LATTICE VIBRATIONS

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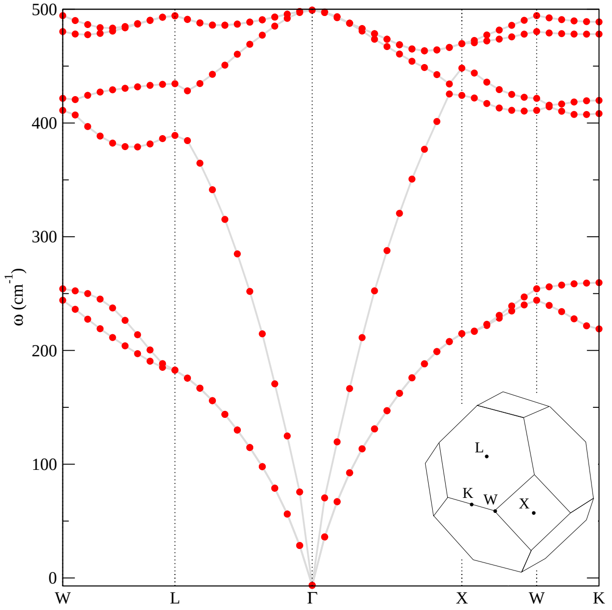
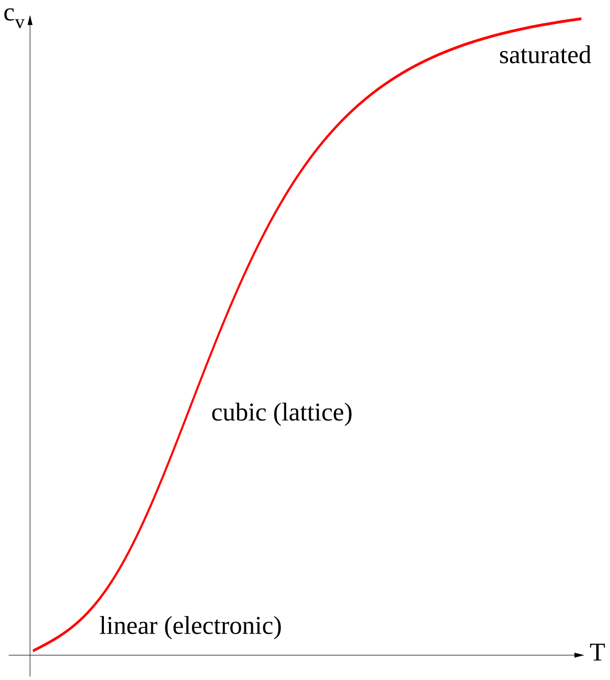


THE BREAKDOWN OF THE STATIC LATTICE MODEL

- The free electron model was refined by introducing a crystalline external potential
- This allows much progress, but is not the full story
- Ions are not infinitely massive, nor held in place by infinitely strong forces
- The classical static lattice can only be valid for T=0K
- It is even wrong for T=0K: $\Delta x \Delta p \geq \hbar \Rightarrow$ *Zero point motion*
- This is a particular problem for insulators: unless $k_B T > E_g$ there are no degrees of freedom to account for their many properties

EQUILIBRIUM PROPERTIES



- Specific heat of a metal:
    - the electronic degrees of freedom alone cannot explain experiment
- Density and cohesive energy
    - zero point motion is important for solid neon and argon, and dominant for solid helium (a *quantum solid*)
- Thermal expansion of insulators
    - electronic contribution negligible for $k_b T < E_g$

TRANSPORT PROPERTIES

- Conductivity
  - in a perfect metallic crystal there are no collisions and perfect conduction
  - lattice vibrations provide the scattering mechanisms
- Superconductivity
  - interaction between two electrons via lattice vibrations
  - no vibrations, no superconductors
- Thermal conductivity of insulators
  - the electronic degrees of freedom are not sufficient
- Transmission of sound
  - sound waves are carried by vibrations of the lattice

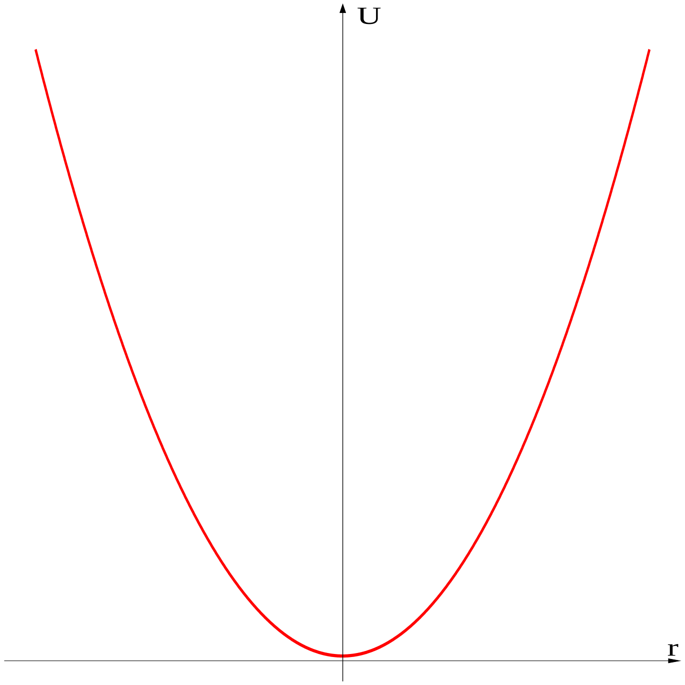
INTERACTION WITH RADIATION

- Reflectivity of ionic crystals
  - Sharp maximum in infrared, far below $\hbar\omega = E_g$
  - E-field applies opposite forces on ± ions
- Inelastic scattering of light
  - small frequency shifts (Brillouin or Raman scattering)
  - understood via lattice vibrations
- X-ray scattering
  - thermal vibrations and zero point motion diminish the intensity of the peaks
  - there is a background in directions not satisfying the Bragg condition
- Neutron scattering
  - momentum transfer with the lattice is discrete, and provides a probe of the lattice vibrations

A CLASSICAL THEORY OF THE HARMONIC CRYSTAL

- A general treatment of the deviation of ions from their equilibrium positions is intractable, so proceed in stages:
  1. Treat small deviations classically
  2. Proceed to a quantum theory
  3. Examine implications of larger movements
- To treat the small deviations, we assume each ion stays in the vicinity of its equilibrium position $\mathbf{R}$, and the Bravais lattice remains as an average of the instantaneous configurations
- Denote the position of an atom whose mean position is $\mathbf{R}$ by $\mathbf{r}(\mathbf{R})$: $\mathbf{r}(\mathbf{R}) = \mathbf{R} + \mathbf{u}(\mathbf{R})$
- The dynamics of the lattice is governed by the classical Hamiltonian: $\sum_{\mathbf{R}} \frac{\mathbf{P}(\mathbf{R})^{\mathbf{2}}}{2M} + U$

The Harmonic Approximation



- 3D Taylor expand the potential energy around the equilibrium configuration: $f(\mathbf{r}+\mathbf{a}) = f(\mathbf{r}) + \mathbf{a}\cdot\nabla f(\mathbf{r}) + \frac{1}{2}(\mathbf{a}\cdot\nabla)^2 f(\mathbf{r}) + O(a^3)$

- At equilibrium the net force is zero, and the potential energy is given by: $U = U^{\text{eq}} + U^{\text{harm}}$

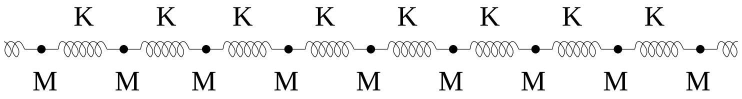
- The general form for U^{harm} is:

$$\boxed{U^{\text{harm}} = \frac{1}{2}\sum_{\mathbf{RR}',\mu\nu} u_\mu(\mathbf{R}) D_{\mu\nu}(\mathbf{R}-\mathbf{R}') u_\nu(\mathbf{R}')}$$

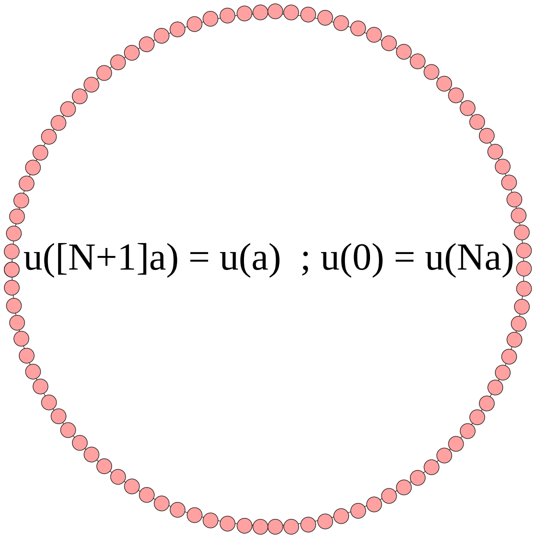
THE ADIABATIC APPROXIMATION

- The quantities D in the harmonic expansion are in general very difficult to calculate
- In ionic crystals the difficulties are the long ranged coulomb interactions
- In covalent/metallic crystals the difficulty comes from the fact that the contribution to the total energy of the valence electrons depends on the ionic configuration $\Rightarrow$ the wavefunctions change as the ions move
- Make the *adiabatic approximation* by separating the typical timescales of the motion of the electrons and ions
  - the electrons are in their groundstate for any configuration
- D is still difficult to calculate

Normal Modes of a 1D Bravais Lattice



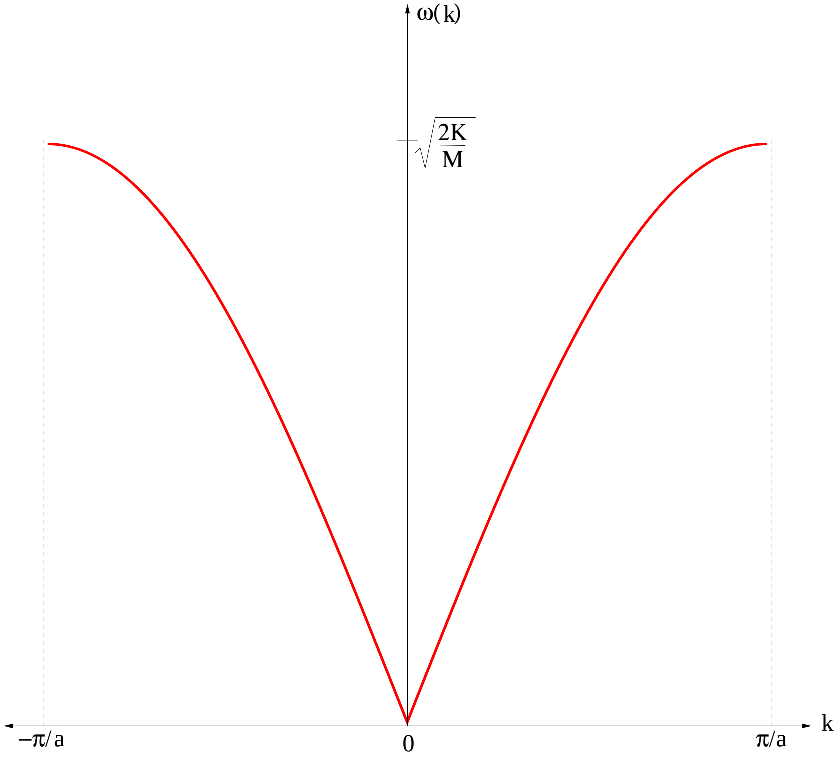
Masses M and springs K



Born-von Karman BCs

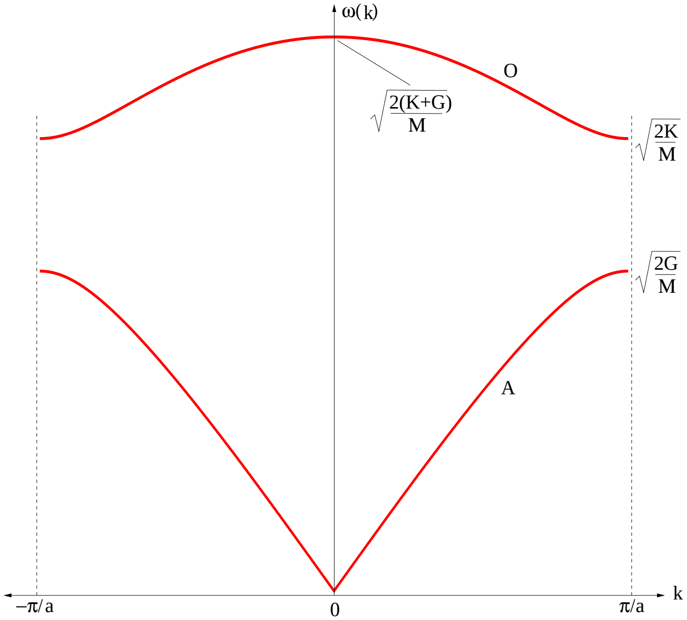
- Consider ions of mass M separated by distance a
- For simplicity, assume nearest neighbour interactions only
- In the Harmonic approximation, this is equivalent to masses connected by springs of strength K: $M\ddot{u}(na) = -\frac{\partial U^{\text{harm}}}{\partial u(na)}$, $U^{\text{harm}} = \frac{1}{2}K\sum_n[u(na) - u((n+1)a)]^2$

Normal Modes of a 1D Bravais Lattice

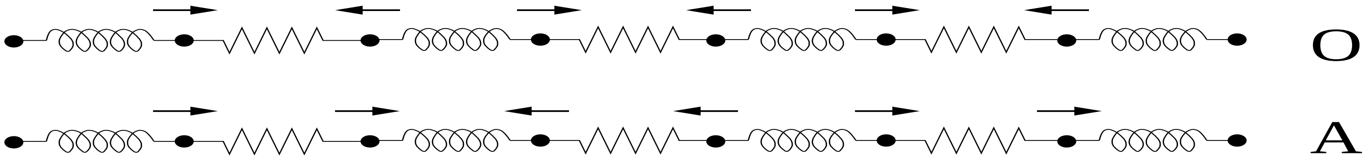


- Seek solutions of the form: $u(na,t) \propto e^{i(kna-\omega t)}$
- The PBCs $\Rightarrow e^{ikNa} = 1 \Rightarrow k = \frac{2\pi}{a}\frac{n}{N}$ with n integer, N solutions and $-\frac{\pi}{a} \leq k < \frac{\pi}{a}$
- Substitution into the dynamical eqn. gives: $\omega(k) = 2\sqrt{\frac{K}{M}}|\sin(ka/2)|$
- The group and phase velocities differ substantially at the zone boundaries

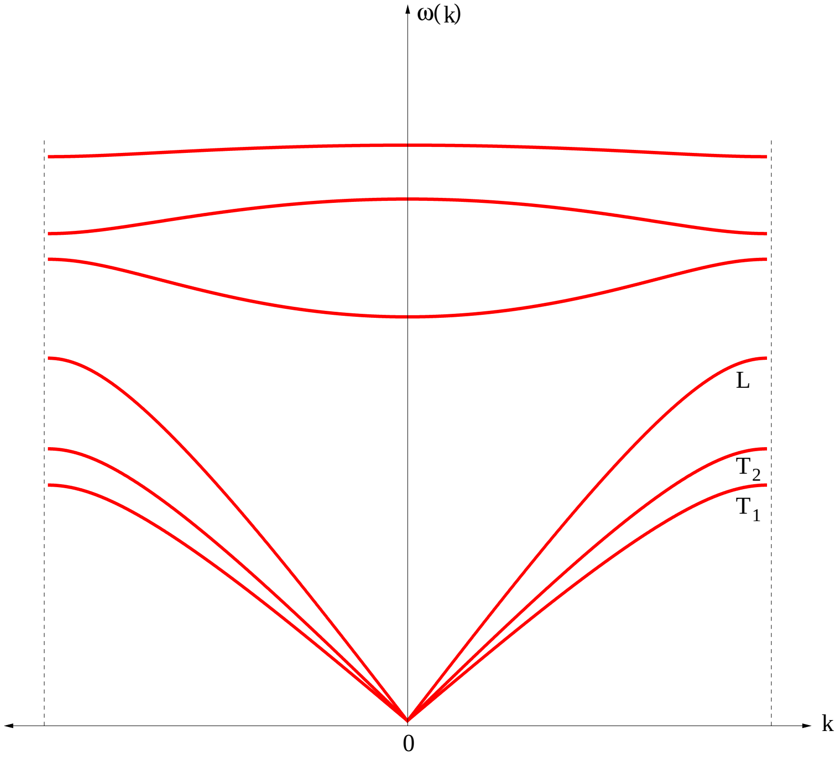
NORMAL MODES OF A 1D BRAVAIS LATTICE WITH A BASIS



- The analysis can be repeated
- The are 2 solutions for each $k \Rightarrow 2N$ solutions in total:
  $\omega^2 = \frac{K+G}{M} \pm \frac{1}{M}\sqrt{K^2 + G^2 + 2KG\cos k$
- There are *acoustic* and *optical* modes



Normal Modes of a 3D Bravais Lattice

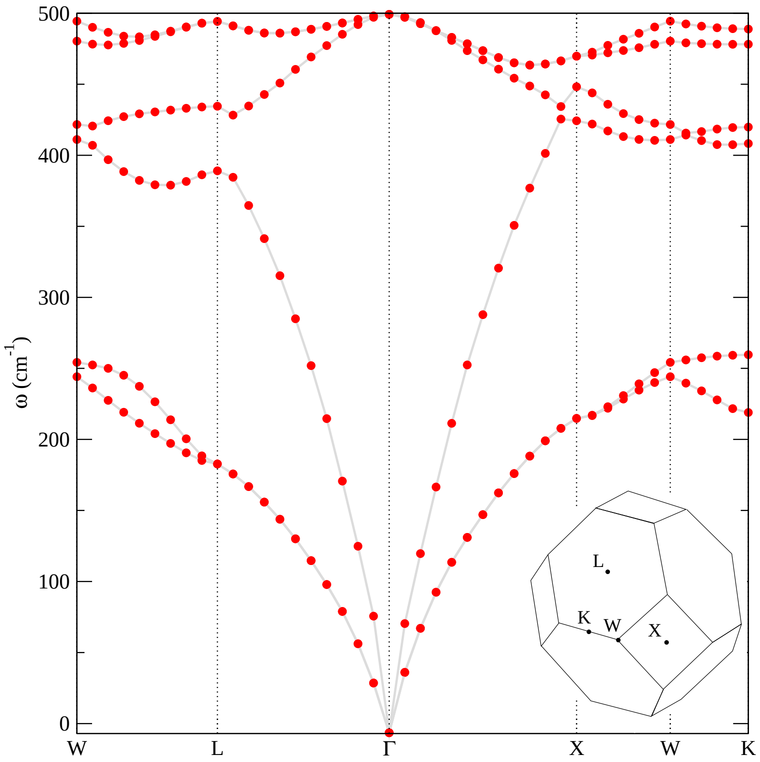


- The *dynamical matrix* is $\mathbf{D}(\mathbf{k}) = \sum_{\mathbf{R}} \mathbf{D}(\mathbf{R}) e^{-i\mathbf{k}\cdot\mathbf{R}}$, where $\mathbf{D}(\mathbf{R}-\mathbf{R}')$ is the second derivative of U with respect to the displacement of ions at $\mathbf{R}$ and $\mathbf{R}'$ at eqbm..

- The solution of the dynamical equation is given by the eigen-equation $M\omega^2\mathbf{e} = \mathbf{D}(\mathbf{k})\mathbf{e}$, where $\mathbf{e}$ is the *polarization vector*

- 3N solutions for each ion in the basis

Normal Modes of a Real Crystal



Dispersion curves for Silicon

- The dynamical matrix can be built up from first principles calculations
- Can use a supercell approach to study certain high symmetry k-vectors
- For arbitary k use linear response theory – a perturbation theory

CONNECTIONS WITH THE THEORY OF ELASTICITY

- The classical theory of elasticity ignores the microscopic atomic structure
- The continuum theory of elasticity can be derived from the theory of lattice vibrations
- Consider displacements that vary slowly over the atomic length scale
- Using the symmetries of $\mathbf{D}$: $\mathbf{U}^{\mathrm{harm}} = \frac{1}{4}\sum_{\mathbf{R}\mathbf{R}'} [\mathbf{u}(\mathbf{R}') - \mathbf{u}(\mathbf{R})]\mathbf{D}(\mathbf{R}-\mathbf{R}')[\mathbf{u}(\mathbf{R}') - \mathbf{u}($
- Slowly varying displacements ⇒ $\mathbf{u}(\mathbf{R}') = \mathbf{u}(\mathbf{R}) + (\mathbf{R}' - \mathbf{R}) \cdot \nabla \mathbf{u}(\mathbf{r})|_{\mathbf{r}=\mathbf{R}}$

$$\mathbf{U}^{\mathrm{harm}} = \frac{1}{2}\sum_{\mathbf{R},\mu\nu\sigma\tau} \left(\frac{\partial u_\mu(\mathbf{R})}{\partial x_\sigma}\right)\left(\frac{\partial u_\nu(\mathbf{R})}{\partial x_\tau}\right) E_{\sigma\mu\tau\nu} \quad \boxed{E_{\sigma\mu\tau\nu} = -\frac{1}{2}\sum_{\mathbf{R}} R_\sigma D_{\mu\nu}(\mathbf{R}) R_\tau}$$

A Quantum Theory of the Harmonic Crystal

- In a Quantum theory the system can be in a set of discrete stationary states
- These stationary states are the eigenstates of the harmonic Hamiltonian: $H^{\mathrm{harm}} = \sum_{\mathbf{R}} \frac{P(\mathbf{R})^2}{2M} + \frac{1}{2}\sum_{\mathbf{RR'}} \mathbf{u}(\mathbf{R})\mathbf{D}(\mathbf{R}-\mathbf{R'})\mathbf{u}(\mathbf{R'})$
- The result is: an N-ion harmonic crystal is equivalent to $3N$ independent oscillators $\Rightarrow$ the $3N$ classical normal modes
- The energy in each mode is discrete, and the total energy is: $E = \sum_{\mathbf{k}s}(n_{\mathbf{k}s} + \frac{1}{2})\hbar\omega_s(\mathbf{k})$
- The integer $n_{\mathbf{k}s}$ is the excitation number of the normal mode in branch s at wave vector $\mathbf{k}$

NORMAL MODES OR PHONONS

- So far we have described the state in terms of the excitation number $n_{\mathbf{k}s}$
- This is clumsy if describing processes involving the exchange of energy – between normal modes, or other systems (electrons, neutrons or X-rays)
- As for the QM theory of the EM field we use an equivalent *corpuscular* description
- Instead of saying that the mode $\mathbf{k}$,s is in the $n_{\mathbf{k}s}$ excited state we say there are $n_{\mathbf{k}s}$ phonons of type s with wave vector $\mathbf{k}$
- Photons $\Rightarrow$ of the correct frequency are visible light
  Phonons $\Rightarrow$ of the correct frequency are sound
- Don't forget phonons/normal modes are equivalent

Classical Specific Heat: Dulong-Petit

- The thermal energy density is given by averaging over all configurations weighted by $e^{-\beta E}$ with $\beta = \frac{1}{k_B T}$

  $$u = \frac{1}{V} \frac{\int d\Gamma e^{-\beta H} H}{\int d\Gamma e^{-\beta H}}$$
  $$= -\frac{1}{V} \frac{\partial}{\partial \beta} ln \int d\Gamma e^{-\beta H}$$

- By making a change of variables:
  $\int d\Gamma e^{-\beta H} = e^{-\beta U^{\mathrm{eq}}} \beta^{-3N} \times \mathrm{constant}$

- The thermal energy density is:
  $u = u^{\mathrm{eq}} + 3nk_B T, \ (n = N/V)$

- The specific heat is independent of T:
  $c_v = 3nk_B$

- This is not observed experimentally – only approximately at high temperature where the harmonic approximation is bad anyway

The Quantum Mechanical Lattice Specific Heat

- The QM thermal energy density is:
  $u = \frac{1}{V}\sum_i E_i e^{-\beta E_i} / \sum_i e^{-\beta E_i}$
  $= -\frac{1}{V}\ \frac{\partial}{\partial \beta} ln \sum_i e^{-\beta E_i}$

- The sum is over the stationary states with energy:
  $E_i = \sum_{\mathbf{k}s} (n^i_{\mathbf{k}s} + \frac{1}{2}) \hbar \omega_s(\mathbf{k})$,
  $n^i_{\mathbf{k}s} = 0, 1, 2, \ldots$
  $\sum_i e^{-\beta E_i} = \Pi_{\mathbf{k}s} \frac{e^{-\beta \hbar \omega_s(\mathbf{k})/2}}{1 - e^{-\beta \hbar \omega_s(\mathbf{k})}}$

- The energy density is :
  $u = \frac{1}{V} \sum_{\mathbf{k}s} \hbar \omega_s(\mathbf{k}) [n_s(\mathbf{k}) + \frac{1}{2}]$

- The mean excitation number $n_s(\mathbf{k}) = \frac{1}{e^{\beta \hbar \omega_s(\mathbf{k})} - 1}$ is the Bose-Einstein distribution function

- The specific heat is given by:
  $c_v = \frac{1}{V} \sum_{\mathbf{k}s} \frac{\partial}{\partial T} \frac{\hbar \omega_s \mathbf{k}}{e^{\beta \hbar \omega_s(\mathbf{k})} - 1}$

THE HIGH-TEMPERATURE LATTICE SPECIFIC HEAT

- When $k_B T \gg \hbar\omega_s(\mathbf{k})$ all the normal modes are highly excited

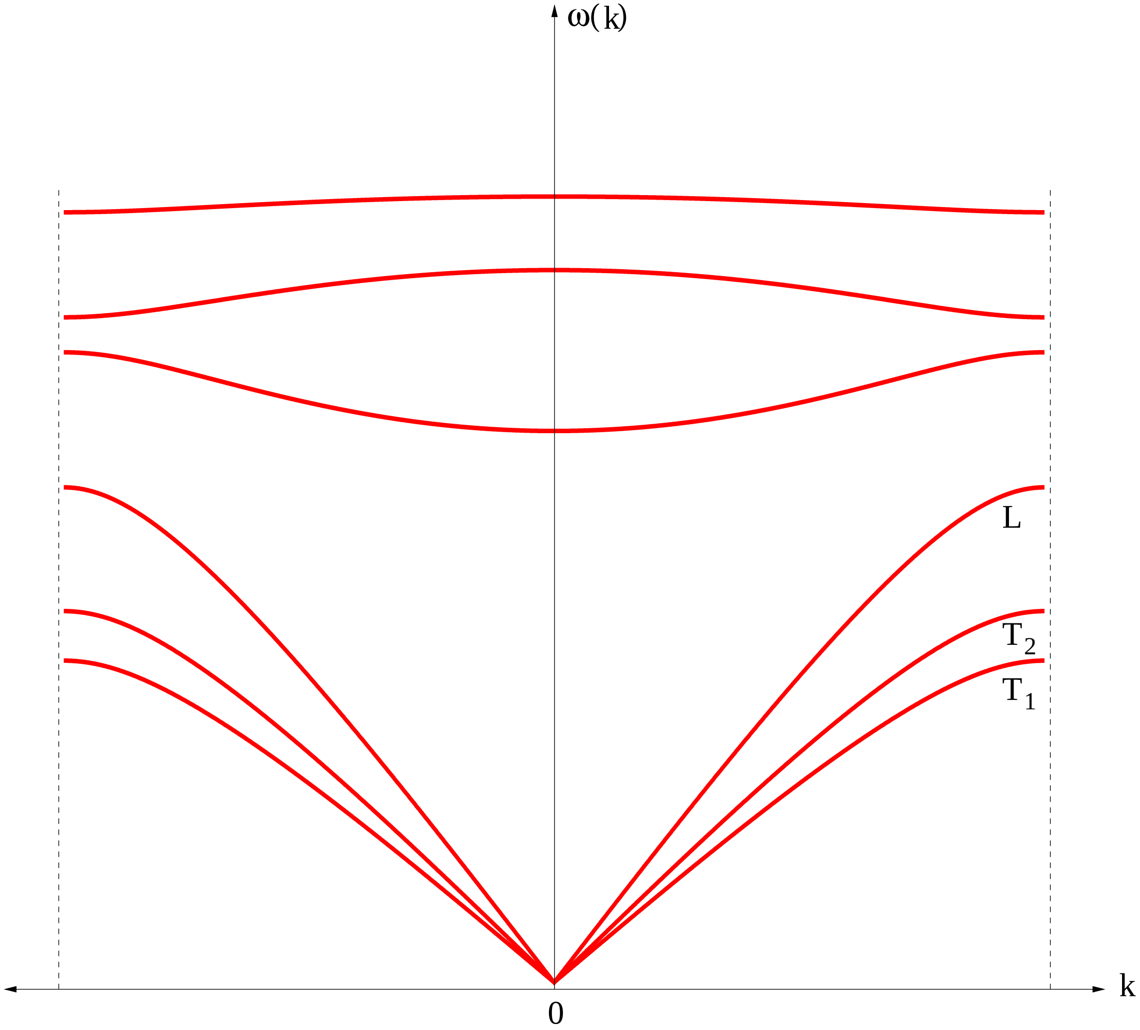
- Writing $\beta\hbar\omega_s(\mathbf{k}) = x$, then x is small and we can expand: $\frac{1}{e^x-1} = \frac{1}{x}[1 - \frac{x}{2} + \frac{x^2}{12} + O(x^3)]$

- Keeping just the leading term we regain the Dulong-Petit law:

$$c_v = \frac{1}{V}\sum_{\mathbf{k}s} \frac{\partial}{\partial T} k_B T = \frac{3N}{V} k_B$$

- The next term is constant in T

- We might try to correct the Dulong-Petit law, but anharmonic terms are likely to dominate where the expansion holds – or the crystal melts!


ω(k)
L
T2
T1
k
0

THE LOW-TEMPERATURE LATTICE SPECIFIC HEAT

- In the limit of a large crystal integrate over the 1st Brillouin zone:
  $c_v = \frac{\partial}{\partial T} \sum_i \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{\hbar\omega_s(\mathbf{k})}{e^{\beta\hbar\omega_s(\mathbf{k})}-1}$

- Modes with $\hbar\omega_s(\mathbf{k}) \gg k_B T$ will not contribute – but the acoustic branches will at long enough wavelengths for any T

- Make some approximations:

1. Ignore the optical modes
2. Use the dispersion relationship: $\omega_s(\mathbf{k}) = c_s(\hat{\mathbf{k}})k$
3. Integrate over all $\mathbf{k}$

- Making the substitution $\beta\hbar c_s(\hat{\mathbf{k}})k = x$ we obtain, and c as the average speed of sound:

$$\boxed{c_v = \frac{\partial}{\partial T}\, \mathrm{const} \times \frac{(k_B T)^4}{(\hbar c)^3} \propto T^3}$$

INTERMEDIATE TEMPERATURE: THE DEBYE AND EINSTEIN MODELS

- The T^3 relation only remains valid while the thermal energy is small compared to the energy of phonons with a non-linear dispersion (much lower than room temperature)
- The Debye and Einstein models approximate the dispersion relations
- Debye: all branches modelled by 3 acoustic modes, all with $\omega = ck$, and integrate up to k_D
- Einstein: optical modes represented by modes of ω_E
- The Debye temperature divides the quantum and classical statistical regimes: $k_B\Theta_D = \hbar\omega_D = \hbar c k_D = \hbar c\sqrt[3]{6\pi^2 n}$

Measuring Phonon Dispersion Relations

- Normal mode dispersion relations $\omega_s(\mathbf{k})$ can be extracted from experiments in which lattice vibrations exchange energy with an external probe

- Energy lost (or gained) by a neutron $\Rightarrow$ emission (or absorption) of a phonon

- The same applies or X-rays or visible light

- Neutrons carry more momentum than photons in the energy range of interest

NEUTRON SCATTERING BY A CRYSTAL

- Neutrons only interact strongly with the atomic nuclei, and so will pass through a crystal, possibly with a changed $E = p^2/2M_n$ and $\mathbf{p}$

- Conservation laws allow the extraction of information from the scattering

- The conservation of energy: $E' = E - \sum_{\mathbf{k}s} \hbar\omega_s(\mathbf{k})\Delta n_{\mathbf{k}s}$,

$\Delta n_{\mathbf{k}s} = n'_{\mathbf{k}s} - n_{\mathbf{k}s}$

- The conservation of crystal momentum: $\mathbf{p}' - \mathbf{p} = \sum_{\mathbf{k}s} \hbar\mathbf{k}\Delta n_{\mathbf{k}s} + \mathbf{K}$

- This is the same crystal momentum as for the Bloch states – important for theories of electron-phonon scattering

- Different numbers of phonons can be involved in a scattering event

Zero Phonon Scattering

- The final state is identical to the initial state
- Energy conservation implies that the energy of the neutron is unchanged (elastically scattered): $q' = q$
- Crystal momentum conservation implies that the neutron's momentum changes by $\hbar\mathbf{K}$: $\mathbf{q}' = \mathbf{q} + \mathbf{K}$
- These are just the von Laue conditions
- We can extract the same crystallographic information of the static lattice as from X-ray diffraction experiments

ONE PHONON SCATTERING

- The situation where one phonon is absorbed or emitted conveys the most information
- The conservation laws imply:
  $E' = E \pm \hbar\omega_s(\mathbf{k})$
  $\mathbf{p}' = \mathbf{p} \pm \hbar\mathbf{k} + \hbar\mathbf{K}$
- The additive $\mathbf{K}$ can be ignored because $\omega_s(\mathbf{k}+\mathbf{K}) = \omega_s(\mathbf{k})$
- For the absorption case:
  $\frac{p'^2}{2M_n} = \frac{p^2}{2M_n} + \hbar\omega_s(\frac{\mathbf{p}'-\mathbf{p}}{\hbar})$
- In an experiment we control $\mathbf{p}$ and E
- We can choose a direction in which to measure, and record the energy E' to map out the dispersion curves $\omega_s(\mathbf{k})$
- Multi-phonon scattering events produce a background