Lecture 7
Beyond Harmonic Phonons

<u>All</u> materials are an-harmonic

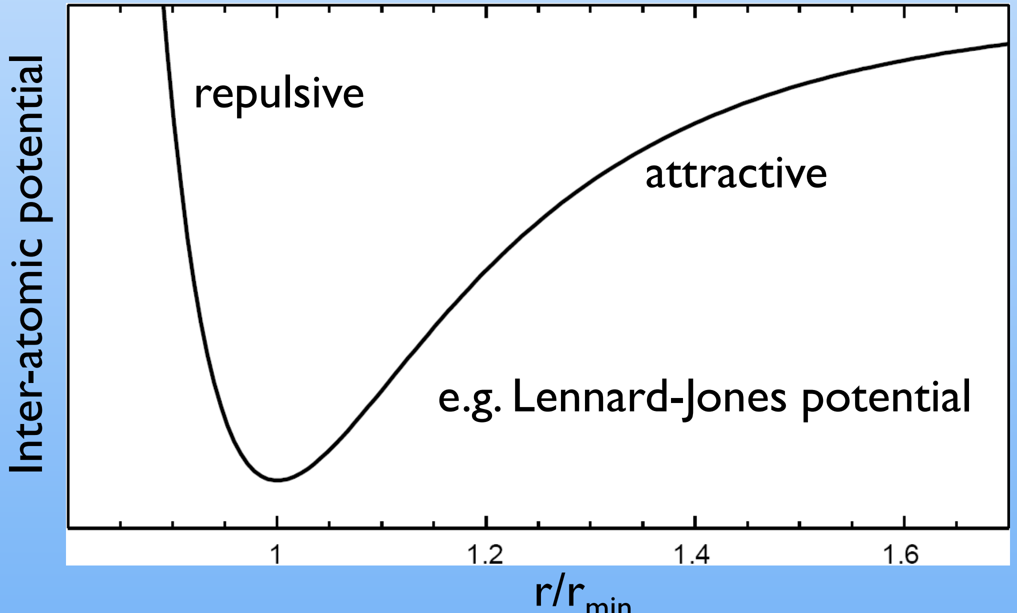
Harmonic Approx is NOT enough

If harmonic approximation was enough …

- No Thermal Expansion
- Infinite thermal conductivity
- C_v and C_p are the same
- Adiabatic and isothermal compressibilities are the same

Limits of Harmonic Approximation

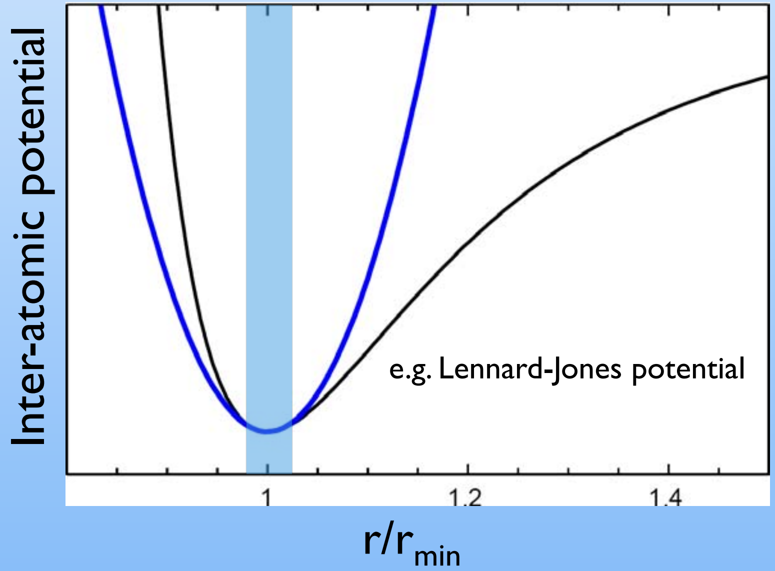
- No T-dependence of lattice constant
- Phonon is an exact eigen-state – i.e. infinite thermal conductivity

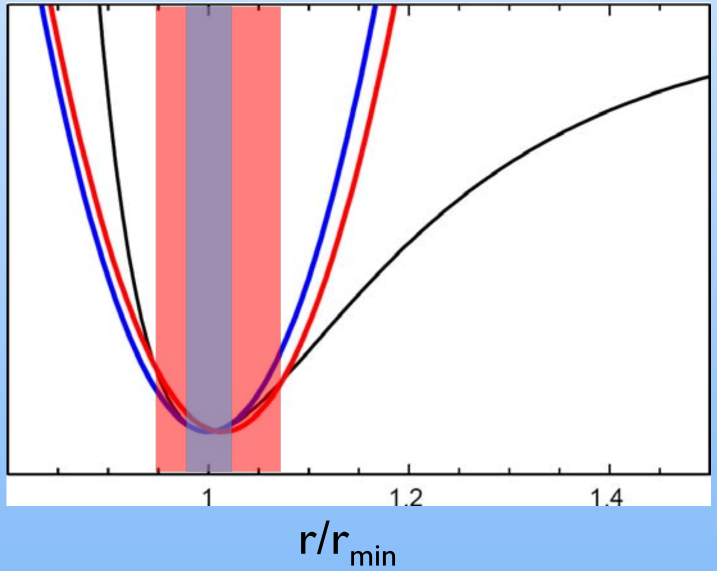


Limits of Harmonic Approximation

This harmonic approx will not change the bond length

In reality, temperature increases the phonon amplitude, and at high temperature the bond length changes (blue → red)





Thermal Expansion, Gruneisen Parameter

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

Sum of all inter-atomic potentials — Euler chain rule — B: bulk modulus

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

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

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

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

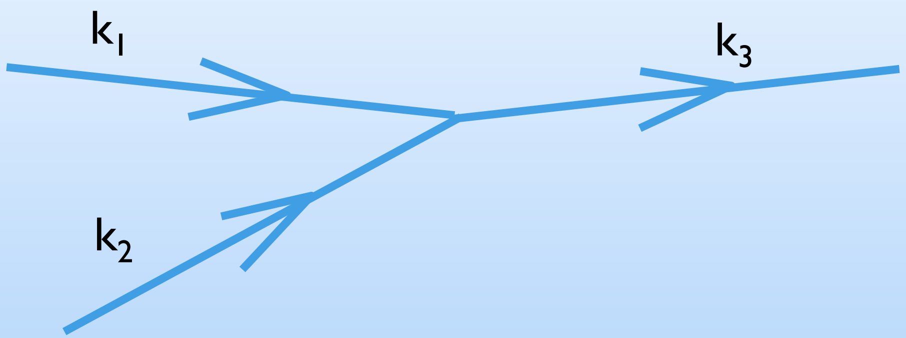
$$U(r) = U(a) + \frac{(r-a)^2}{2}U''(a) + \frac{(r-a)^3}{6}U'''(a) + \cdots$$

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

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

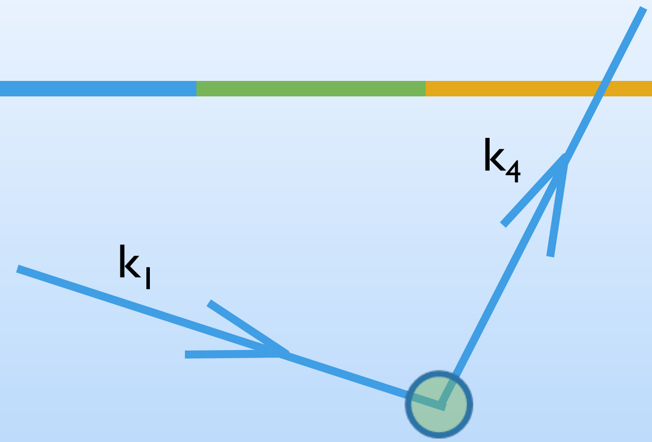
$$\gamma = -\frac{d\ln\omega}{d\ln V} = -\frac{\frac{1}{2}d\ln K}{3\ d\ln a} = -\frac{a}{6K}\frac{dK}{da} \approx -\frac{aU'''(a)}{6U''(a)}$$

Thermal Conductivity for Insulators



Phonon-Phonon Scattering

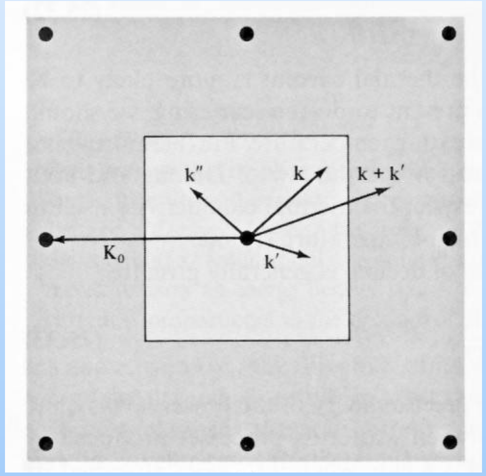
- By convention, k_1 and k_2 are taken within one BZ.
- If $k_3 = k_1 + k_2$ ends up in the other BZ, then the process is called "Umklapp process"
- **Only Umklapp** changes the total momentum – **source for finite conductivity**.

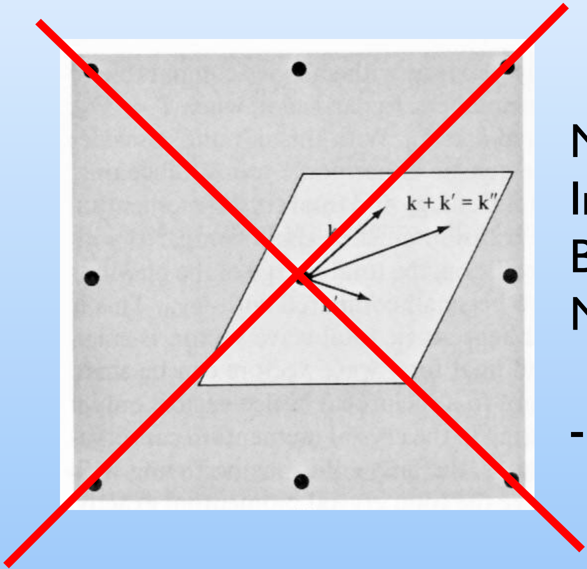


Phonon-Impurity Scattering

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

Umklapp Process





Normal
In Principle
But Really
NOT

- Refer to **BZ**

Always think in terms of the (1st) **BZ** – highly symmetric object
Normal process cannot bring equilibrium
Only umklapp process can bring equilibrium

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 mean free path

Phonon heat capacity

	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 (**Size Effect**)	$Nk_B(T/\theta_D)^3$	$\propto T^3$