Lecture 5
Phonon Branches, Thermos

Crystal, the broken symmetry state, is NOT an eigen-state of the underlying Hamiltonian, while acoustic phonons emerge as quantum Goldstone modes ($\omega \rightarrow 0$ as $k \rightarrow 0$) of the broken symmetry state.

Some Terminology – Important!

- Branch – dispersion relation in the (k,ω) plane

  (accoustic branch, optical branch)
- Mode – each point of the dispersion relation

  A specific k is implied

  (accoustic mode, optical phonon mode, soft mode)

Acoustic and Optical Branches

- **# of branches = dm**

  d = spatial dimension

  m = # of atoms in the primitive basis

  (proof: Consider k=0 only, as the number of branches should be indep. of k. Number of possible branches = number of possible normal modes for each primitive basis = dm.)

- **# of acoustic branches = d**

  i.e. 1 in 1d, 2 in 2d, 3 in 3d

  1 LA – "longitudinal" acoustic,

  and the rest are TA – "transverse"

- # of optical branches = dm – d

General Formulation of Harmonic Approximation

$$U(\{\vec{u}_j(\boldsymbol{R})\}) \approx U_0 + \sum_{\boldsymbol{R},j,\boldsymbol{R}',j'} \frac{1}{2}\vec{u}^T{}_j(\boldsymbol{R})\,\overleftrightarrow{D}_{jj'}(\boldsymbol{R},\boldsymbol{R}')\vec{u}_{j'}(\boldsymbol{R}')$$

$\vec{u}_j(\boldsymbol{R})$ Displacement at Bravais Lattice **R** and element-index j within the basis

(1) Bravais Lattice translation symmetry: $\overleftrightarrow{D}_{jj'}(\boldsymbol{R},\boldsymbol{R}') = \overleftrightarrow{D}_{jj'}(\boldsymbol{R}-\boldsymbol{R}')$

(2) Real and symmetric, from definition: $\overleftrightarrow{D}_{jj'}(\boldsymbol{R},\boldsymbol{R}') = \overleftrightarrow{D}^T{}_{j'j}(\boldsymbol{R}',\boldsymbol{R})$

(3) Uniform translation does not add energy: $\sum_{\boldsymbol{R},j} \overleftrightarrow{D}_{jj'}(\boldsymbol{R},\boldsymbol{R}') = 0$

A and O Branches – example

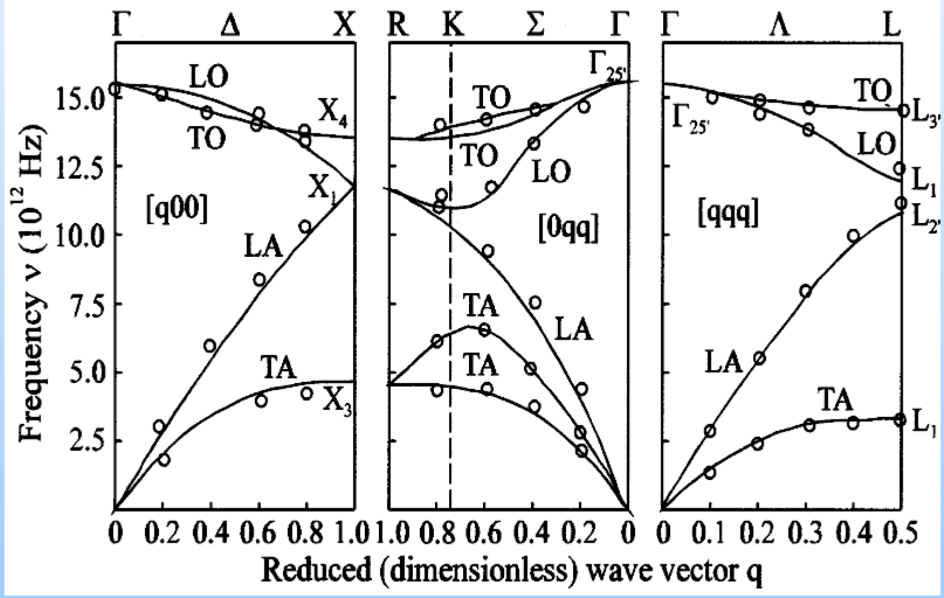
Material = Si

(note: 10^{12} Hz = THz

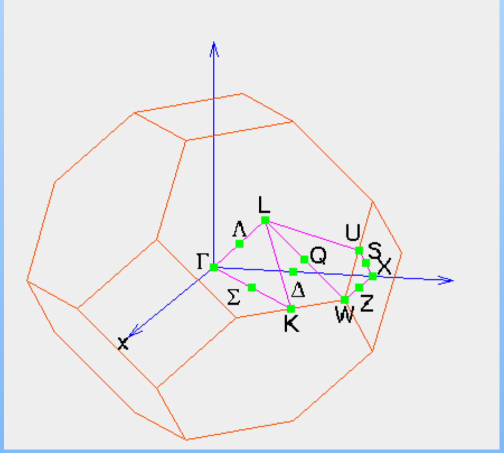
= 4.1 meV)

Diamond structure

2 atom basis in fcc



http://www.ioffe.rssi.ru/SVA/NSM/Semicond/SiGe/mechanic.html



http://cst-www.nrl.navy.mil/~mehl/phonons/fcczone.png

Generally, TA has lower energy than LA, and tends to be degenerate.

Phonons

- So far, we used only classical mechanics. But, once we find classical normal modes, it is trivial to treat the problem in quantum mechanics, since each normal mode is described by an independent harmonic oscillator Hamiltonian (by definition of a normal mode).
- Energy levels for each normal mode is then given by

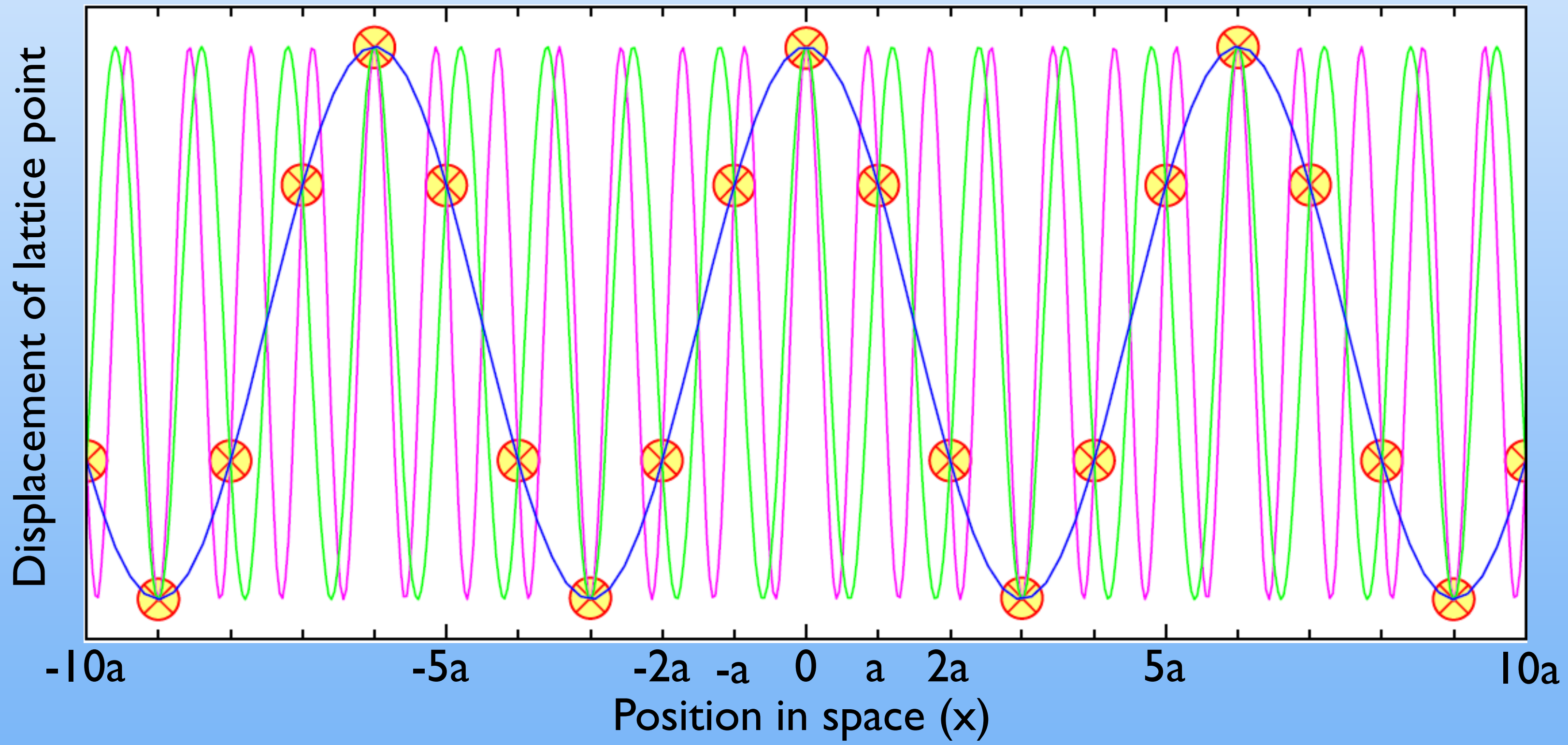
  $$(n + \tfrac{1}{2})\, \hbar\omega$$

  where $\omega=\omega(k, \text{other quantum numbers})$, and

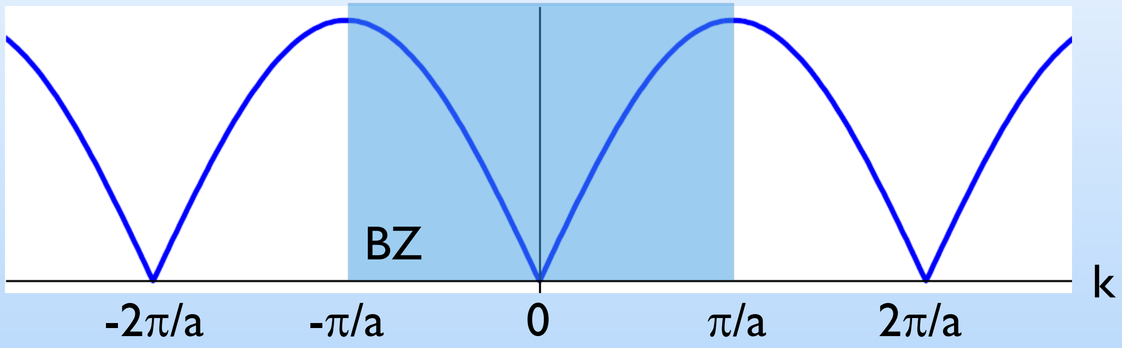
  $n = 0, 1, 2, \ldots$
- Quantum of these (vibrational) normal modes is called **phonon**, i.e. n describes the number of phonons.
- As we have seen, k is a good quantum number for describing phonons. Other good quantum numbers are polarizations, i.e. T or L – transverse or longitudinal.

Crystal Momentum

cos(kx) with k = π/(3a) (blue), π/(3a)–2π/a (green), π/(3a)+2π/a (magenta).
Crystal (yellow circles) is defined by lattice constant a.
There is no difference between all these waves if they represent lattice displacment, i.e. phonon amplitude, in the crystal.

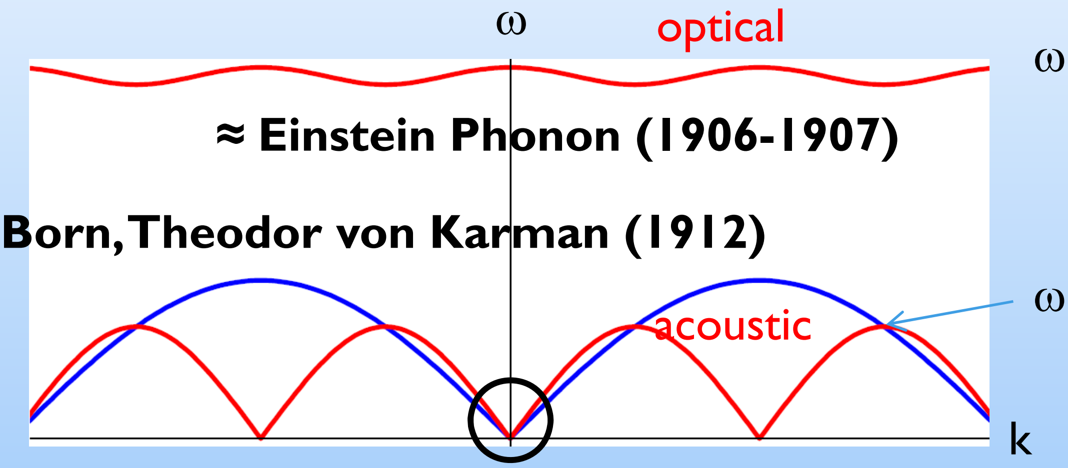


Crystal Momentum



- k is a good quantum number (i.e. eigenvalue $\omega=\omega(k)$), but is ambiguous up to wave vector $2\pi/a$, or **K** (R.L. vector) in general.
- $\hbar k$ (or sloppily just k) is called "**crystal momentum**"
- A continuous translational symmetry is broken but there is a discrete translational symmetry. Symmetry implies a conserved quantity, which in this case is the crystal momentum.
- It is as though the "new vacuum," i.e. the lattice, is able to impart momentum $\hbar\mathbf{K}$ to any wave (phonon, electron, neutron, photon, …) that exist in it (remember Bragg's law $\mathbf{q}=\mathbf{K}$).

How phonons came to be



$\omega \approx \sqrt{(2K/m)}$

≈ **Einstein Phonon (1906-1907)**

Max Born, Theodor von Karman (1912)

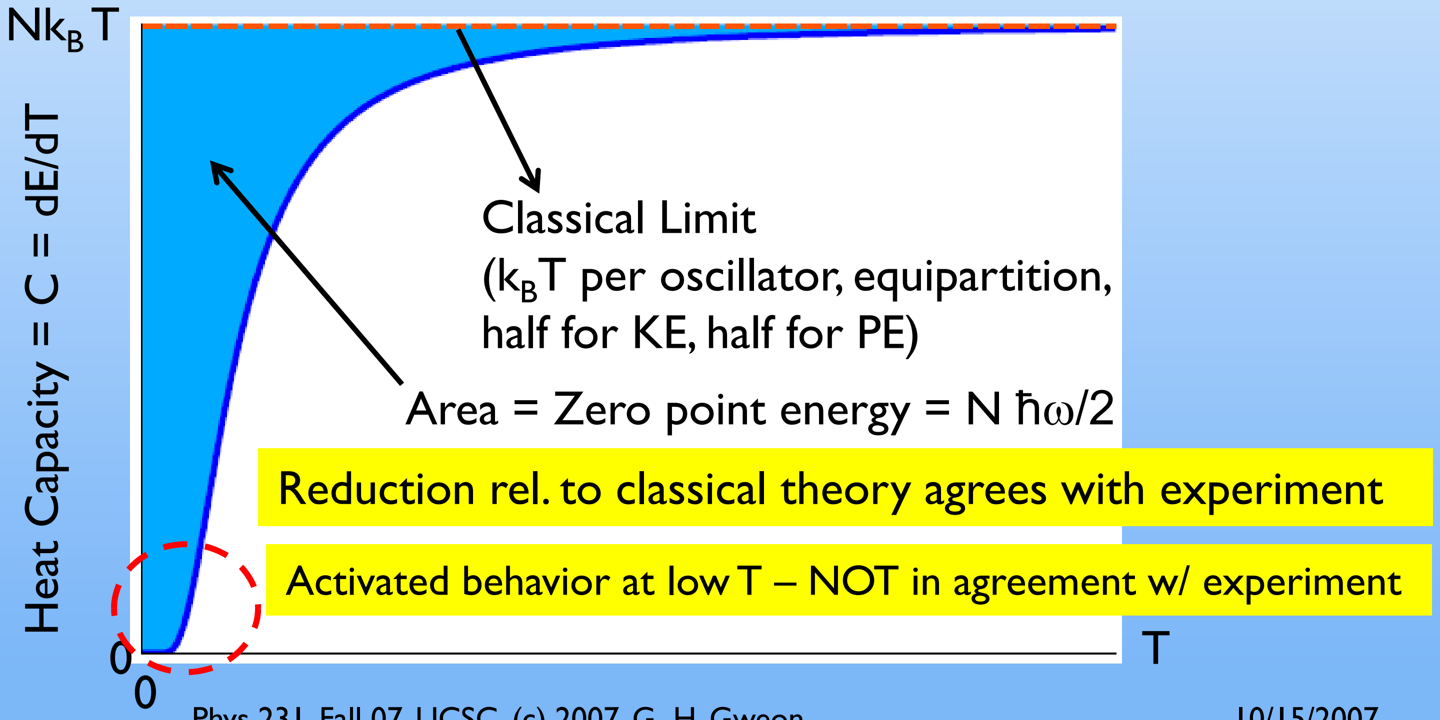
$\omega \approx \sqrt{(2K/M)}$

≈ **Debye Phonon (1912)**

- Einstein Phonon: $\omega = \omega_0$ = **constant**
  Independent single oscillator at each atom
- Debye Phonon: ω = **vk**
  Sound wave

Thermodynamics of Einstein Phonon

- Single frequency mode per lattice point and no coupling between neighboring mode → ω is independent of k ("dispersion-less")
- Just treat like N independent oscillators.



Classical Limit
($k_B T$ per oscillator, equipartition, half for KE, half for PE)

Area = Zero point energy = $N \hbar\omega/2$

Reduction rel. to classical theory agrees with experiment

Activated behavior at low T – NOT in agreement w/ experiment

Single Oscillator Problem (x N = Einstein Model)

Stat. Mech.

$$E = \frac{\Sigma_{n=0}^{\infty}\left(n+\frac{1}{2}\right)\hbar\omega \exp\left[-\frac{\left(n+\frac{1}{2}\right)\hbar\omega}{k_B T}\right]}{\Sigma_{n=0}^{\infty}\exp\left[-\frac{\left(n+\frac{1}{2}\right)\hbar\omega}{k_B T}\right]} = \frac{1}{Z}\frac{\partial Z}{\partial(-\beta)} = -\frac{\partial(\ln Z)}{\partial\beta}$$

$$\beta = \frac{1}{k_B T}$$

$$Z = \sum_{n=0}^{\infty} \exp[-\left(n+\frac{1}{2}\right)\beta\hbar\omega] = \exp\left(-\frac{1}{2}\beta\hbar\omega\right)\frac{1}{1-\exp(-\beta\hbar\omega)}$$

$$-\ln(Z) = \frac{1}{2}\beta\hbar\omega + \ln[1-\exp(-\beta\hbar\omega)]$$

n(ω): Bose Einstein Func

$$E = \frac{1}{2}\hbar\omega + \hbar\omega\frac{\exp(-\beta\hbar\omega)}{1-\exp(-\beta\hbar\omega)} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{\exp(\beta\hbar\omega)-1} = \boxed{\frac{1}{2}\hbar\omega + \hbar\omega\cdot n(\omega)}$$

Low Temperature $\beta\hbar\omega \to \infty$

Gapped, or Activated behavior

$$n(\omega) \approx \exp(-\beta\hbar\omega)$$

$$E \approx \frac{1}{2}\hbar\omega + \hbar\omega\exp\left(-\frac{\hbar\omega}{k_B T}\right)$$

$$C \approx k_B\left(\frac{\hbar\omega}{k_B T}\right)^2 \exp\left(-\frac{\hbar\omega}{k_B T}\right)$$

Heat Capacity

$$C = \frac{\partial E}{\partial T}$$

High Temperature $\beta\hbar\omega \to 0$

$$n(\omega) \approx (\beta\hbar\omega)^{-1}\cdot\left(1-\frac{1}{2}\beta\hbar\omega\right)$$

$$E \approx k_B T\left(1 + O\left(\frac{\omega}{T}\right)^2\right)$$

$$C \approx k_B$$

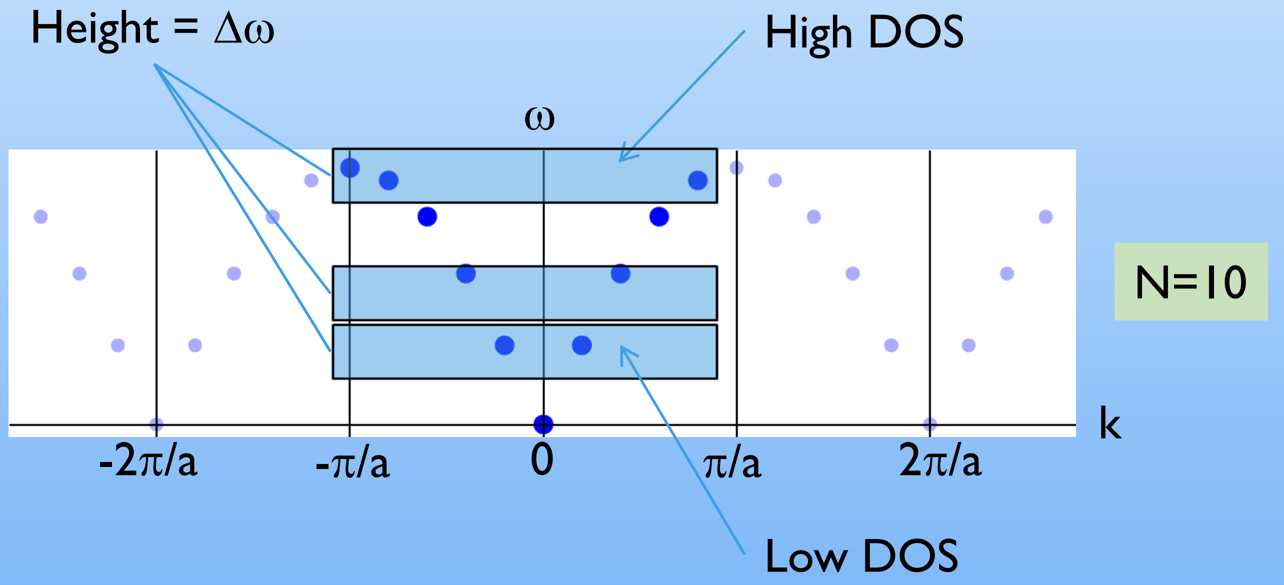
Classical Mech

$$\int_0^{k_B T} dT\, C = \int_0^{k_B T} dT\, \hbar\omega\frac{\partial n(\omega,T)}{\partial T} = \hbar\omega[n(\omega,T) - n(\omega,T=0)] \to k_B T - \frac{1}{2}\hbar\omega = \text{classical energy} - \frac{1}{2}\hbar\omega$$ as $\frac{k_B T}{\hbar\omega} \to \infty$

Thus, $\int_0^{\infty} dT\, C_{classical} - \int_0^{\infty} dT\, C_{quantum} = \frac{1}{2}\hbar\omega$

Density of States (DOS)

- For a given constant $\Delta\omega$, the number of available quantum states = number of blue dots = Density of States

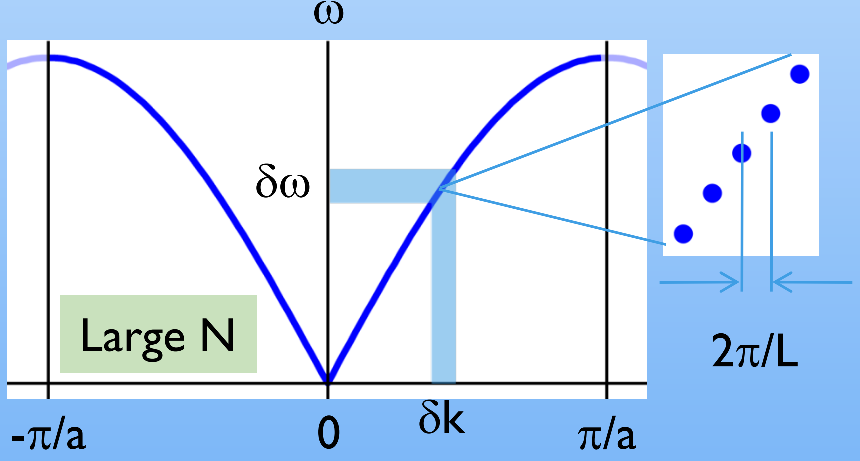


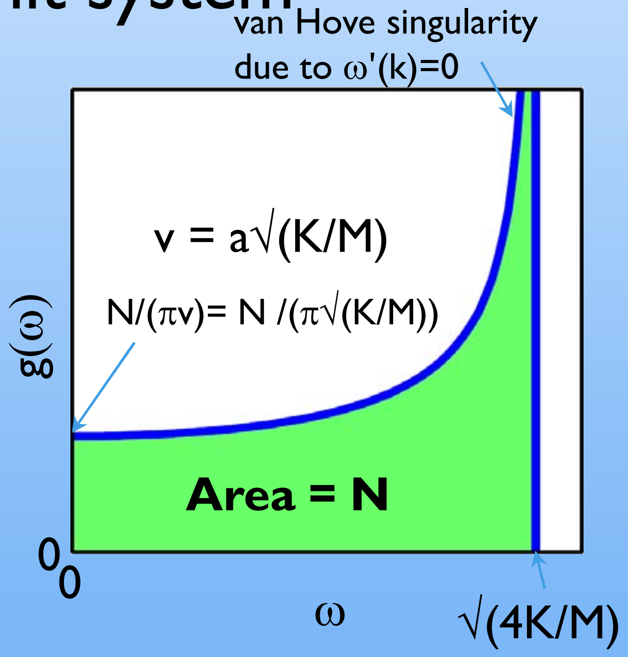
Density of States (DOS)
1d example

- Given $\omega = \omega(k)$, # of quantum states for $\delta\omega$

  $= \delta k \cdot 2 / (2\pi/L)$

  $= (\delta k/\delta\omega) \cdot \delta\omega \cdot L/\pi \equiv \boxed{g(\omega)}\, \delta\omega$
- $g(\omega) \equiv$ DOS per unit energy and unit system "volume" $= 1/(\pi \boxed{\omega'(k)})$

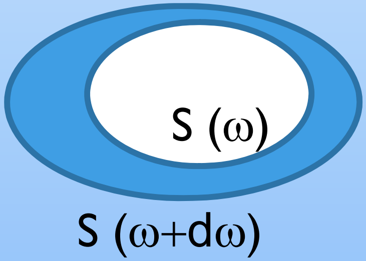




Density of States (DOS) General Formula

$$g(\omega) = \sum_s \int \frac{d\mathbf{k}}{(2\pi)^3}\, \delta(\omega - \omega_s(\mathbf{k})).$$

$$g(\omega) = \sum_s \int \frac{dS}{(2\pi)^3} \frac{1}{|\nabla\omega_s(\mathbf{k})|},$$



s – branch index
S (**k**, ω) – constant energy surface $\omega_s(\mathbf{k}) = \omega$.

DOS
3d example (Debye Model)

- Special case of $\omega = vk$ where $k = |\mathbf{k}|$

  (Easily generalized to $\omega = \omega(k)$)
- Number of states in small volume element in **k** space = $\delta k_x \delta k_y \delta k_z / (2\pi/L)^3 = \delta(\cos\theta)\delta\phi\delta k/(2\pi/L)^3 = \delta(\cos\theta)\delta\phi k^2 \delta k \, V/(2\pi)^3$ $(V=L^3)$
- To calculate DOS, note that ω depends only on k, $\delta\omega = v\,\delta k$. I.e., integrate over θ, ϕ.

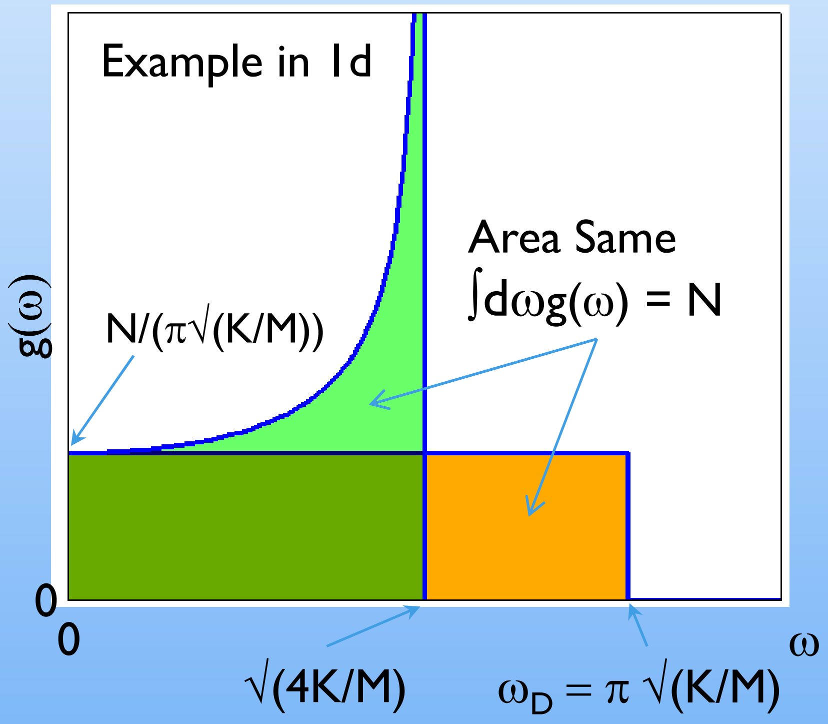
  $g(\omega)\delta\omega = 4\pi k^2 \delta k \, V/(2\pi)^3 = \omega^2 \delta\omega V/(2\pi^2 v^3)$
- Now consider 1 longitudinal and 2 transverse:

  $g(\omega) = V\omega^2(1/v_L{}^3 + 2/v_T{}^3)/(2\pi^2)$
- Determine ω_D from $\int_0^{\omega_D} d\omega \, g(\omega) = 3N$

  (N = # of primitive lattice points)

Debye Model

- $\omega = vk$
- ω_D (Debye Frequency) is determined by $\int_0^{\omega_D} d\omega\, g(\omega) = 3N$ (or dN)
- θ_D (Debye Temperature)
  $k_B \theta_D = \hbar \omega_D$
  165 K for Au,
  2200 K for Diamond,
  Generally, 10~100 meV
  (Remember 300 K = 26 meV)



Notations:
v = c_s in A&M
C = c_vV in A&M

Debye Model in 3D – Math

In the Einstein model, we saw that for a single mode ω, Energy $= \frac{1}{2}\hbar\omega + \hbar\omega \cdot n(\omega)$

In the Debye model, a continuous distribution of modes from energy 0 to ω_D.

$$g(\omega) = \frac{V\omega^2}{2\pi^2}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right) = \frac{3}{2\pi^2}\frac{V\omega^2}{\tilde{v}^3} \qquad \int_0^{\omega_D} d\omega g(\omega) = 3N \qquad \frac{3}{2\pi^2}\frac{V}{\tilde{v}^3}\frac{\omega_D^3}{3} = 3N \qquad \boxed{g(\omega) = \frac{9N}{\omega_D^3}\omega^2}$$

$$\omega_D = \tilde{v}\,\sqrt[3]{6\pi^2 N/V}$$

$n(\omega,T)$ = Bose-Einstein function

$$E = \int_0^{\omega_D} d\omega\, g(\omega)\left(\frac{1}{2}\hbar\omega + \hbar\omega\, n(\omega,T)\right) = E_0 + \frac{9N}{\omega_D^3}\hbar\int_0^{\omega_D} d\omega\, \omega^3\, n\left(\frac{\hbar\omega}{k_B T}\right) \qquad E_0 = \frac{9}{8}N\hbar\omega_D$$

$$\boxed{E - E_0 = 9N\frac{(k_B T)^4}{(\hbar\omega_D)^3}\int_0^{\frac{\theta_D}{T}} dx\, x^3\, n(x) = 9Nk_B T\left(\frac{T}{\theta_D}\right)^3\int_0^{\frac{\theta_D}{T}} dx\, x^3\, n(x)} \quad \boxed{C = \frac{\partial E}{\partial T}}$$

Heat Capacity

$$\boxed{N_{ph} = \int_0^{\omega_D} d\omega\, g(\omega) n\left(\frac{\hbar\omega}{k_B T}\right) = \frac{9N}{\omega_D^3}\int_0^{\omega_D} d\omega\, \omega^2\, n\left(\frac{\hbar\omega}{k_B T}\right) = 9N\left(\frac{T}{\theta_D}\right)^3\int_0^{\frac{\theta_D}{T}} dx\, x^2\, n(x)}$$

Number of Phonons

$$\frac{\theta_D}{T} \to \infty \qquad E - E_0 \approx \frac{3\pi^4}{5}N\left(\frac{T}{\theta_D}\right)^3 k_B T \qquad \boxed{C \approx \frac{12\pi^4}{5}N\left(\frac{T}{\theta_D}\right)^3 k_B} \qquad N_{ph} \approx 18c_A N\left(\frac{T}{\theta_D}\right)^3$$

Low T

$$\int_0^\infty dx\, x^3\frac{1}{e^x - 1} = \frac{\pi^4}{15}$$

Deby T^3 low

$$\int_0^\infty dx\, x^2\frac{1}{e^x - 1} = 2.404\ldots \equiv 2c_A$$

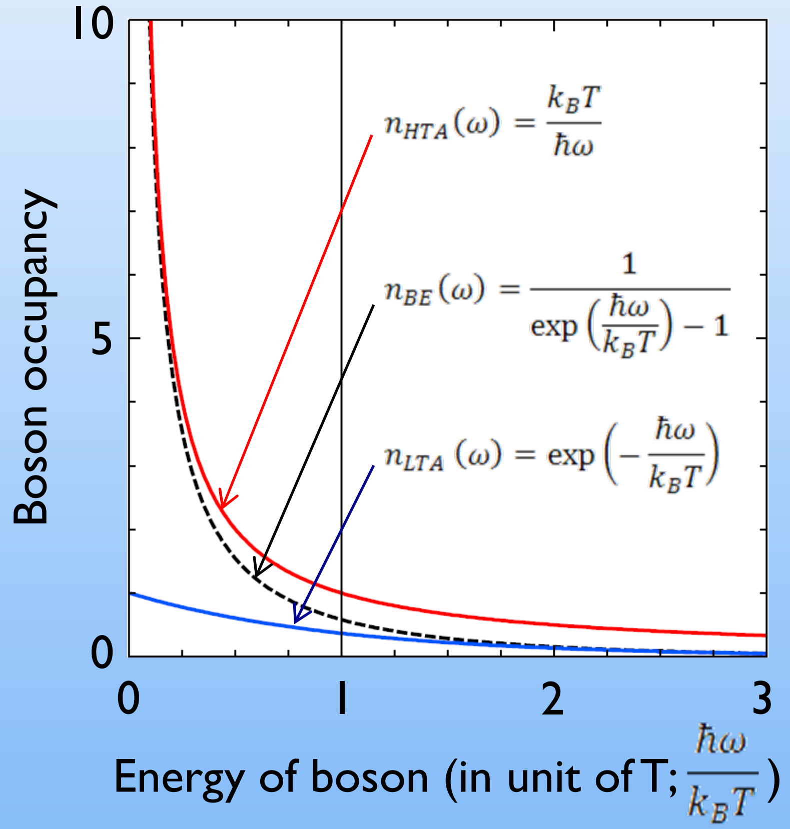
$$\frac{\theta_D}{T} \to 0 \qquad E - E_0 \approx 3Nk_B T \qquad C \approx 3Nk_B \qquad N_{ph} \approx \frac{9}{2}N\frac{T}{\theta_D}$$

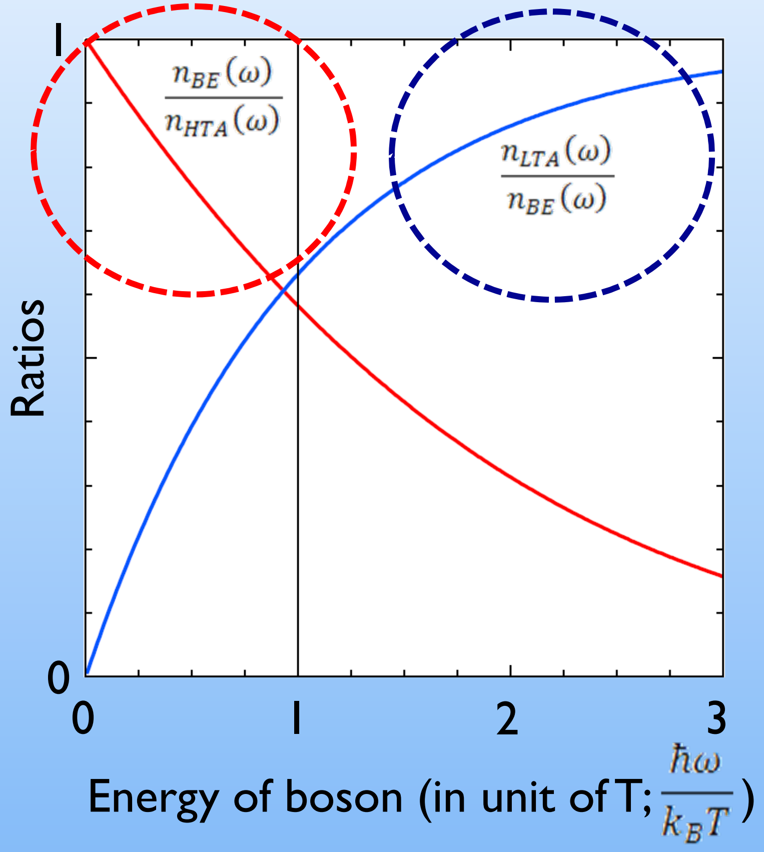
High T

$$n(x) \approx \frac{1}{x} \qquad \int_0^{\frac{\theta_D}{T}} dx\, x^3\, n(x) \approx \int_0^{\frac{\theta_D}{T}} dx\, x^2 = \frac{1}{3}\left(\frac{\theta_D}{T}\right)^3$$

$$\int_0^{\frac{\theta_D}{T}} dx\, x^2\, n(x) \approx \int_0^{\frac{\theta_D}{T}} dx\, x = \frac{1}{2}\left(\frac{\theta_D}{T}\right)^2$$

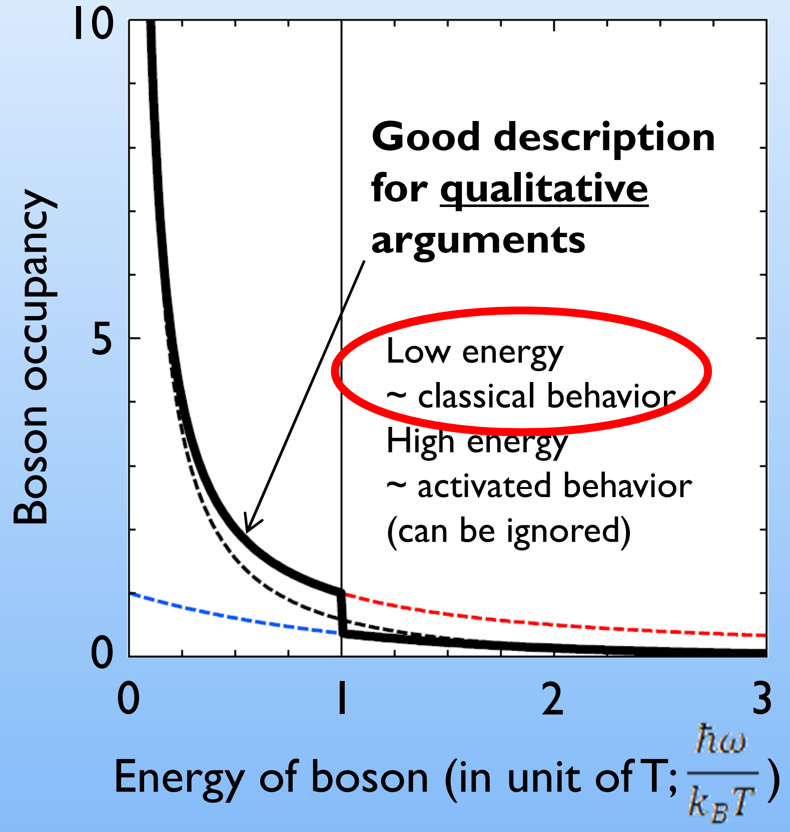
Qualitative Inspection of Bose-Einstein Distribution Function





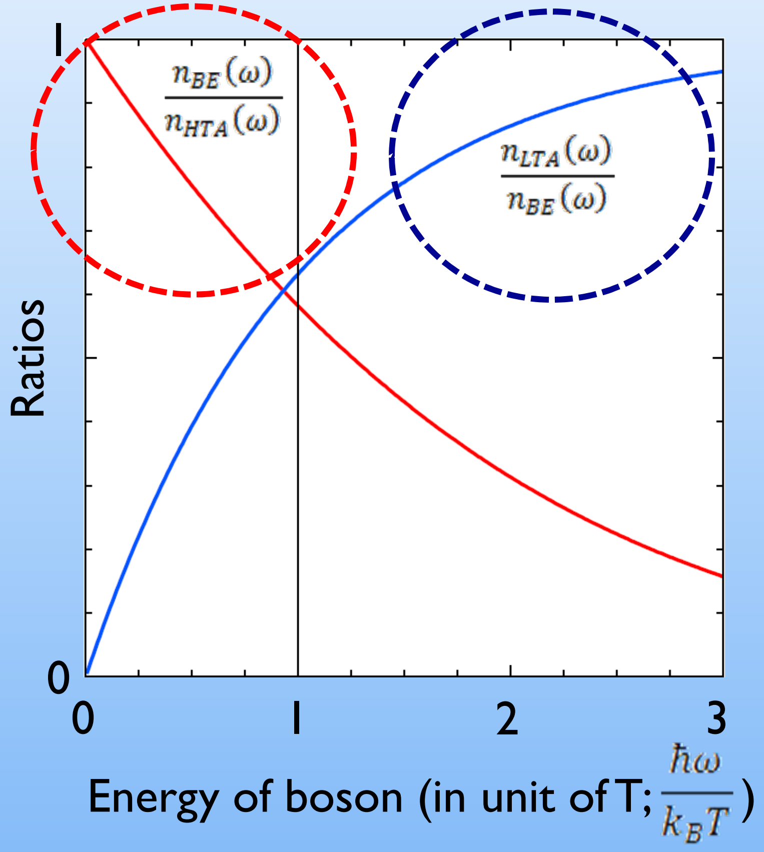
HTA=high temperature approx.
LTA = low temperature approx.

Qualitative Inspection of Bose-Einstein Distribution Function



Good description for qualitative arguments

Low energy
~ classical behavior
High energy
~ activated behavior
(can be ignored)

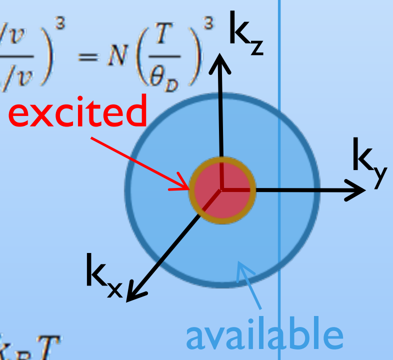


As long as classical phonons exist ($\omega < T$), they determine the thermodynamics.

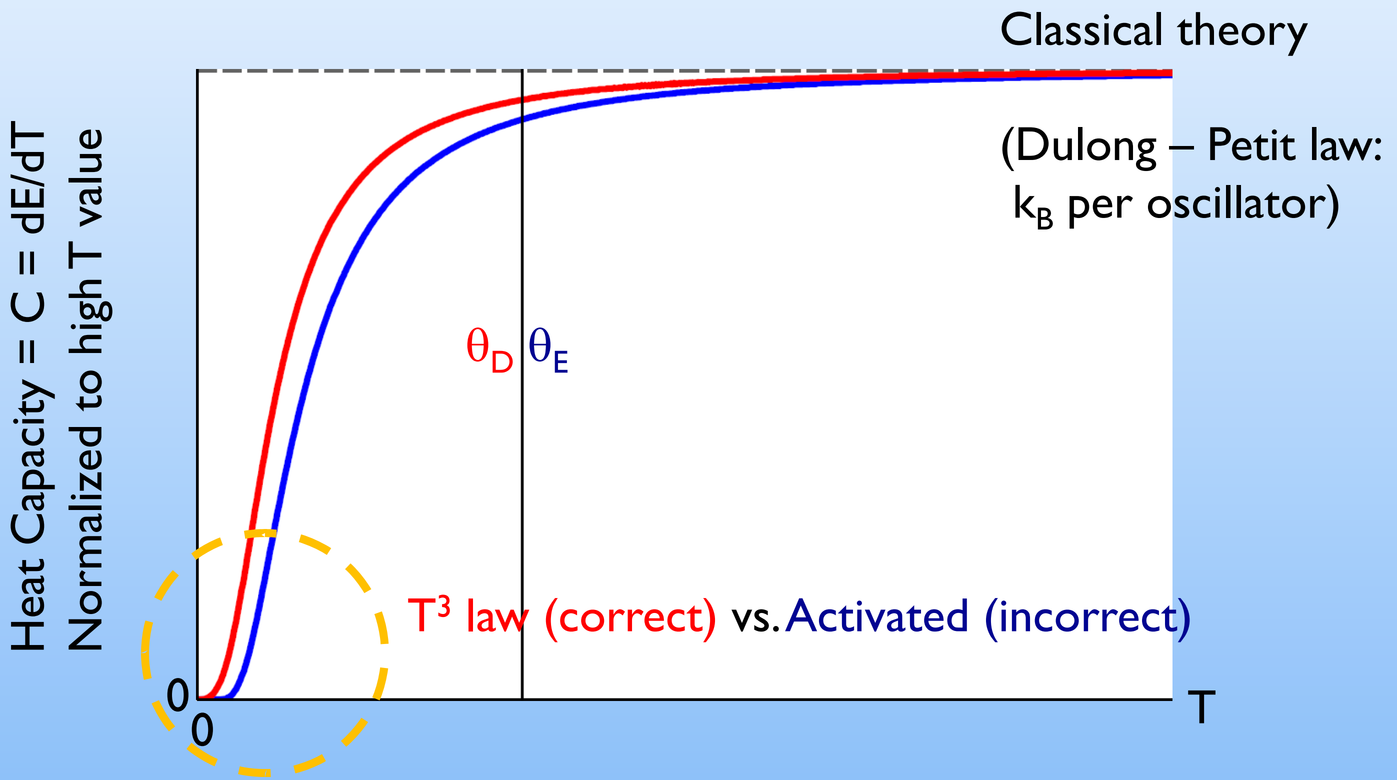
Debye Model in 3D – Physics

To a first approximation, a phonon is not excited at all (if $\omega < \omega_D$) or excited ($\omega > \omega_D$).
All numerical factors (3, π and so on) are omitted below.

	Low T ($T \ll \theta_D$)	High T ($T \gg \theta_D$)
(1) Equi-partition energy	k_BT	k_BT
(2) Number of excited phonon modes	$N\left(\frac{k_{thermal}}{k_{Debye}}\right)^3 \sim N\left(\frac{k_BT/v}{k_B\theta_D/v}\right)^3 = N\left(\frac{T}{\theta_D}\right)^3$	N
(3) Characteristic eigen-energy of excited phonons	k_BT	$k_B\theta_D$
E = (1) x (2)	$N\left(\frac{T}{\theta_D}\right)^3 k_BT$	Nk_BT
C = dE/dT	$N\left(\frac{T}{\theta_D}\right)^3 k_B$	Nk_B
N_{ph} = E / (3)	$N\left(\frac{T}{\theta_D}\right)^3$	$N\frac{T}{\theta_D}$



Debye and Einstein - Comparison



Classical theory

(Dulong – Petit law:
k_B per oscillator)

T^3 law (correct) vs. Activated (incorrect)

Warning: θ_D and θ_E are generally different – here they are taken to be the same just for the comparison of the form of C. Generally $\theta_E > \theta_D$.