). The entropy per unit volume at each point is given by:

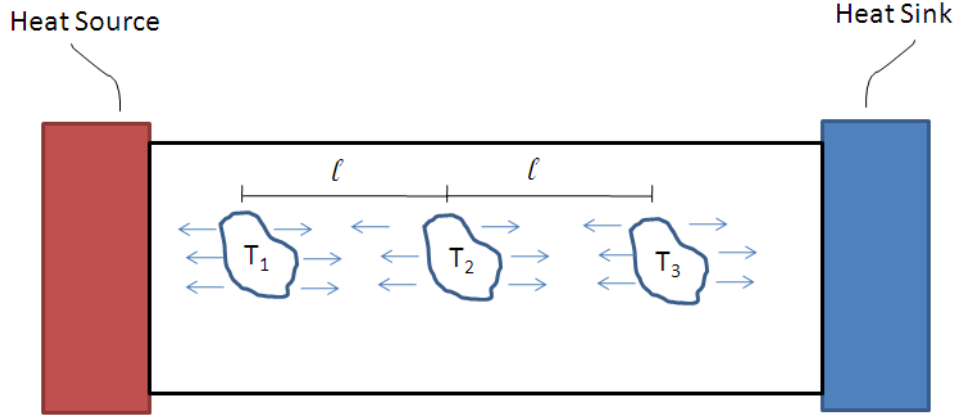


Figure 11: Schematic representation of thermal transport.

$$s = \int_0^T dT \frac{c_v}{T} \quad (34)$$

The entropy balance at the mid position T_2 is given by the entropy flowing *in* the domain and released therein minus that flowing *out*:

$$\begin{aligned} \Delta s_{in} &= \frac{1}{2}(s_1 + s_3) \\ \Delta s_{out} &= s_2 \\ \Delta s_{tot} &= \frac{1}{2} \frac{c_v}{T} (T_1 - T_3) = \frac{c_v}{T} \ell_x \nabla T \end{aligned} \quad (35)$$

where ℓ_x is the mean free path projected along the direction of the gradient. The transported quantity is the heat transfer per unit volume

$$\frac{Q}{V} = c_v \ell_x \nabla T \quad (36)$$

while the relevant velocity is the projection c_x of the phonon (sound) velocity c along the x direction. In order to obtain the thermal conductivity, we need to average the expression $c_x \ell_x = c \ell \cos^2 \theta$ over the hemisphere in the direction of the gradient (θ is the angle between the phonon velocity and the x axis). It is a simple calculation to show that this average is $\ell c/3$.

- We have made the approximation that the average velocities do not depend on temperature, which is about (but not exactly) correct for both phonons and electrons (but, of course, would be very wrong for bosons with a mass). Our discussion is summarised in tab. 2

Table 2: Various parameters relevant to thermal and electrical transport.

| Transport | Transported quantity | Velocity | Current | Conductivity |
|------------------|--------------------------|---------------|-----------------------------------------|----------------------------------------------|
| Electrical | $-en_e$ | $-eE\tau/m^*$ | $e^2n_e\tau/m^* E$ | $\sigma = e^2n_e\tau/m^*$ |
| Phonon Thermal | $c_v^{ph} \ell \nabla T$ | $c/3$ | $\frac{1}{3}c_v^{ph} \ell c \nabla T$ | $\kappa^{ph} = \frac{1}{3}c_v^{ph} \ell c$ |
| Electron Thermal | $c_v^{el} \ell \nabla T$ | $v_F/3$ | $\frac{1}{3}c_v^{el} \ell v_F \nabla T$ | $\kappa^{el} = \frac{1}{3}c_v^{el} \ell v_F$ |

- The mean free path ℓ and the relaxation time τ in eq 2 have in general a complex temperature dependence, making exact theory of transport a very difficult problem. However, we can write:

$$\ell = (n_s \Sigma)^{-1} \quad (37)$$

where n_s is the density of scatterers and Σ is the scattering cross section; this simply shifts the problem to determining the temperature (or energy) dependence of the cross section.

- Note that, in the free electron model

$$c_v^{el} = n_e k_B \frac{\pi^2}{2} \left(\frac{k_B T}{\mathcal{E}_F} \right) = n_e k_B \pi^2 \left(\frac{k_B T}{m^* v_F^2} \right) \quad (38)$$

and $\ell = v_F \tau$, so the electronic thermal conductivity becomes:

$$\kappa^{el} = \frac{n_e \tau \pi^2}{m^* 3} k_B^2 T \quad (39)$$

whence the famous **Wiedemann-Franz law**:

$$\kappa^{el} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 T \sigma \quad (40)$$

2.4 Thermal conductivity due to phonons

- In a perfect crystal, harmonic phonons would propagate without hindrance as free particles; furthermore, in an insulator, we have removed the possibility for them to scatter off electrons. We would therefore conclude that phonons can only be scattered by **crystal imperfections**, i.e., defects and, ultimately, the surfaces of the crystal themselves.

- In both cases, **real momentum is transferred between the phonons and the crystal as a whole**. These collisions are therefore efficient in thermalising the phonon energy distribution and therefore in transferring entropy.
- Taking Σ as a constant in eq. 37, we can as a first approximation write $\ell \propto 1/n_d$, n_d being the defect density. If n_d is very small, ℓ is eventually limited by the crystal size. In either case, **the harmonic approximation predicts that the phonon thermal conductivity should be proportional to the phonon specific heat**, that is, $\propto T^3$ at least up to temperatures where the optical phonons become important. In most materials, the relation $\kappa^{ph} \propto T^3$ should therefore hold in a wide domain up to a significant fraction of the Debye temperature.
- The relation $\kappa^{ph} \propto T^3$ is indeed obeyed at very low temperatures (typically to $\sim 10K$), but **the lattice thermal conductivity drops rather abruptly above this temperature**. This is exemplified in fig. 12.
- The crystals employed in the Thacher experiment (fig. 12) were very pure, so that the scattering from defects was negligible. Therefore, at low temperatures, we can clearly see the effect of crystal size, which determines the mean free path ℓ . In assessing the data, we have to acknowledge that, above $\sim 10K$ something starts scattering the phonons more than the crystal boundaries, and this can be nothing other than other phonons.
- In the harmonic approximation, phonons have infinite lifetime and do not scatter off each other. Phonon-phonon scattering is an intrinsically **inelastic process**. 3- and 4- phonon processes are depicted in fig. 13.
- The assumption $l^{ph} \propto (\Sigma_{ph} n^{ph})^{-1}$, would seem logical, but would give a completely wrong temperature dependence. In fact, in the Debye model, the low-temperature phonon density scales like T^3 (like the specific heat), so we would get $c_v^{ph} l^{ph} = const.$ **We should therefore expect the thermal conductivity to saturate at the point where the phonon mean free path becomes smaller than the crystal size.**
- One way to reproduce the data is to introduce a **low-energy cutoff** for the phonons that contribute to reducing the mean free path. Phonons below this energy cut-off will be ineffective. This amounts to introduce a “density of effective phonons” (effective in reducing the mean free path). The total and “effective” phonon densities in the Debye model are:

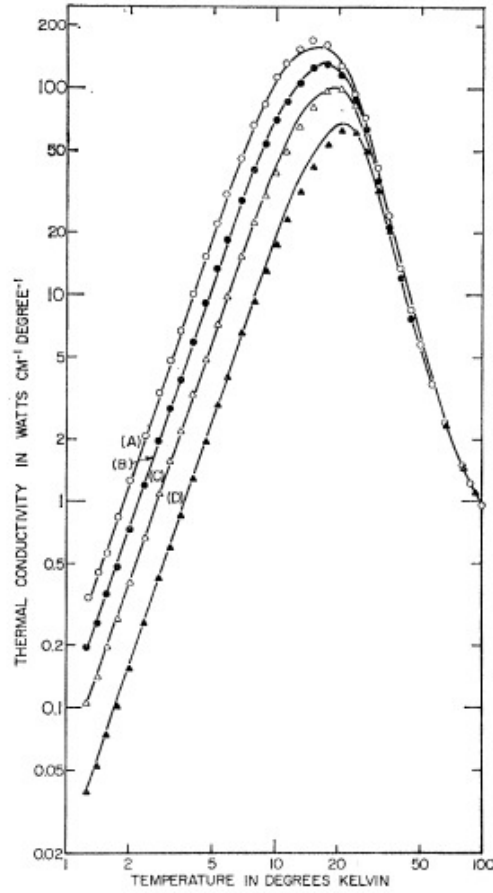


Figure 12: Thermal conductivity of isotopically pure LiF. The different curves at low temperatures correspond to different crystal sizes: (A) 7.25 mm, (B) 4.00 mm (C) 2.14 mm and (D) 1.06 mm. The figure is the same as in Ashcroft and Mermin, and is reproduced from P.D. Thacher, Phys. Rev. **156**, 957 (1967).

$$\begin{aligned}
 n^{ph} &= 3n \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} dx \frac{x^2}{e^x - 1} \\
 n_{eff}^{ph} &= 3n \left(\frac{T}{\Theta_D} \right)^3 \int_{\Theta_C/T}^{\Theta_D/T} dx \frac{x^2}{e^x - 1}
 \end{aligned}
 \tag{41}$$

where Θ_C is the cut-off temperature, and, as we shall see, is a significant fraction of room temperature.

- At low temperatures, $x \gg 1$ and we can ignore the additive term -1 in the denominator and the terms with $e^{-\Theta_D/T}$ as a pre-factor in the integral; we obtain

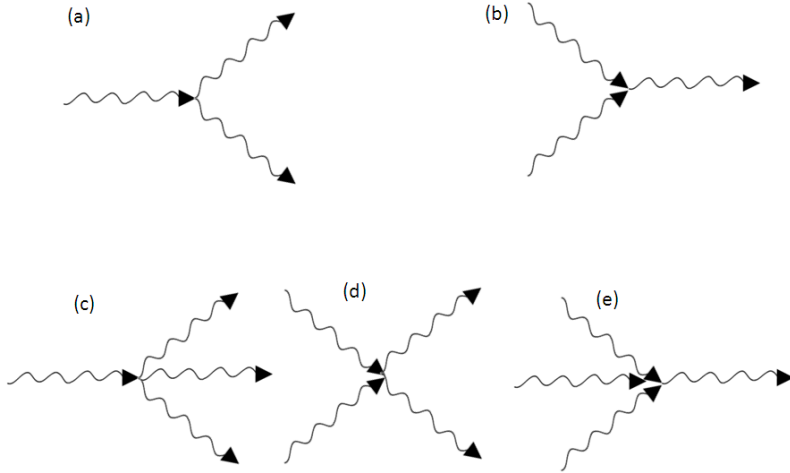


Figure 13: Multi-phonon processes enabled by cubic — (a) and (b)— and quartic —(c), (d) and (f) — terms in the Hamiltonian.

$$n_{eff}^{ph} \approx 3n \left(\frac{T}{\Theta_D} \right)^3 e^{-\Theta_C/T} \left((\Theta_C/T)^2 + 2(\Theta_C/T) + 2 \right) \approx 3n \left(\frac{\Theta_C^2}{\Theta_D^3} \right) T e^{-\Theta_C/T} \quad (42)$$

In other words

With the introduction of a cut-off frequency, the number of “effective” phonons grows exponentially with temperature in the relevant low-temperature range.

- These results and the last general statement in particular, can be understood by the fact that

Only unklapp processes can bring about the release of entropy and the attainment of thermal equilibrium.

This can be simply understood by looking again at the diagram in fig. 11. Phonons that transfer entropy from T_1 to T_2 will carry a net crystal momentum, whereas phonons in thermal equilibrium will have $\sum_i \mathbf{k}_i = 0$

Since normal processes conserve real momentum exactly, they can never restore a thermal equilibrium configuration of crystal momenta.

- The low-energy cut-off arises naturally from the fact that only unklapp processes can reduce the mean free path. In fact, simple kinematics accounting for the simultaneous energy and crystal momentum conservation (the latter to within a non-zero RL vector) imposes that

The crystal momentum of *all* the phonons involved in an umklapp process must be a significant fraction of a non-zero reciprocal lattice vector. This means also that their energy must be a significant fraction of the Debye energy.

3 Lecture 10 — Phase Transitions

3.1 Continuous and discontinuous phase transitions

- All phase transitions entail a change in the entropy of a system. We distinguish between:
 - ◊ **First-order (discontinuous) transitions:** 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**.
 - ◊ **Second-order (continuous) transitions:** 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.
- Phase transition lines can be crossed as a function of many parameters, for example temperature, pressure, chemical composition, magnetic or electric field etc.
- In some cases, phase transitions occur without a change in symmetry of the material — for example the vapour–liquid transitions. In other cases, there is a change of symmetry — for example, the liquid–crystalline solid transitions. Second-order transitions with symmetry changes are particularly important.
- The **low-temperature** phase usually has the **lowest symmetry**. The *symmetry group* of the low-temperature phase is usually a **subgroup** of that of the high-temperature phase.

3.2 Phase transitions as a result of symmetry breaking

- There is a close connection between the theory of normal modes and that of phase transitions resulting from symmetry breaking (first- or second-order). For a large class of crystallographic phase transitions, one employs the same decomposition in fully-reduced modes as for the construction of normal modes. For these phase transition:

- ◇ At the transition temperature T_c , a *single* fully-reduced normal mode becomes frozen in a given macroscopic part of the crystal (**domain**)—neither its symmetry-equivalent nor any symmetry-inequivalent modes freeze in that domain. The symmetry within that domain will be therefore *lowered* by that frozen mode.
 - ◇ Overall symmetry is restored because symmetry-equivalent modes freeze in **different domains**.
 - ◇ A phase transition of this kind is described by the *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.
- These phase transitions are called **displacive**, because they are described in terms of atomic displacements. Other phase transitions in crystals (particularly alloys), called **order-disorder**, are characterised by the **degree of chemical ordering** on each site, i.e., the positive or negative deviation from a random occupancy of each site by a certain atomic species. These phase transitions can also be described by *scalar* modes. **Magnetic phase transitions** are also usually described using vectors — in this case **axial vectors** .

3.3 Macroscopic quantities: the Neumann principle

- 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**.

3.3.1 Polarisation and ferroelectricity

- Macroscopic polarisation describes the overall electrical dipole moment of a crystal, resulting from the sum of microscopic electrical dipole moments. It is measured in C/m^2 . Ferroelectric 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 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 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.

3.3.2 Magnetisation and ferromagnetism

- The magnetisation 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).
- Ferromagnets cannot be truly cubic, since the direction of M in itself breaks the cubic symmetry. For example, iron is ferromagnetic with M in the $\langle 111 \rangle$ direction, and in the magnetic state one can measure a very slight rhombohedral distortion away from cubic — an effect known as **magnetostriction**.
- Many more crystals are **antiferromagnetic** without breaking crystal symmetries than what one may expect from simple symmetry considerations. This is because magnetic moments are **time-reversal-odd** (M can be thought as resulting of microscopic circulating currents), whereas the crystal structure is **time-reversal-even**. By including the reversal symmetries combined with ordinary operators, one can describe complex magnetic structures in highly-symmetric crystals.

3.4 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.
- 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, 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.

- In the Landau construction, one 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:

$$\mathcal{F} = \mathcal{F}_0 + \Delta\mathcal{F}(\eta^i) \quad (43)$$

where \mathcal{F}_0 does not depend on the order parameter, while $\Delta\mathcal{F}(\eta^i)$ is **small** in the vicinity of the phase transition.

- 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 .

- Since $\Delta\mathcal{F}$ is small one can perform a **Taylor expansion** of $\Delta\mathcal{F}(\eta^i)$ in powers of η^i . For each η^i , the expansion will look like:

$$\Delta\mathcal{F} = -\eta H + \frac{a}{2}\eta^2 + \frac{c}{3}\eta^3 + \frac{b}{4}\eta^4 + o(\eta^5) \quad (44)$$

- H is an external field. The term in H is only present for **ferroic transitions**.
- Note the absence of a linear term in η that does not contain H . This is because η must break at least some symmetry of the high-symmetry phase.
- If we look, for example, at the modes described in the top row of fig. 5, we find that:
 - ◊ The dipole moment of the molecule is $\eta' \mathbf{d}$, where \mathbf{d} is along x and y for the left and right mode, respectively. .
 - ◊ The linear terms for coupling with the electric field are $-\eta' d_x E_x$ and $-\eta' d_y E_y$.
 - ◊ We can now redefine the order parameter $\eta = d\eta'$ and get the form in eq. 44 .
- With this, we can define the **generalised polarisation**:

$$\mathcal{P} = -\frac{\partial \mathcal{F}}{\partial H} = \eta \quad (45)$$

- Note that some of the symmetry operators of the undistorted molecule transform the two modes into each other. This can be fully accounted for in a slightly more complex formulation.
- Note that some of the symmetry operators of the undistorted molecule transform the two modes into each other. This can be fully accounted for in a slightly more complex formulation of the Landau free energy.
- In order for the high-temperature phase to be stable, one must have $a > 0$ for $T > T_c$. Likewise, the phase transition can only occur if $a < 0$ for $T < T_c$.

In the Landau theory, phase transitions occur when the coefficient of the quadratic term in the order parameter expansion *changes sign* (from positive to negative, e.g., as a function of temperature). 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. *Only one fully reduced mode or several modes having the same transformation rules can drive the phase transition, so only one of the η^i is involved in a phase transition.*

- in many cases, cubic terms in η^3 are not allowed by symmetry. For example, in an expansion as in eq. 44, the cubic term (or any other odd-order term) would not be allowed if a transformation $\eta \rightarrow -\eta$ existed in the high-symmetry group.

- If the cubic term exists **it always force the transition to be first-order.**
See for this the analysis of the following paragraphs and in particular fig. 14

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.

- 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 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.**

3.5 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. 44 without the odd-order terms. 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.

$$\Delta\mathcal{F} = -\eta H + \frac{a}{2}\eta^2 + \frac{b}{4}\eta^4 + o(\eta^4) \quad (46)$$

3.5.1 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:

$$-H + a'(T - T_c)\eta + b\eta^3 = 0 \quad (47)$$

- In zero field, $\mathcal{P}(H = 0) = \eta(H = 0)$ is known as the **spontaneous generalised polarisation**. Eq. 47 has the simple solutions:

$$\begin{aligned}\eta &= 0 \\ \eta &= \pm \sqrt{\frac{a'}{b}}(T_c - T)^{\frac{1}{2}}\end{aligned}\quad (48)$$

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. 14

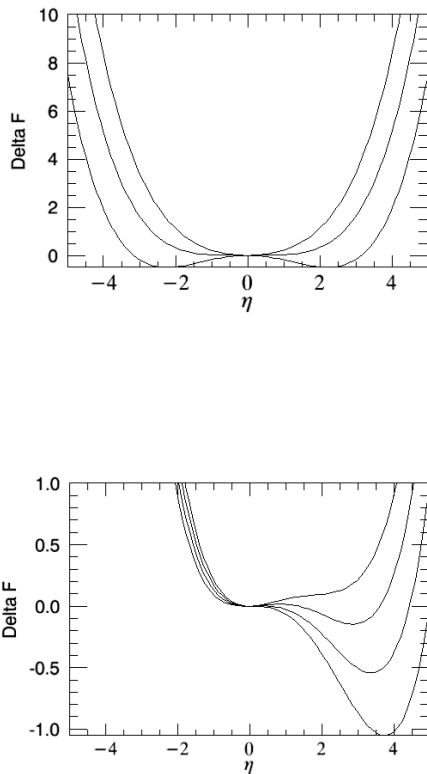


Figure 14: Two examples of the temperature dependence of the Landau free energy. **Top:** the simple form with quadratic and quartic terms produces a 2nd-order phase transition. **Bottom:** adding a cubic term produces a 1st-order phase transition.

The case $H \neq 0$ is analysed in details in the book by Landau; 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.**

3.5.2 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

$$\chi = \frac{\partial \mathcal{P}}{\partial H} = \frac{\partial \eta}{\partial H} \quad (49)$$

By differentiating eq. 44 with respect to H , one finds the general formula:

$$\chi^{-1} = \frac{\partial^2 \Delta \mathcal{F}}{\partial \eta^2} \quad (50)$$

which, in the specific case of eq. 46 yields:

$$\chi^{-1} = a'(T - T_c) + 3\eta^2 b \quad (51)$$

Eq. 51 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 :

$$\begin{aligned} \chi^{-1}(H = 0) &= a'(T - T_c) \quad \text{for } T > T_c \\ \chi^{-1}(H = 0) &= 2a'(T_c - T) \quad \text{for } T < T_c \end{aligned} \quad (52)$$

Note that **the zero-field susceptibility diverges at the critical temperature**. In fact, above T_c , eq. 52 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**.

3.5.3 The specific heat

It is easy to see that, within Landau theory, the entropy *below* the phase transition is:

$$\Delta S = S - S_0 = - \left. \frac{\partial \mathcal{F}}{\partial T} \right|_V = - \frac{a'^2}{2b} (T_c - T) \quad (53)$$

where S_0 is the component of the entropy not related to the phase transition.

$\Delta S = 0$ above T_c .

The specific heat is:

$$\Delta c_v|_{T < T_c} = -T \left. \frac{\partial^2 \mathcal{F}}{\partial T^2} \right|_V = \frac{a'^2}{2b} T \quad (54)$$

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.

3.6 Displacive transitions and soft modes

- Most displacive phase transitions have a dynamical character, and are caused by *softening and “freezing” of a particular phonon*.
- **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:

$$\omega^2 \propto \chi^{-1} \quad (55)$$

Eq. 55, combined with eq. 52, gives the temperature dependence of the soft phonon frequency.

- PbTiO_3 : a classic example of a displacive soft-mode transition. See the extended version for a full analysis of PbTiO_3 and the agreement of the experimental data with the linear Cochran relation.