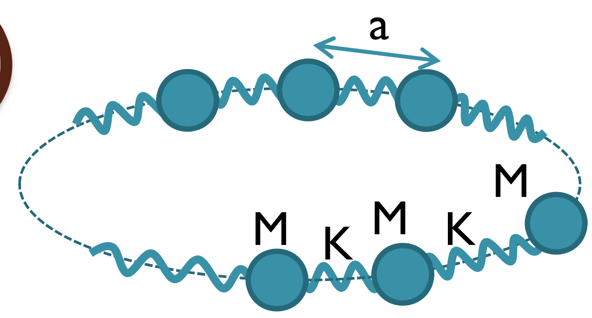
Lecture 7

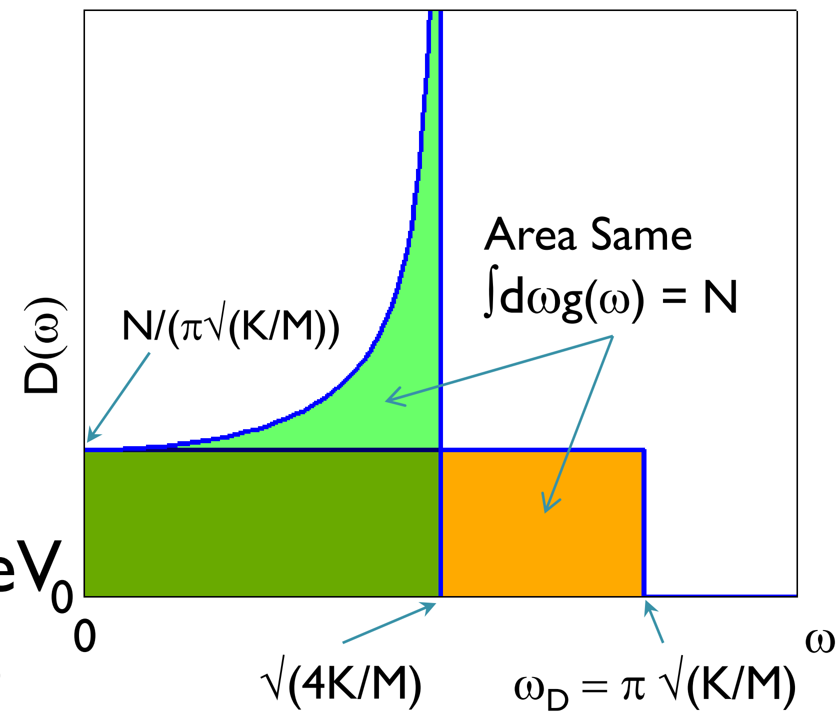
Phonon Dynamics (continued)

Debye Model (1D)

- $\omega = vk$
- 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)



N balls on a circle



Debye Model (3D)

- Obtain g(ω), considering all three acoustic branches

$$g(\omega) = \frac{V\omega^2}{2\pi^2}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right) = \frac{3}{2\pi^2}\frac{V\omega^2}{\tilde{v}^3}$$

$$\int_0^{\omega_D} d\omega g(\omega) = 3N$$

N = number of p. B.L. points (unit cells)

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

$$\boxed{g(\omega) = \frac{9N}{\omega_D^3}\omega^2}$$

- Do Stat-Mechanics, like for photons
- Keep in mind that the number of phonons is un-restricted as in the case of photons

Debye Model in 3D – Math

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

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

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

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

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

$\frac{\theta_D}{T} \to \infty$ **Low T**

$$E - E_0 \approx \frac{3\pi^4}{5} N\left(\frac{T}{\theta_D}\right)^3 k_B T \qquad \int_0^\infty dx\, x^3 \frac{1}{e^x - 1} = \frac{\pi^4}{15}$$

$$C \approx \frac{12\pi^4}{5} N\left(\frac{T}{\theta_D}\right)^3 k_B$$

Deby T^3 low

$$N_{ph} \approx 18 c_A N\left(\frac{T}{\theta_D}\right)^3 \qquad \int_0^\infty dx\, x^2 \frac{1}{e^x - 1} = 2.404\ldots \equiv 2c_A$$

$\frac{\theta_D}{T} \to 0$ **High T**

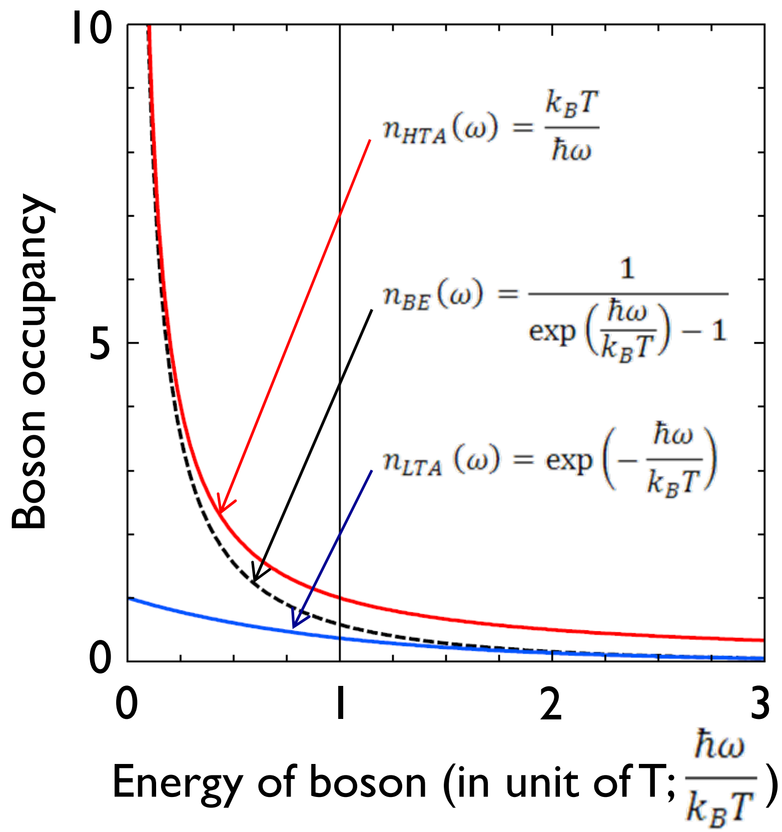
$$E - E_0 \approx 3Nk_BT \qquad n(x) \approx \frac{1}{x} \qquad \int_0^{\frac{\theta_D}{T}} dx\, x^3\, n(x) \approx \int_0^{\frac{\theta_D}{T}} dx\, x^2 = \frac{1}{3}\left(\frac{\theta_D}{T}\right)^3$$

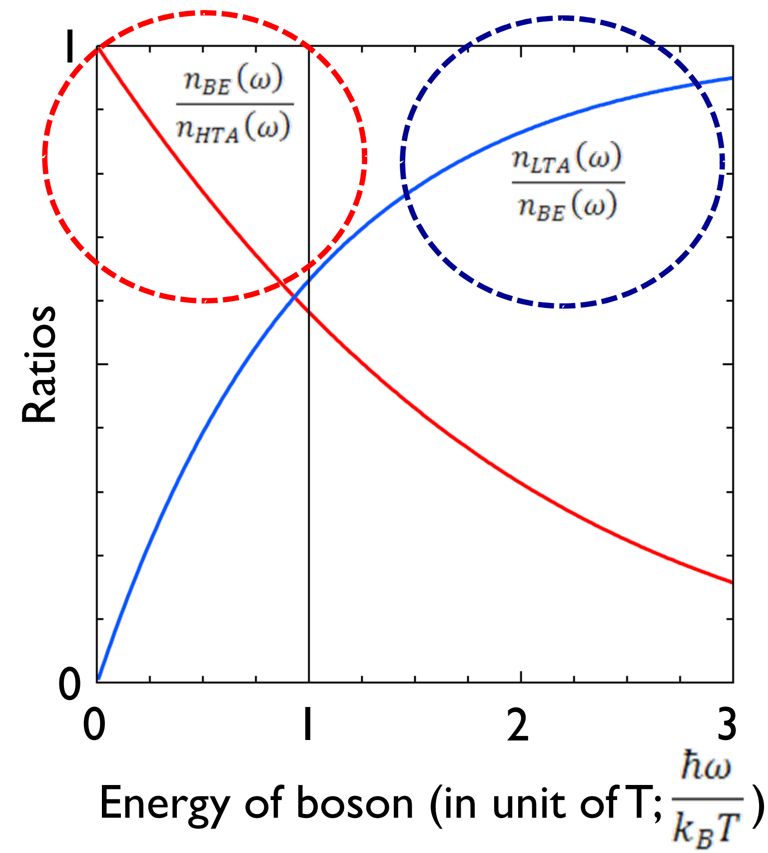
$$C \approx 3Nk_B$$

$$N_{ph} \approx \frac{9}{2} N \frac{T}{\theta_D} \qquad \int_0^{\frac{\theta_D}{T}} dx\, x^2\, n(x) \approx \int_0^{\frac{\theta_D}{T}} dx\, x = \frac{1}{2}\left(\frac{\theta_D}{T}\right)^2$$

But beware of optical phonons at high T

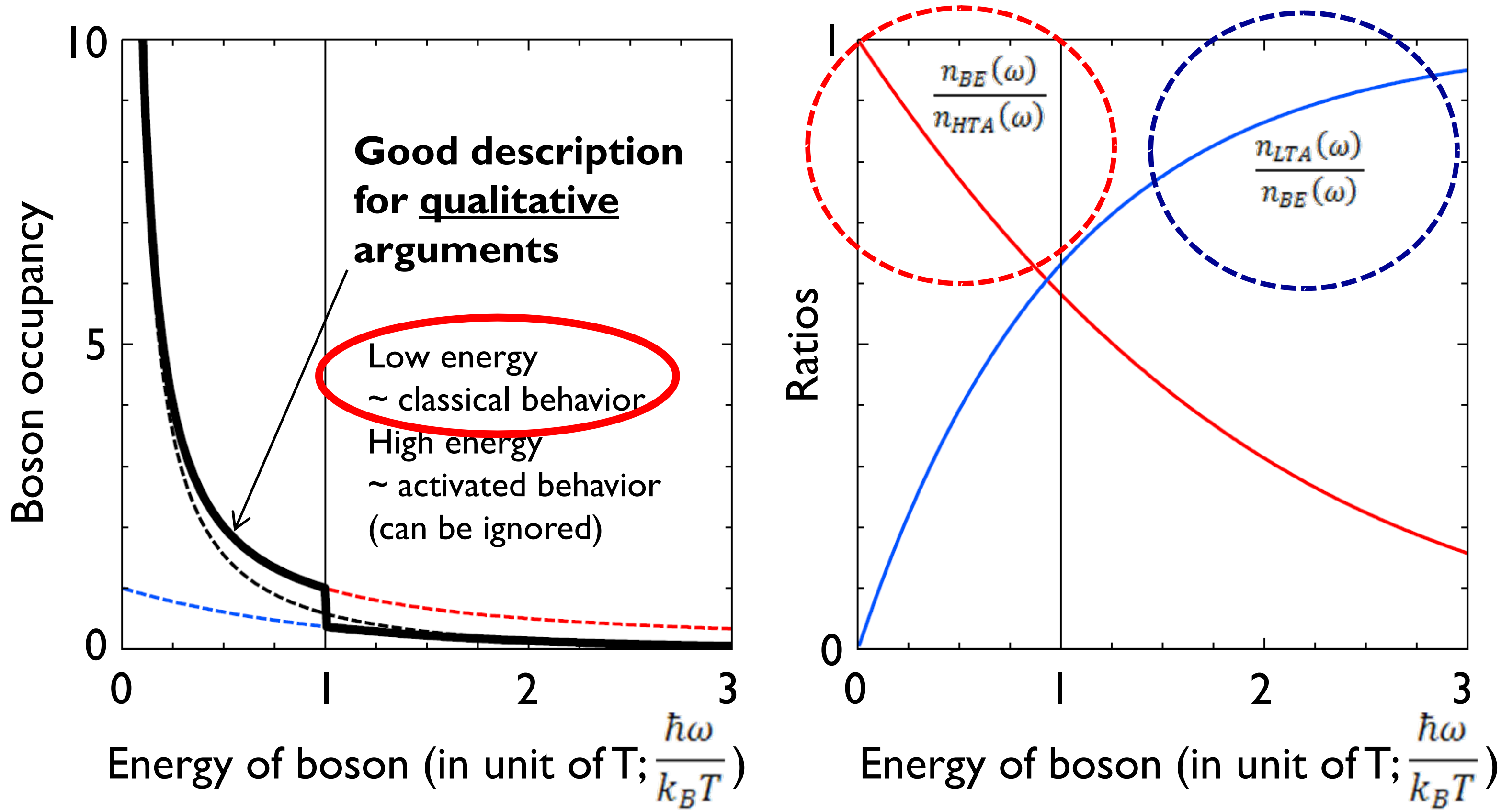
Qualitative Inspection of Bose-Einstein Distribution Function





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

Qualitative Inspection of Bose-Einstein Distribution Function

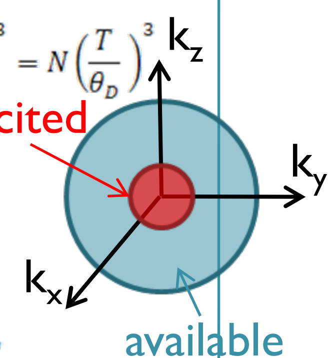


As long as classical phonons exist (ω < T), they determine the thermodynamics.

Debye Model in 3D – Physics

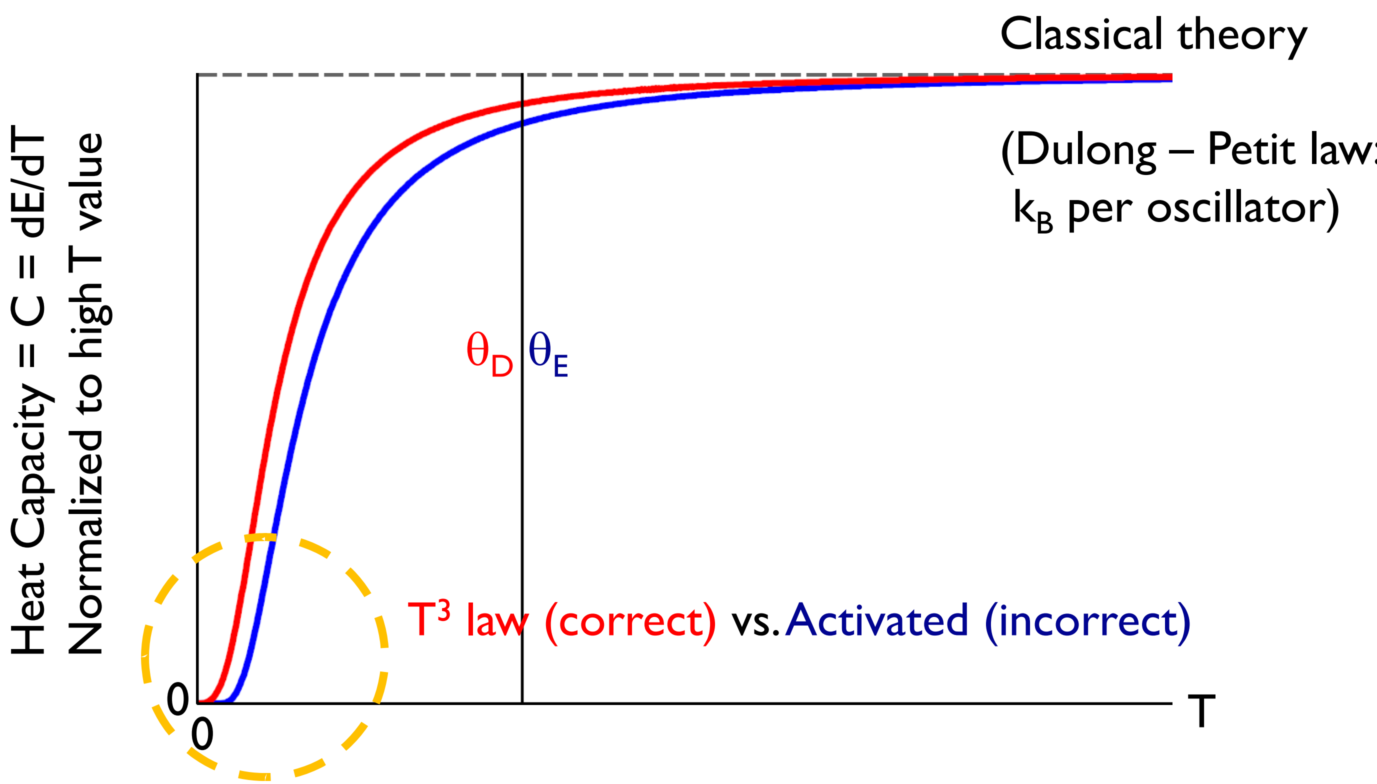
To a first approximation, a phonon is not excited at all (if $\omega < \omega_D$) or excited ($\omega > \omega_D$).
All numerical factors (3, π and so on) are omitted below.

	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) x (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)	$N\left(\frac{T}{\theta_D}\right)^3$	$N\frac{T}{\theta_D}$



IMPORTANT!!

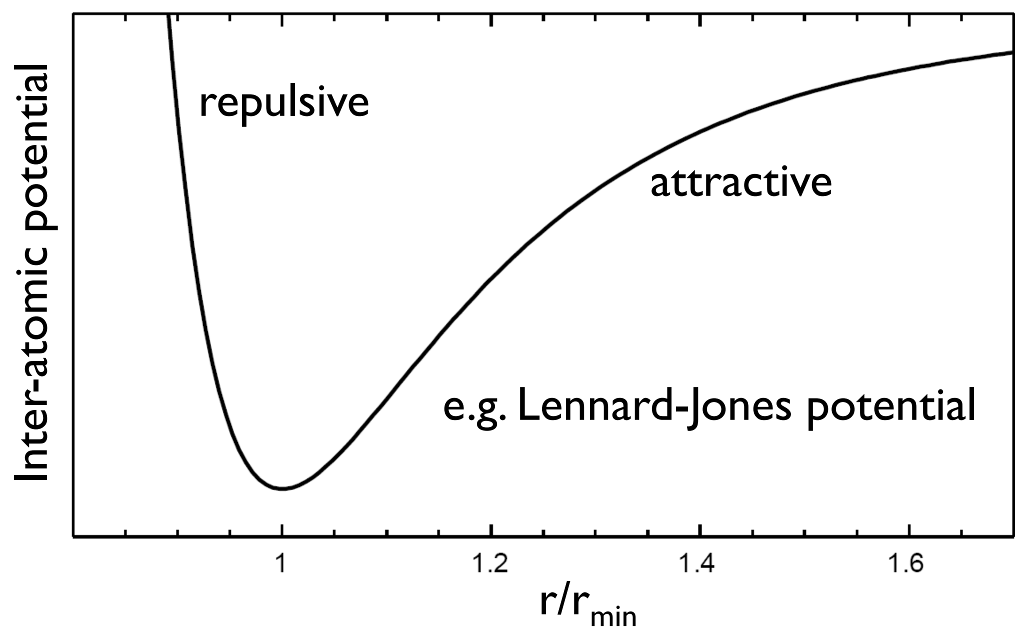
Debye and Einstein - Comparison



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



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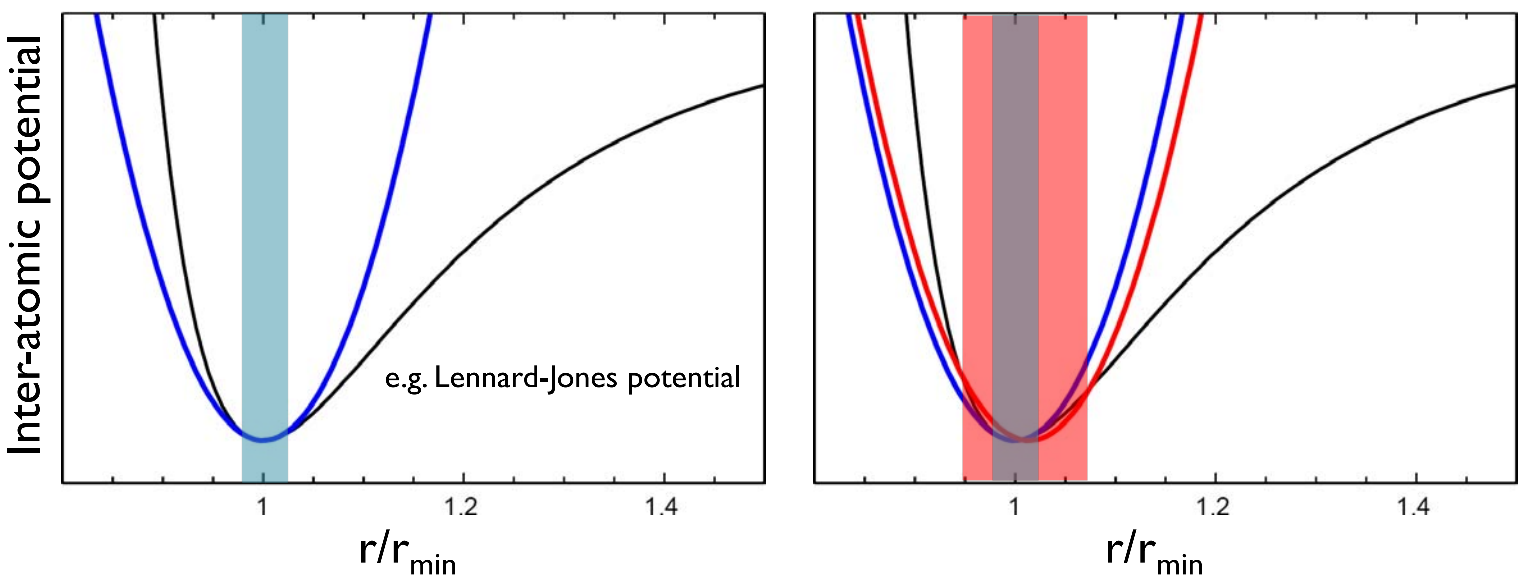


Thermal Expansion

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

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

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

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

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

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

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

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

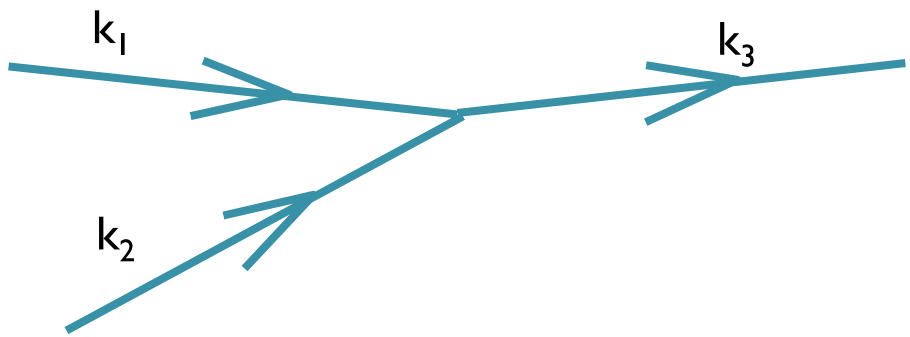
$$K(a') = U''(a') = U''(a) + (a'-a)U'''(a) + \cdots$$

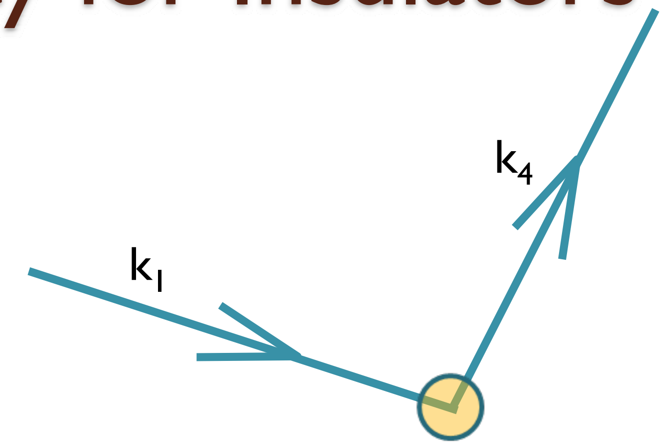
$\omega \propto \sqrt{K} \qquad V \propto a^3$

$$\gamma = -\frac{d\ln\omega}{d\ln V} = -\frac{\frac{1}{2}d\ln K}{3\,d\ln a} = -\frac{a}{6K}\frac{dK}{da} \approx -\frac{aU'''(a)}{6U''(a)}$$

Reading

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

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

Phonon heat capacity

Phonon mean free path

	Mean free path	Heat capacity	Thermal Conductivity
High T	$\propto 1/T$ due to N_{ph}	Nk_B	$\propto 1/T$ ($1/T^x$ x =1..2)
Intermediate T	$\exp(O(\theta_D)/T)$	--	$\exp(O(\theta_D)/T)$
Low T	sample size	$Nk_B(T/\theta_D)^3$	$\propto T^3$