

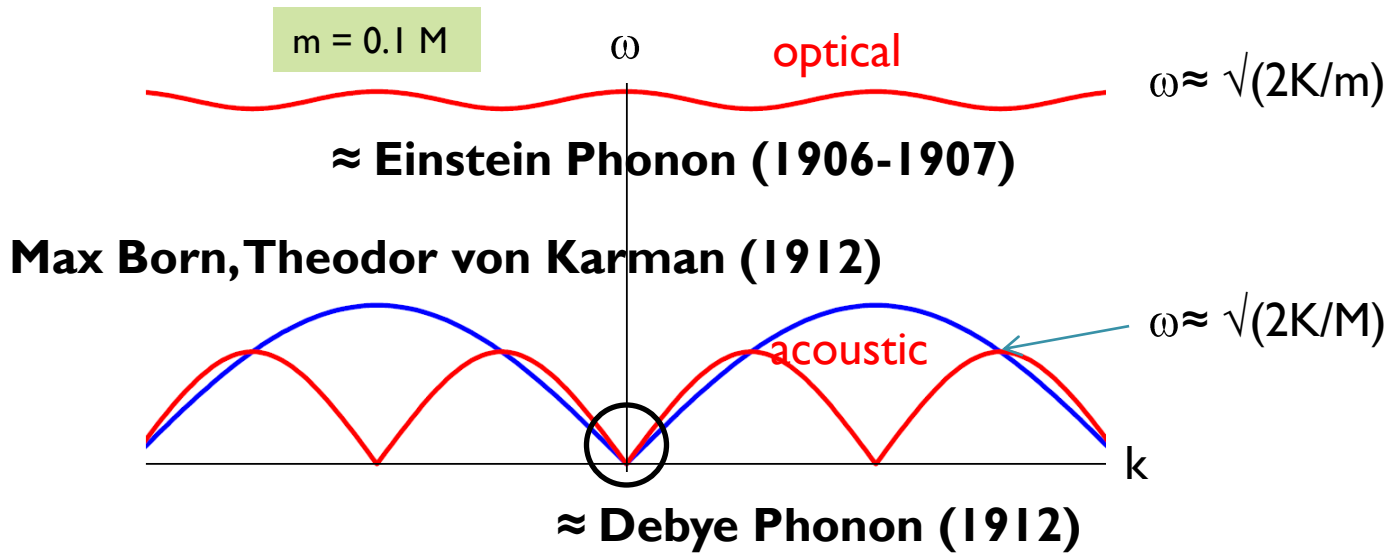
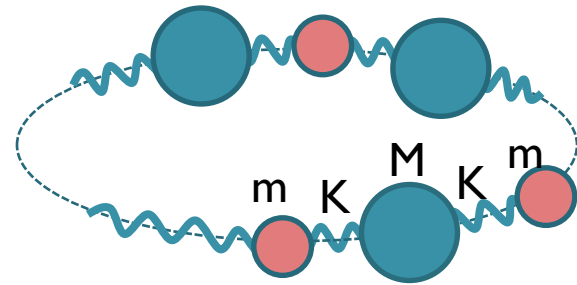


Lecture 4

Phonon Dynamics

It's a little like photons.

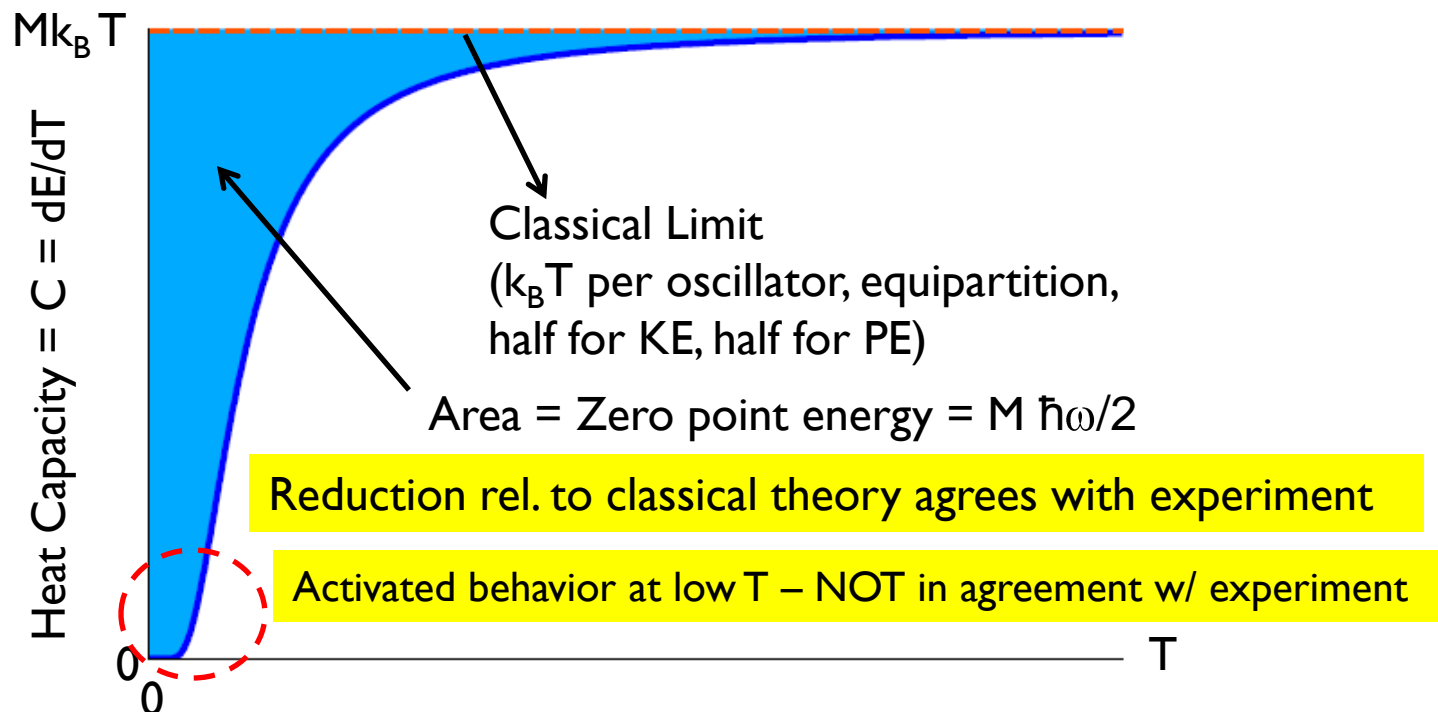
How phonons came to be



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

Thermodynamics of Einstein Phonon

- Single frequency mode per lattice point and no coupling between neighboring mode $\rightarrow \omega$ is independent of k (“dispersion-less”)
- Just treat like M independent oscillators.



Einstein Phonon Problem (M=1)

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

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

$n(\omega)$: Bose Einstein Func

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

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

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 $\beta \hbar \omega \rightarrow 0$

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

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

$$C \approx k_B$$

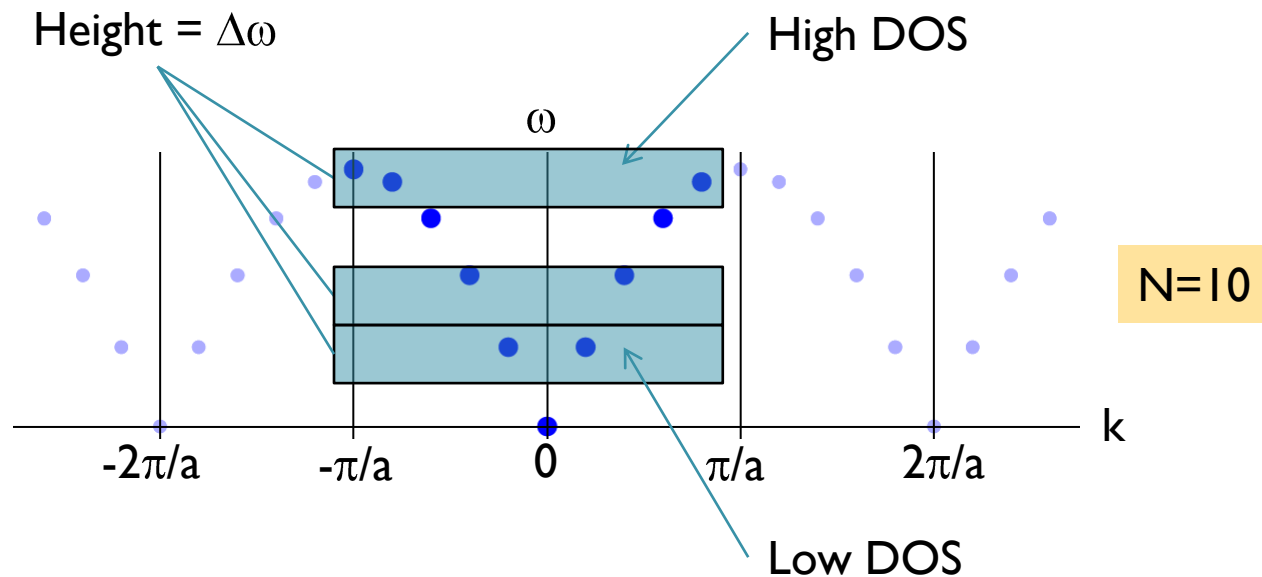
Classical Mech

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

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

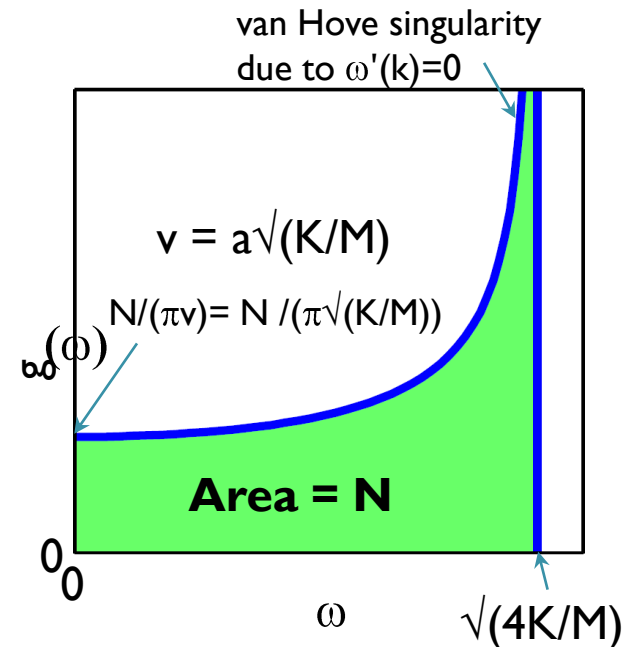
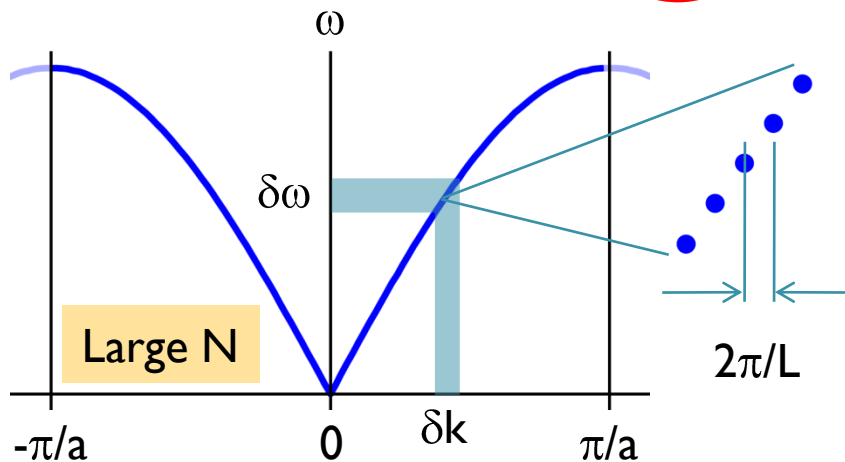
Density of States (DOS)

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



Density of States (DOS)

- Given $\omega = \omega(k)$, # of quantum states for $\delta\omega$
 $= \delta k \cdot 2 / (2\pi/L)$
 $= (\delta k / \delta\omega) \cdot \delta\omega \cdot L / \pi \equiv g(\omega) \delta\omega$
- $g(\omega) \equiv$ DOS per unit energy and unit system
 “volume” = $L / (\pi \omega'(k))$



DOS in 3D

- Special case of $\omega = vk$ where $k = |\mathbf{k}|$
(Easily generalized to $\omega = \omega(k)$)
- Number of states in small volume element in \mathbf{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

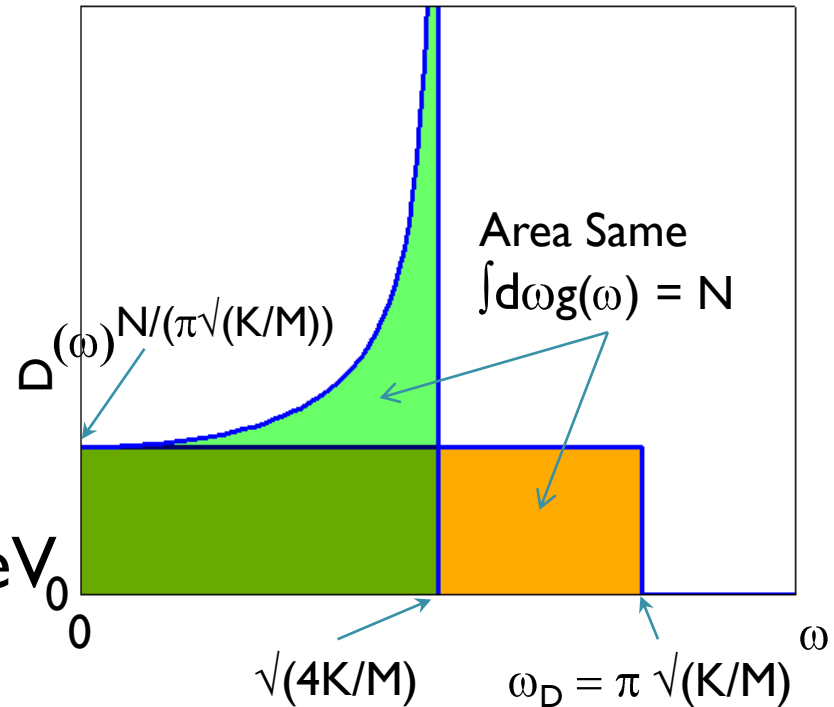
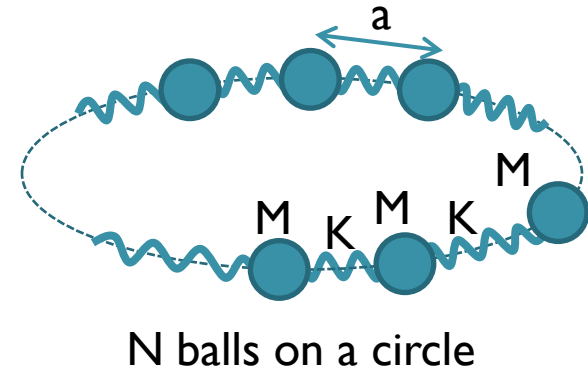
- $\omega = vk$
- ω_D (Debye Frequency) is determined by

$$\int_0^{\omega_D} d\omega g(\omega) = N$$
- 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 = 25 meV)



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, we need to consider a continuous distribution of modes from energy 0 to ω_D .

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

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

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

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

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

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

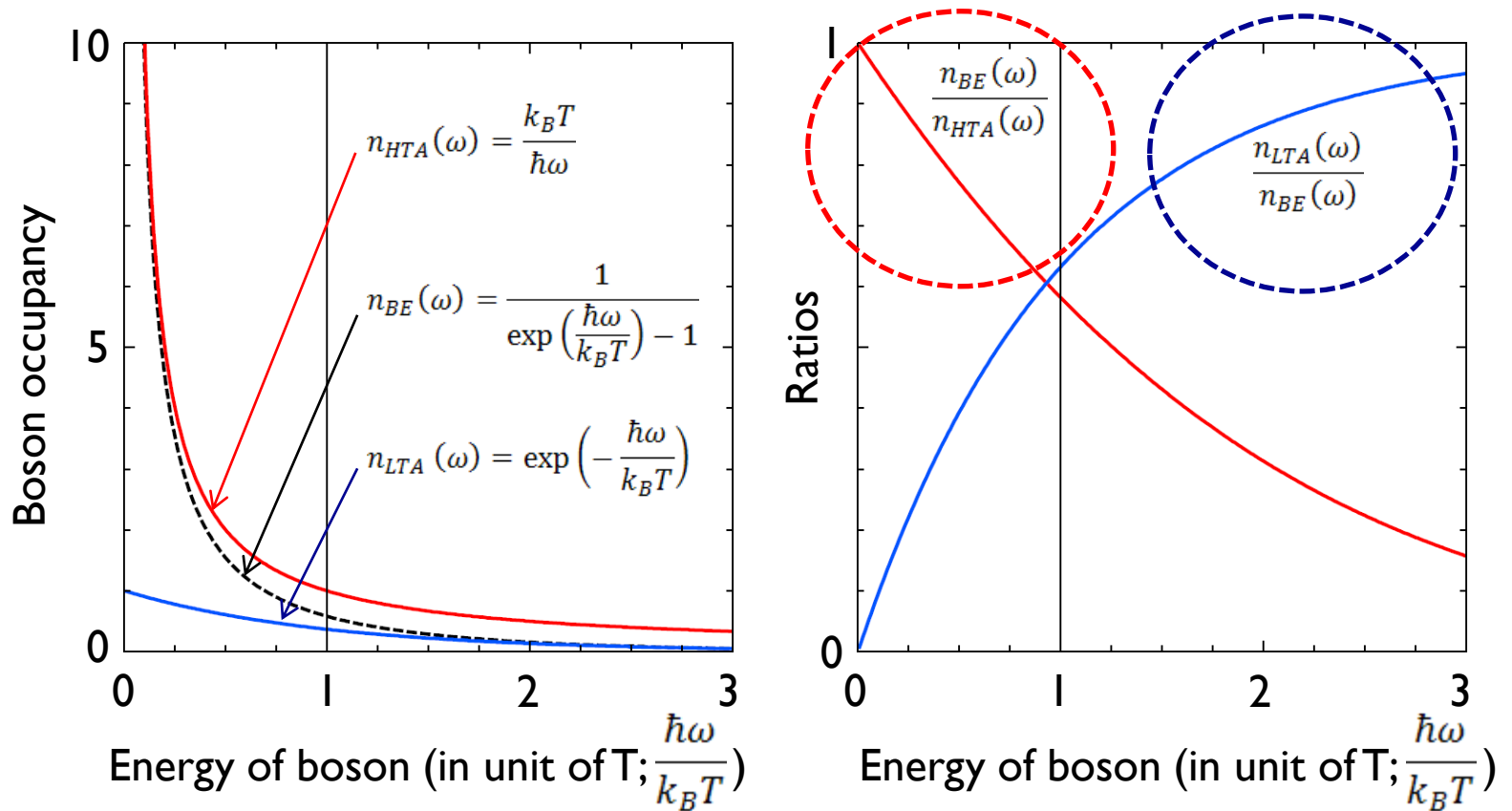
$$\frac{\theta_D}{T} \rightarrow \infty \quad \text{Low T} \quad E - E_0 \approx \frac{3\pi^4}{5} N \left(\frac{T}{\theta_D} \right)^3 k_B T \quad \boxed{C \approx \frac{12\pi^4}{5} N \left(\frac{T}{\theta_D} \right)^3 k_B} \quad N_{ph} \approx 18c_A N \left(\frac{T}{\theta_D} \right)^3$$

$$\int_0^\infty dx x^3 \frac{1}{e^x - 1} = \frac{\pi^4}{15} \quad \text{Deby } T^3 \text{ low} \quad \int_0^\infty dx x^2 \frac{1}{e^x - 1} = 2.404 \dots \equiv 2c_A$$

$$\frac{\theta_D}{T} \rightarrow 0 \quad \text{High T} \quad E - E_0 \approx 3N k_B T \quad C \approx 3N k_B \quad N_{ph} \approx \frac{9}{2} N \frac{T}{\theta_D}$$

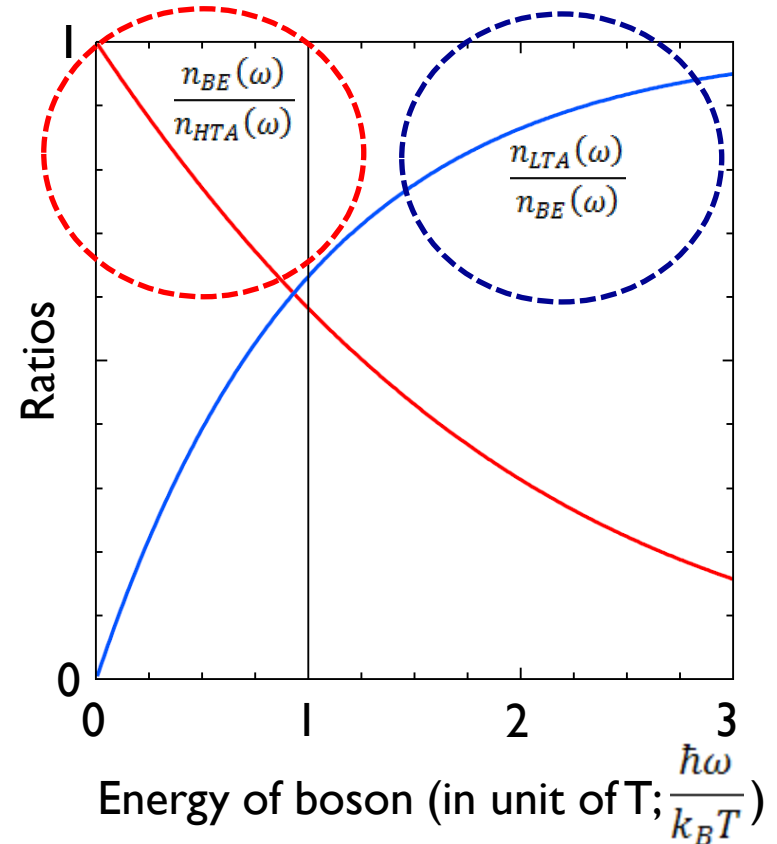
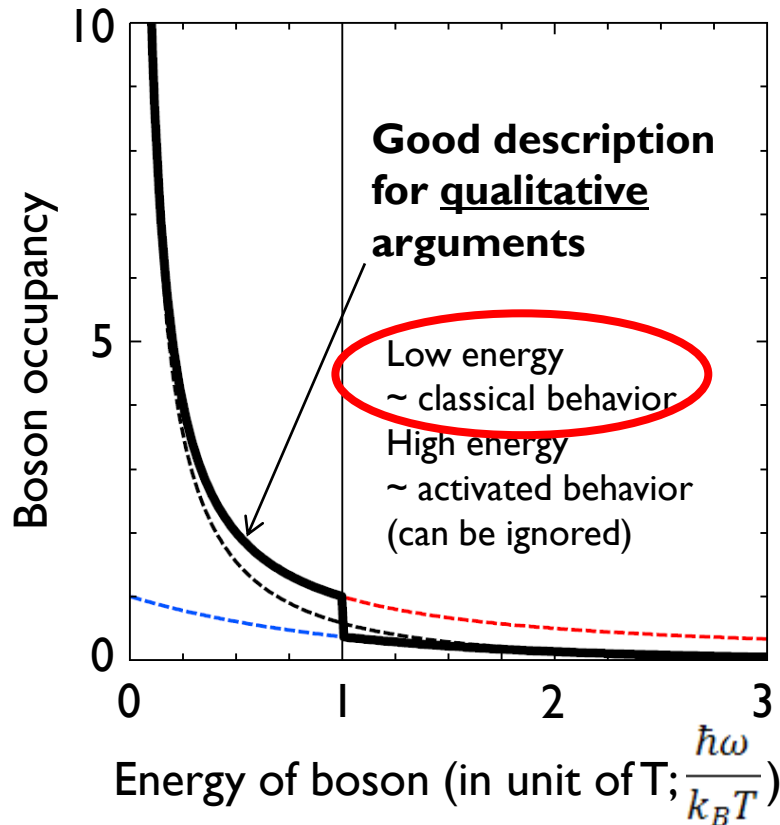
$$n(x) \approx \frac{1}{x} \quad \int_0^{\frac{\theta_D}{T}} dx x^3 n(x) \approx \int_0^{\frac{\theta_D}{T}} dx x^2 = \frac{1}{3} \left(\frac{\theta_D}{T} \right)^3 \quad \int_0^{\frac{\theta_D}{T}} dx x^2 n(x) \approx \int_0^{\frac{\theta_D}{T}} dx x = \frac{1}{2} \left(\frac{\theta_D}{T} \right)^2$$

Qualitative Inspection of Bose-Einstein Distribution Function



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

Qualitative Inspection of Bose-Einstein Distribution Function



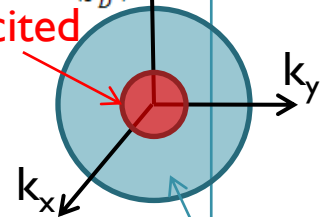
As long as classical phonons exist ($\omega < T$), they determine the thermodynamics.

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.

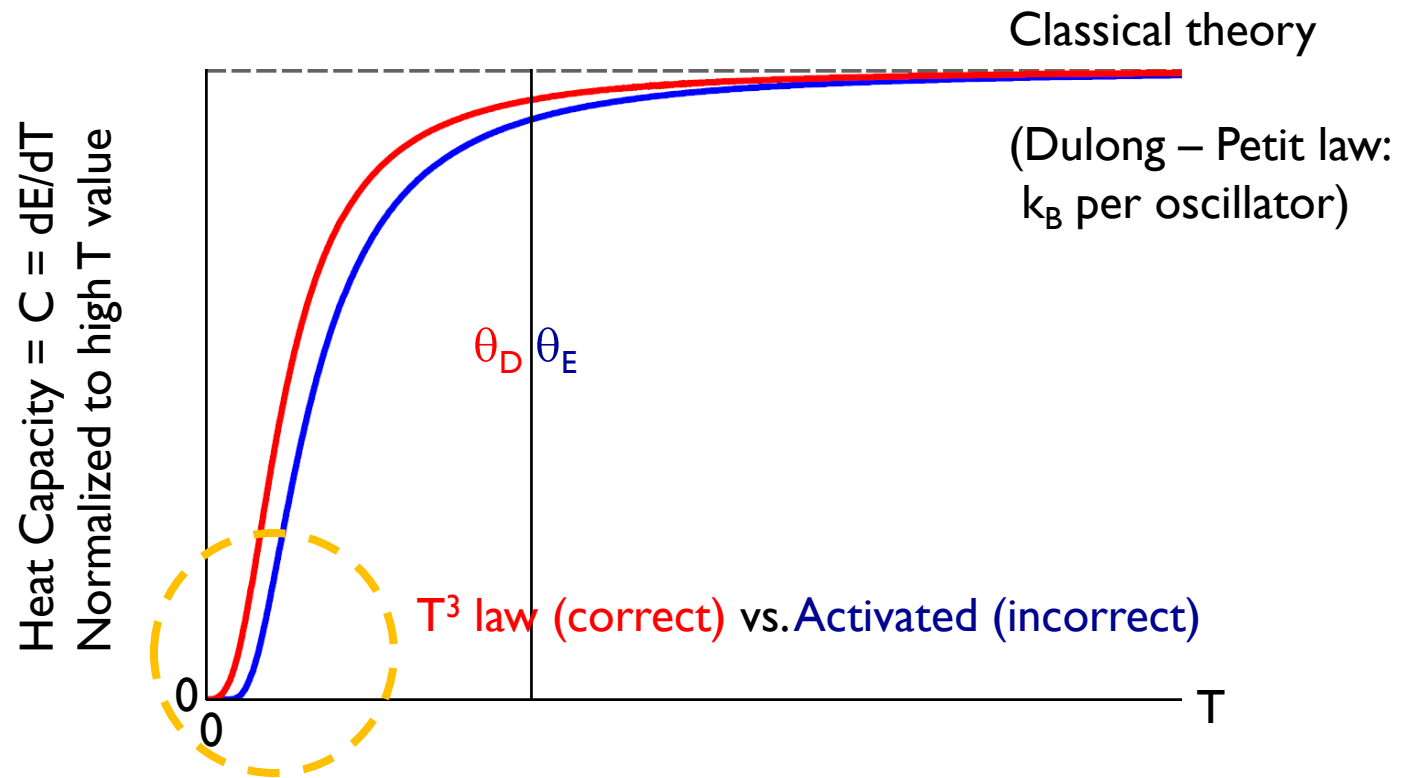
	Low T ($T \ll \theta_D$)	High T ($T \gg \theta_D$)
(1) Equi-partition energy	$k_B T$	$k_B T$
(2) Number of excited phonon modes	$N \left(\frac{k_{thermal}}{k_{Debye}} \right)^3 \sim N \left(\frac{k_B T / v}{k_B \theta_D / v} \right)^3 = N \left(\frac{T}{\theta_D} \right)^3$	N
(3) Characteristic eigen-energy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

excited



available

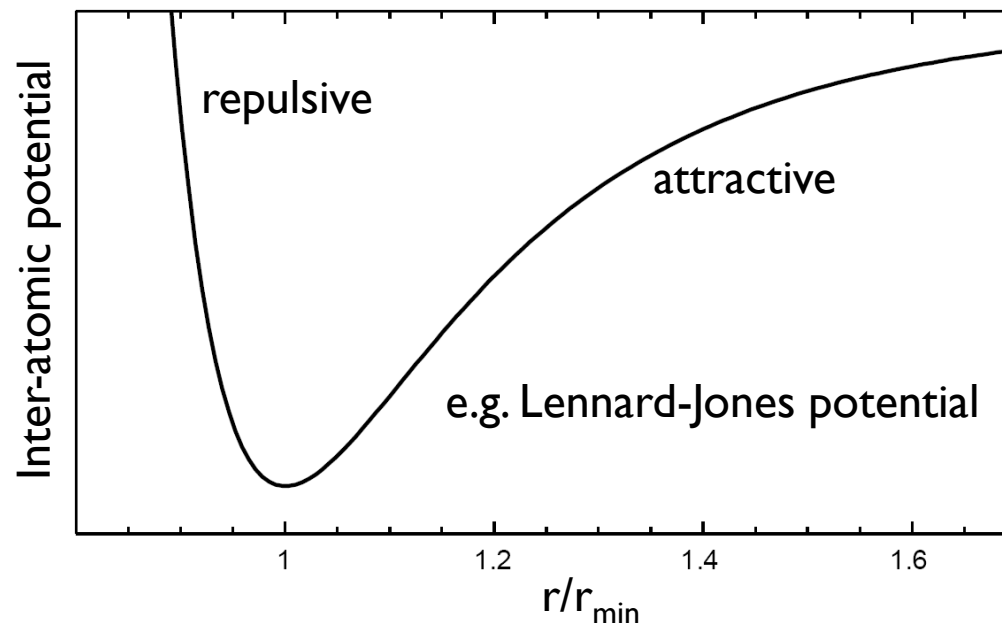
Debye and Einstein - Comparison



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 $\theta_E > \theta_D$.

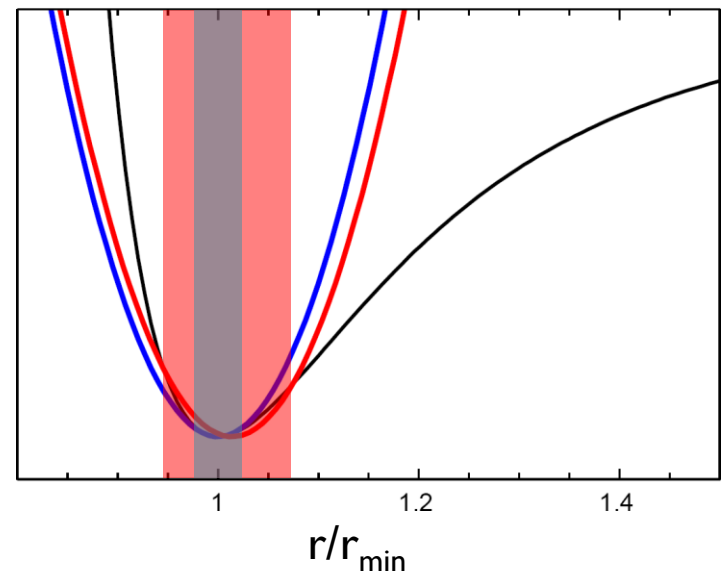
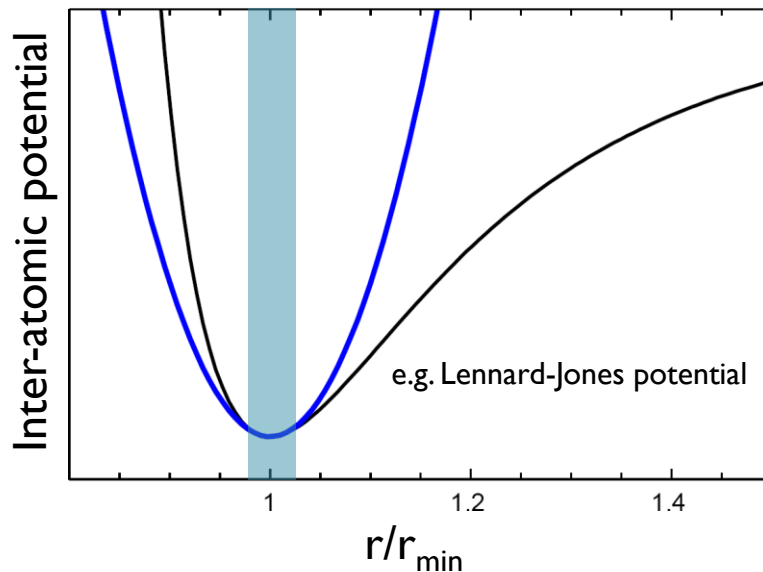
Limits of Harmonic Approximation

- No T-dependence of lattice constant
- Phonon is an exact eigen-state – i.e. infinite thermal conductivity



Limits of Harmonic Approximation

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- Phonon is an exact eigen-state – i.e. infinite thermal conductivity



Thermal Expansion

Thermal Expansion Coefficient $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = -\frac{1}{V} \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{B} \left(\frac{\partial P}{\partial T} \right)_V$

Euler chain rule B: bulk modulus

Sum of all inter-atomic potentials

$$F = E_{pot} - k_B T \sum_{modes} \ln Z \quad Z = \sum_{n=0}^{\infty} \exp \left[-\beta \left(n + \frac{1}{2} \right) \hbar \omega \right] = \frac{\exp(-\frac{1}{2} \beta \hbar \omega)}{1 - \exp(-\beta \hbar \omega)}$$

$$F = E_{pot} + \sum_{modes} \left\{ \frac{1}{2} \hbar \omega + k_B T \ln [1 - \exp(-\beta \hbar \omega)] \right\}$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = - \left(\frac{\partial E_{pot}}{\partial V} \right)_T - \sum_{modes} \hbar \left(\frac{\partial \omega}{\partial V} \right)_T \left\{ \frac{1}{2} + \frac{\exp(-\beta \hbar \omega)}{1 - \exp(-\beta \hbar \omega)} \right\} = - \frac{\partial E_{pot}}{\partial V} - \sum_{modes} \hbar \frac{\partial \omega}{\partial V} \left\{ \frac{1}{2} + \frac{1}{\exp(\beta \hbar \omega) - 1} \right\} = - \frac{\partial E_{pot}}{\partial V} - \sum_{modes} \hbar \frac{\partial \omega}{\partial V} \left\{ \frac{1}{2} + n(\beta \omega) \right\}$$

Gruneisen assumption $\omega \propto V^{-\gamma}$ γ : Gruneisen parameter, 1~3

$$P = - \frac{\partial E_{pot}}{\partial V} - \sum_{modes} \frac{\hbar(-\gamma)\omega}{V} \left\{ \frac{1}{2} + n(\beta \omega) \right\} = - \frac{\partial E_{pot}}{\partial V} + \frac{\gamma}{V} E_{modes} \quad \left(\frac{\partial P}{\partial T} \right)_V = \frac{\gamma}{V} C_V$$

C_V : heat capacity at constant volume

Gruneisen relation $\beta = \frac{\gamma C_V}{BV}$

γ is finite only because of the anharmonic term

γ from interatomic potential $U(r)$ and spring constant K

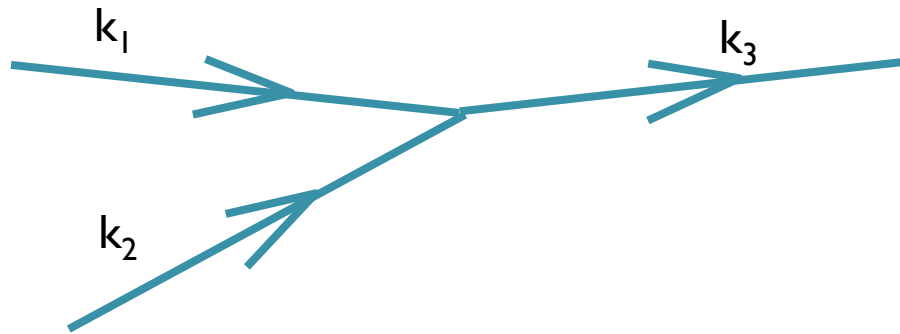
$$U(r) = U(a) + \frac{(r-a)^2}{2} U''(a) + \frac{(r-a)^3}{6} U'''(a) + \dots$$

$$K(a') = U''(a') = U''(a) + (a' - a) U'''(a) + \dots$$

$\omega \propto \sqrt{K} \quad V \propto a^3$

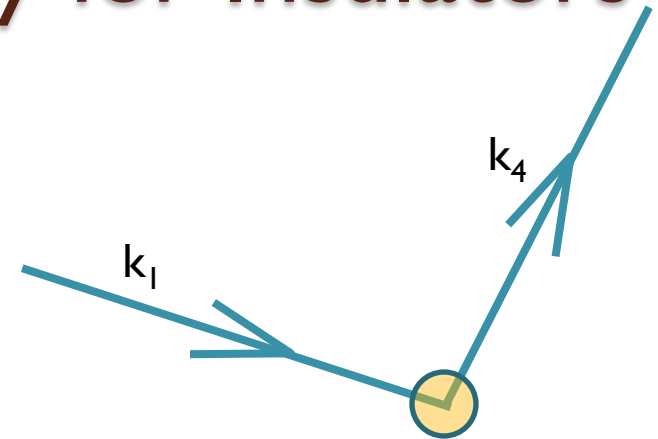
$$\gamma = - \frac{d \ln \omega}{d \ln V} = - \frac{1}{2} \frac{d \ln K}{d \ln a} = - \frac{a}{6K} \frac{dK}{da} \approx - \frac{a U'''(a)}{6 U''(a)}$$

Thermal Conductivity for Insulators



Phonon-Phonon Scattering

- By convention, k_1 and k_2 are taken within one BZ.
- If $k_3 = k_1 + k_2$ ends up in the other BZ, then the process is called “Umklapp process”
- **Only Umklapp** changes the total momentum – **source for finite conductivity.**



Phonon-Impurity Scattering

- Momentum changing and thus source for finite conductivity also
- Important only when wave-vector of phonon is large.

Thermal Conductivity for Insulators

$$\text{Heat current} = -\frac{1}{3} v l \frac{d(\frac{E}{V})}{dz} = -\frac{1}{3} v l \frac{dE}{V dT} \frac{dT}{dz} \equiv -\kappa \frac{dT}{dz}$$

Thermal conductivity $\kappa = \frac{1}{3} v l \frac{C}{V}$

Sound velocity \swarrow
 Phonon mean free path \nearrow
 Phonon heat capacity \nearrow

	Mean free path	Heat capacity	Thermal Conductivity
High T	$\propto 1/T$ due to N_{ph}	Nk_B	$\propto 1/T$
Intermediate T	$\exp(O(\theta_D)/T)$	--	$\exp(O(\theta_D)/T)$
Low T	sample size	$Nk_B(T/\theta_D)^3$	$\propto T^3$