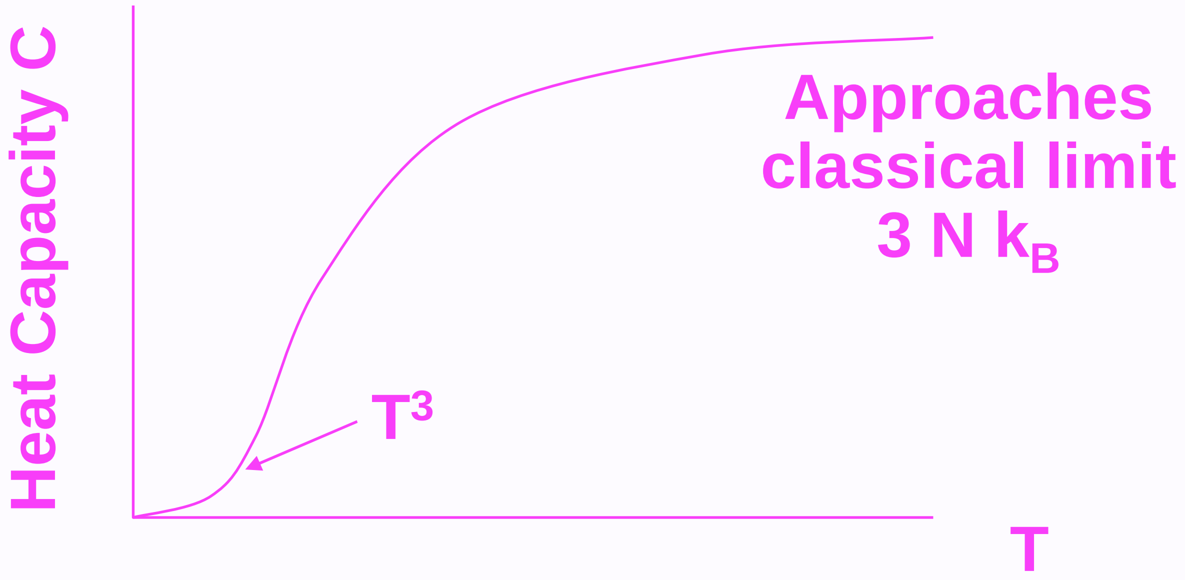
Phonons II - Thermal Properties (Kittel Ch. 5)



Approaches classical limit $3\ N\ k_B$

Outline

- What are thermal properties?
  - Fundamental law for probabilities of states in thermal equilibrium
- Planck Distribution
  - Start of quantum mechanics
  - Applied to solids in early days of q. m.
  - Bose-Einstein statistics - Planck distribution

- Density of states, Internal energy, Heat capacity
- Normal mode enumeration
- Debye Model -- $C \sim T^3$ law at low T
- Einstein Model
- (Read Kittel Ch 5)

Keys Today

- **Fundamental laws**
- **How to make good approximations**

Beginnings of quantum mechanics

- **Max Planck - 1901**
- **Observations and experimental facts that showed problems with classical mechanics**
- **One was radiation – the laws of classical mechanics predicted that light radiated from hot bodies would be more intense for higher frequency (blue and ultraviolet) – totally wrong!**

- **Planck proposed that light was emitted in "quanta" – units with energy $E = h\nu = \hbar\omega$**

- **One key result is the distribution of the frequencies of waves as a function of temperature**
- **Applies to all waves!**

Thermal Properties - Key Points

- **Fundamental law a system in thermal equilibrium**:

  If two states of the system have total energies E_1 and E_2, then the ratio of probabilities for finding the system in states 1 and 2 is:
  $P_1 / P_2 = \exp(-(E_1 - E_2) / k_B T)$
  where
  k_B is the Boltzman constant

- **Applies to all systems** - whether treated as classical or as quantum and whether the particles are bosons (like phonons) or fermions (like electrons)
- **Quantum Mechanics makes the problem easier**, with final formulas for thermal energy, etc., that depend upon whether the particles are bosons or fermions

Thermal Properties - Phonons

- Phonons are examples of bosons that do not obey an exclusion principle. There can be any number n phonons for each oscillator, i.e., the energy of each oscillator can be $E_n = (n + ½)\hbar\omega$, n = 0,1,2,. . .

  Thus the probability of finding the oscillator with n phonons :

  $$P_n = \exp(-E_n / k_B T) \; / \; \sum_{n'=0}^{\infty} \exp(-E_{n'} / k_B T)$$

  Note : $\sum_{n=0}^{\infty} P_n = 1$ as it must for probabilities

- And the average phonon occupation is

  $$\langle n \rangle = \sum_{n=0} P_n \, n$$

  $$= \sum_{n=0}^{\infty} n \exp(-E_n / k_B T) \; / \; \sum_{n'=0}^{\infty} \exp(-E_{n'} / k_B T)$$

- See next slide

Planck Distribution

- Using the formulas:
  $1/(1 - x) = \sum_{s=0}^{\infty} x^s$ and $x/(1 - x)^2 = \sum_{s=0}^{\infty} s\, x^s$
  (simple proof in class)
  it follows that:

$$\langle n \rangle = \frac{1}{\exp(\hbar\omega / k_B T) - 1}$$

Planck Distribution

- Average energy of an oscillator at temperature T:

$$U = \hbar\omega\left(\langle n \rangle + \tfrac{1}{2}\right)$$

$$= \hbar\omega\left(\frac{1}{\exp(\hbar\omega / k_B T) - 1} + \tfrac{1}{2}\right)$$

- At high T, $U \rightarrow \hbar\omega / [\hbar\omega / k_B T] \rightarrow k_B T$
  which is the classical result

Mean square displacement

- Consider an oscillator with $E = \frac{1}{2} C(x - x_0)^2$
- We can estimate the mean square displacement by setting $\frac{1}{2} C\overline{(x - x_0)^2}$ equal to the average energy of an oscillator $\hbar\omega$ ($<n> + \frac{1}{2}$). Using $\omega = (C/M)^{1/2}$ we find $\overline{(x - x_0)^2} \sim 2\hbar(1/CM)^{1/2}$ ($<n> + \frac{1}{2}$).
- For low temperature $T \sim 0$, we find the quantum zero point motion (ZPM) :

$$\overline{(x - x_0)^2} \sim \hbar\,(1/CM)^{1/2}$$

Note: the ZPM decreases as C and/or M increases

- At high T, $E \rightarrow k_B T$, and $\overline{(x - x_0)^2} \sim 2\, k_B T / C$ which is independent of the mass

Mean square displacement

- Homework problem to estimate the root mean square displacement $\Delta x_{rms} = [\, \overline{(x - x_0)^2} \,]^{1/2}$
- One can use typical values for C and M
- Result – for most cases Δx_{rms} << near neighbor distance at T=0
- Δx_{rms} increases and it is ~ near neighbor distance when the solid melts (Lindeman criterion)

Total thermal energy of a crystal

- The crystal is a sum, of independent oscillators (in the harmonic approximation). The independent oscillators are waves labeled by **k** and an index m = 1, ..., 3N. Therefore, the total energy of the crystal is:

3 dimensions

atoms per cell

Fixed atoms

$$U = U_0 + \sum_{\underline{\mathbf{k}},m} \hbar\omega_{\underline{\mathbf{k}},m} \left(\frac{1}{\exp(\hbar\omega_{\underline{\mathbf{k}},m} / k_B T) - 1} + \tfrac{1}{2} \right)$$

Added thermal energy

Zero point energy

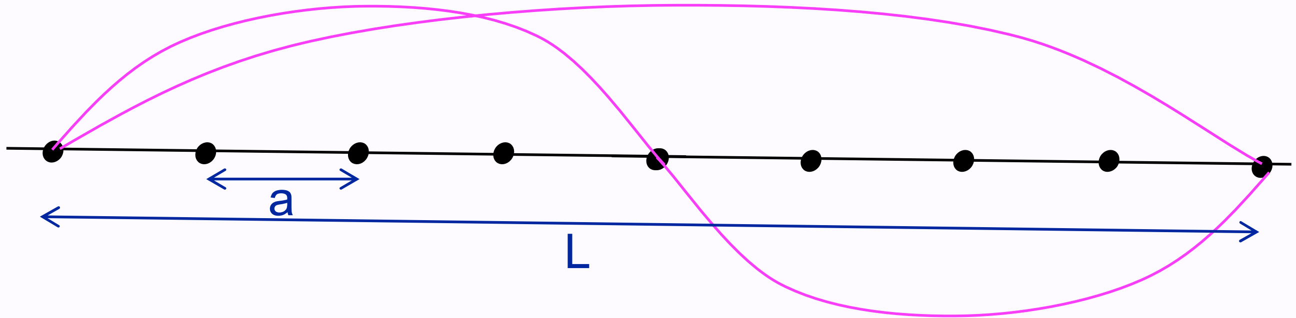
Question: How to do the sum over **k** ??

Sum over vibration modes of a crystal

- We can derive this and we can also see that it MUST be true without doing any work!
  - 1. A crystal in 3 dimensions with N cells and N_{cell} atoms/cell has 3 N N_{cell} “degrees of freedom” (i.e. number of ways the atoms can move).
  - 2. This does not change when we transform to the independent oscillators (i.e. the oscillators with frequencies $\omega_{k,m}$)
  - 3. Therefore there are 3 N N_{cell} independent oscillators!
- This can be thought of as follows:
  - There is one **k** point for each primitive cell in the crystal (see next slide)
  - For each **k** point there are 3 N_{cell} ways the atoms in the cell can move, i.e., 3 N_{cell} dispersion curves labeled by the index m with frequency $\omega_{k,m}$
  - This is a total of 3 N N_{cell} independent oscillators!

Counting k points

- Demonstration that the sum over **k** is equivalent to one **k** point for each primitive cell
  - See notes and Kittel p. 109-110 and Ch 5, Figs 2-4
- Consider all the possible waves for atoms moving in 1 dimension with the ends fixed



$u_s = u \sin(ksa)$, $k = \pi/L, 2\pi/L, 3\pi/L, \ldots (N-1)\pi/L$

For a large crystal: $N-1 \sim N$

Conclusion: # k points = # cells

Also $\Delta k = \pi/L$ and the k points approach a continuum

The frequencies ω_k form a smooth curve for $k=0$ to $k = \pi/a$

Counting k points

- If we consider the states on a circle (the line wrapped into a circle), it is easier to consider u_s = u exp(i ksa)
  - See Kittel, Ch 5, Fig. 4
- Consider all the possible waves u_s = u exp(iksa) that can fit in a circle of circumference L

$k = -N\pi/L, \ldots -6\pi/L, -4\pi/L, -2\pi/L, 0, 2\pi/L, 4\pi/L, 6\pi/L, \ldots N\pi/L$

N values of k in Brillouin Zone

Conclusion: # k points = # cells (same as before)

$\Delta k = 2\pi/L$ -- approaches a continuum -- smooth curve for ω_k

$$(2\pi/L)\Sigma_{k \text{ inside BZ}} f(k) \Rightarrow \int_{BZ} dk\, f(k)$$

Using L = Na

$$(1/N)\, \Sigma_{k \text{ inside BZ}} f(k) \Rightarrow (a/2\pi) \int_{BZ} dk\, f(k)$$

Counting k points

- The ideas carry over to 2 and 3 dimensions
- The same derivation can be used for each direction in reciprocal space
- For a 3 dimensional crystal with $N = N_1\ N_2\ N_3$ cells

Each k point corresponds to a volume in reciprocal space

$$(2\pi/L_1)\,(2\pi/L_2)\,(2\pi/L_3) = (2\pi)^3/V = (2\pi)^3/NV_{cell} = (1/N)\,(2\pi)^3/V_{cell}$$
$$= V_{BZ}/N$$

N values of k in Brillouin Zone

Conclusion: # k points = # cells (same as before)

$$(V_{BZ}/N)\,\Sigma_{k\text{ inside BZ}}\ f(k) \Rightarrow \int_{BZ} dk\ f(k)$$

$$(1/N)\,\Sigma_{k\text{ inside BZ}}\ f(k) \Rightarrow (1/V_{BZ}) \int_{BZ} dk\ f(k)$$

Counting k points

- Final result in any dimension

  Equivalent to Kittel Ch 5, Eq. 18
  But I thinkmy version is clearer
- All expressions for total integrated quantities in a crystal involve a sum over the k points in the Brillouin Zone (or any primitive cell of the reciprocal lattice)
- We can express the result as a value per cell as the sum over k points divided by the number of cells N

For any function f(k) the integrated value per cell is

$$f^{\text{Total}}_{\text{per cell}} = (1/N)\, \Sigma_{\text{k inside BZ}}\, f(k) \Rightarrow f^{\text{Total}}_{\text{per cell}} = (1/V_{BZ}) \int_{BZ} dk\, f(k)$$

Total thermal energy

- For the total thermal energy we need a sum over states
  $$U = \text{const} + \sum_{\underline{\mathbf{k}},m} \hbar\omega_{\underline{\mathbf{k}},m} \frac{1}{\exp(\hbar\omega_{\underline{\mathbf{k}},m} / k_B T) - 1}$$
- Then the thermal energy per cell is
  $$U_{th} = (1/V_{BZ}) \int_{BZ} dk \sum_m \hbar\omega_{\underline{\mathbf{k}},m} \frac{1}{\exp(\hbar\omega_{\underline{\mathbf{k}},m} / k_B T) - 1}$$
- Notice that this depends only on the frequency of the phonons $\omega_{\underline{\mathbf{k}},m}$ It does not depend on the type of phonon, etc.
- We can use this to simplify the problem

Density of States

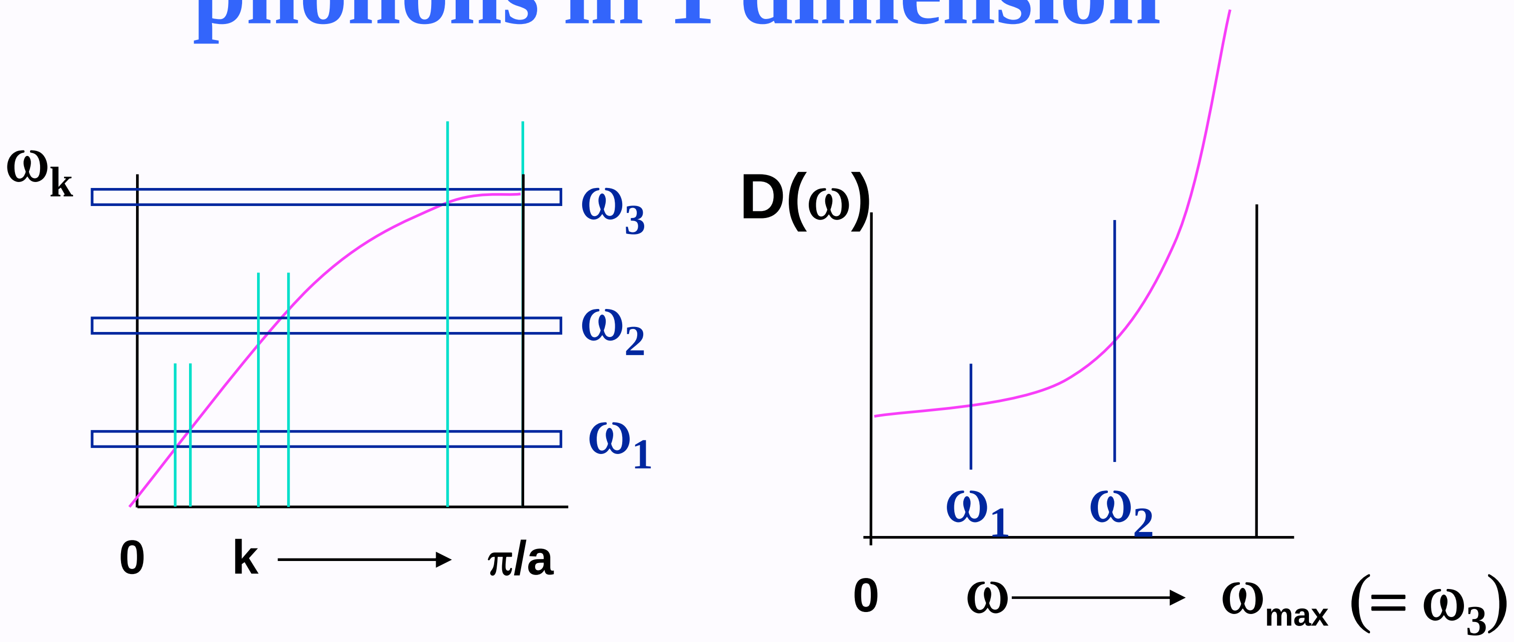
- What is needed is the number of states per unit frequency $D(\omega)$. Then for any function $f(x)$

$$(1/V_{BZ}) \int_{BZ} dk \sum_m f(\omega_{\underline{\mathbf{k}},m}) = \int d\omega\, D(\omega)\, f(\omega)$$

- How do we find $D(\omega)$?
- By finding the number of states in an energy range from ω to $\omega + \Delta\omega$
- The key is that the k points are equally spaced. Thus the number of states per unit k is constant Example - One dimension (homework)

  Next Slide

Density of states for acoustic phonons in 1 dimension

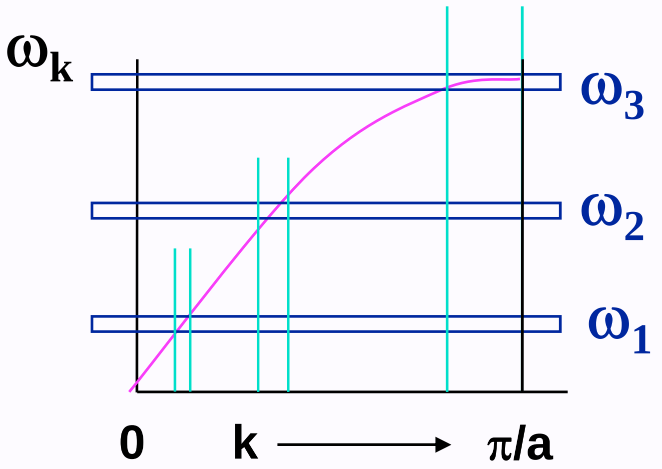


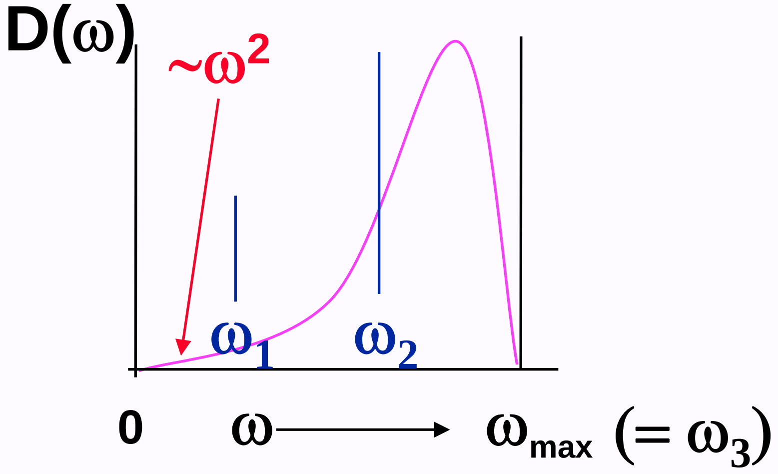
The key is that the k points are equally spaced.
In 1 dimension this means that the number of states per unit k is constant. Thus

$$D(\omega) = dN_{states}/d\omega = (dN_{states}/dk)(dk/d\omega) = (L/2\pi)(dk/d\omega)$$
$$= (L/2\pi)(1/v_{group})$$

Homework)

Density of states for acoustic phonons in 3 dimensions





The k points are equally spaced in each direction.
In 3 dimensions this means that the number of states per unit |k| is $4\pi|k|^2$. Thus

$$D(\omega) = dN_{states}/d\omega = (dN_{states}/d|k|)(d|k|/d\omega) = (V/(2\pi)^3)\, 4\pi|k|^2 (dk/d\omega)$$
$$= (V/2\pi^2)|k|^2\, (1/v_{group})$$

Debye Model for density of states for acoustic phonons in 3 dimensions

- For acoustic phonons at long wavelength (small k), $\omega = v_s\, k$
- The Debye model is to assume $\omega = v_s\, k$ for all k in the Brillouin zone
- Then $D(\omega) = (V/2\pi^2)|k|^2\ (1/v_{group}) = (V/2\pi^2)\omega^2/v_s^3$

- Also we define a cutoff frequency by $\omega_D = v_s\, k_{max}$ where k_{max} is the radius that would give a sphere with the same volume as the Brillouin zone

$$(4\pi/3)k_{max}^3 = V_{BZ} = (2\pi)^3/V_{cell}$$

or

$$\omega_D^3 = 6\pi^2 v_s^3\ /V_{cell}$$

Debye Model for density of states for acoustic phonons in 3 dimensions

- Thus the thermal energy is

$$U = \int d\omega\ D(\omega) < n(\omega) > \hbar\omega =$$

$$= \int d\omega\ (V_{cell}\ \omega^2/2\pi^2 v_s^3) \frac{\hbar\omega}{\exp(\hbar\omega / k_B T) - 1}$$

- If we define $x = \hbar\omega/ k_B T$, and $x_D = \omega_D / k_B T \equiv \Theta/ k_B T$
- Then (see Kittel for details)

$$U = 9\ N\ k_B\ T\ (T/\ \Theta)^3 \int dx\ x^3/(\exp(x) - 1)$$

Note – we have assumed 3 acoustic modes with an average sound speed

Heat capacity

- The heat capacity is the change in energy per unit change in temperature

$$C_V = dU/dT$$

- Thus in the Debye model

$U = 9\ N\ k_B\ T\ (T/\ \Theta)^3 \int_0^{x_D} dx\ x^3/(\exp(x)\ -1)$

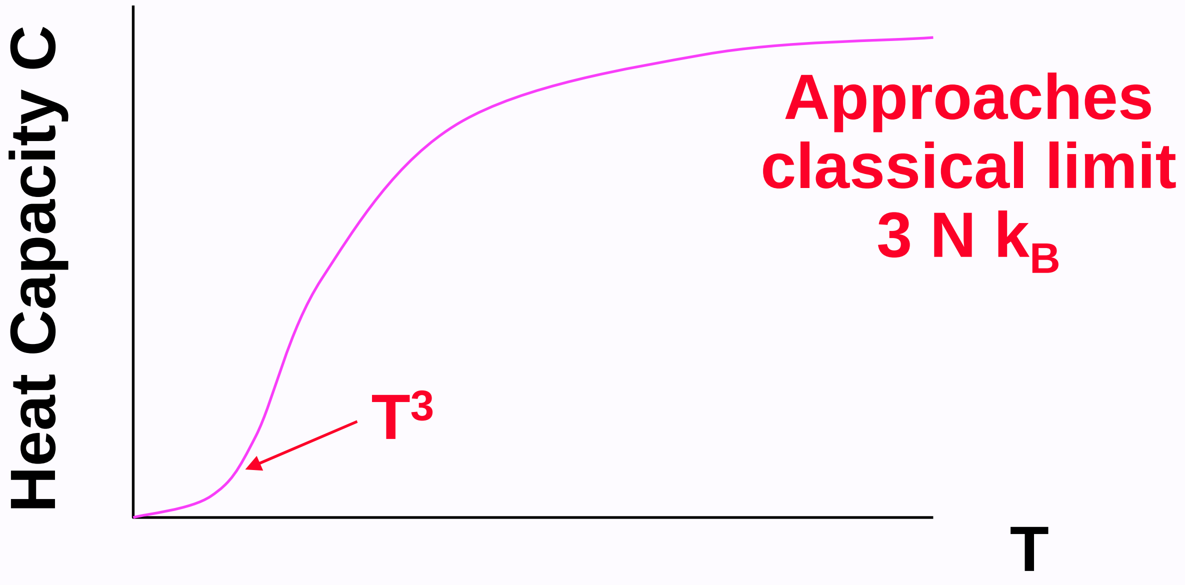
and

$C_V = 9\ N\ k_B\ (T/\ \Theta)^3 \int_0^{x_D} dx\ x^4 \exp(x)\ /(\exp(x)\ -1)$

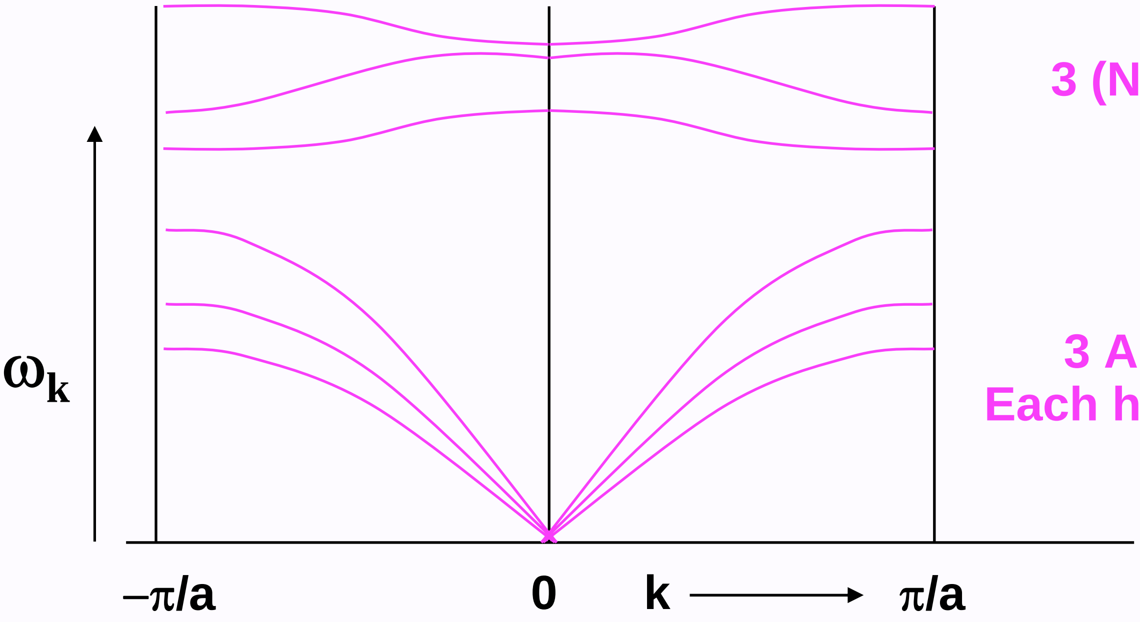
- See Kittel for details

Debye Approximation

- Has correct general behavior that must be found in all crystals. For 3 dimensions:



Oscillations in general 3 dimensional crystal with N atoms per cell



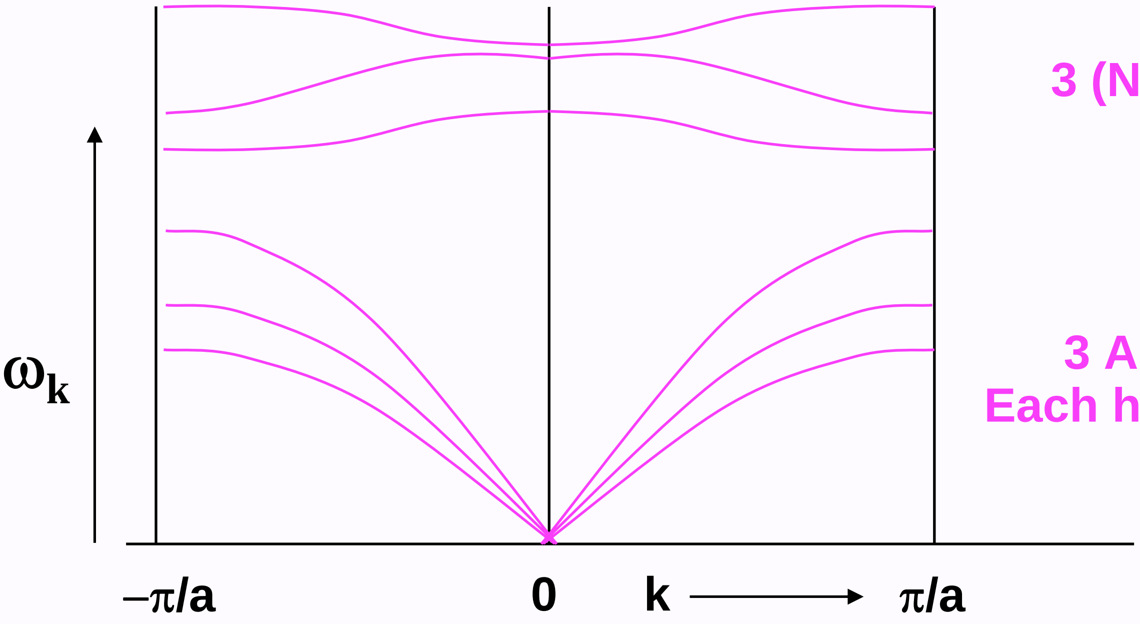
3 (N -1) Optic Modes

3 Acoustic modes
Each has $\omega \sim k$ at small k

Einstein Approximation

- Appropriate for Optic modes
- Use only one frequency – an average frequency for the optic modes

$$U = 3(N_{cell} - 1)\frac{\hbar\omega}{\exp(\hbar\omega / k_B T) - 1}$$



3 (N -1) Optic Modes

3 Acoustic modes
Each has ω ~ k at small k

See Kittel p. 114 for Einstein model.

Summary

- Fundamental law for probability of finding a system in a state if it is in thermal equilibrium
- Only need energies of possible states of the system
- Phonons are particles that obey Bose statistics
- Result is Planck Distribution
- Expression for internal energy and heat capacity
- Limits for heat capacity at low T and high T
- Debye approximation
- Debye temperature used as a characteristic measure for vibrational properties of solids
- Einstein Approximation
- How to make useful approximations!

Next time

- **Thermal Heat Transport**
  Phonon Heat Conductivity

- **Anharmonicity**
  Crucial for Transport

- **Gruneisen Constant**

- **(Read Kittel Ch 5)**