Lecture # 22: Phonon-phonon interactions, thermal expansion

Energy of a solid as a function of strain:

$$\frac{U}{V} = \frac{U_0}{V} + \underbrace{\sum_{ij} C^{(1)}_{ij}\varepsilon_{ij}}_{C^{(1)}_{ij}=0 \text{ at equilibrium}} + \frac{1}{2}\sum_{ijkl} C^{(2)}_{ijkl}\varepsilon_{ij}\varepsilon_{kl} + \frac{1}{6}\sum_{ijklmn} C^{(3)}_{ijklmn}\varepsilon_{ij}\varepsilon_{kl}\varepsilon_{mn} + \mathcal{O}(\varepsilon^4)$$

This is just the elastic constant: $C^{(2)}_{ijkl} \equiv C_{ijkl}$

Drop $\mathcal{O}(\varepsilon^4)$:

$$\frac{U}{V} = \frac{U_0}{V} + \frac{1}{2}\sum_{ijkl} \underbrace{\left(C^{(2)}_{ijkl} + \frac{1}{3}C^{(3)}_{ijklmn}\varepsilon_{mn}\right)}_{\text{New elastic constant: strain dependent}} \varepsilon_{ij}\varepsilon_{kl}$$

New elastic constant: strain dependent
new "spring constant": " "

Quite generally, $\omega = \sqrt{\frac{C}{\rho}}\, K$

$$\Rightarrow d\omega = \frac{d\omega}{dC}dC = \frac{K}{\sqrt{\rho}}\frac{1}{2}C^{-\frac{1}{2}}dC = \frac{1}{2}\omega\frac{dC}{C} = \frac{1}{2}\frac{\omega}{C}\underbrace{\left(\frac{1}{3}C^{(3)}\varepsilon\right)}_{\Delta C}$$

Define the Grüneisen parameter as:

$$\gamma = \frac{1}{\omega}\frac{\Delta\omega}{\varepsilon} = \frac{1}{\omega}\frac{1}{\cancel{\varepsilon}}\frac{1}{2}\frac{\omega}{C}\frac{1}{3}C^{(3)}\cancel{\varepsilon} = \frac{1}{6}\frac{C^{(3)}}{C} = \text{CONST}$$

(INDEPENDENT of ε, K)

②

The Gruneisen parameter can be measured from the change in frequency of phonons with strain.

<u>Phonon-phonon interactions:</u>

$$H_{anh} = \int d^3r \quad \gamma C \varepsilon^3$$

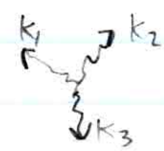
Recall $\vec{u}(\vec{r}) = \sum_{\vec{k},\lambda} \hat{n}_{k,\lambda} \sqrt{\frac{\hbar}{2\rho V \omega_k}} \left(\hat{a}_{k\lambda} e^{i\vec{k}\cdot\vec{r}} + \hat{a}^{\dagger}_{k\lambda} e^{-i\vec{k}\cdot\vec{r}} \right)$

$\varepsilon = \frac{\partial u}{\partial x} = uk$ (neglecting polarizations and indices):

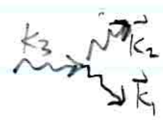
$$H_{anh} = \gamma C \sum_{k_1,k_2,k_3} \left(\frac{\hbar}{2\rho V v} \right)^{3/2} \frac{1}{\sqrt{k_1 k_2 k_3}} k_1 k_2 k_3$$

$$\times \Big[\hat{a}_{k_1} \hat{a}_{k_2} \hat{a}_{k_3} \, \delta_{0,k_1+k_2+k_3}$$

$$+ \hat{a}^{\dagger}_{k_1} a^{\dagger}_{k_2} a^{\dagger}_{k_3} \, \delta_{0,k_1+k_2+k_3}$$



$$+ 3 \hat{a}^{\dagger}_{k_1} \hat{a}^{\dagger}_{k_2} a_{k_3} \, \delta_{k_3,k_2+k_1}$$



$$+ 3 \hat{a}^{\dagger}_{k_1} \hat{a}_{k_2} \hat{a}_{k_3} \, \delta_{k_2+k_3,k_1} \Big]$$

rates for these processes: For a phonon to turn into two others:

$$\frac{1}{\tau_{k_3}} = \frac{1}{\cancel{N_{k_3}}} \frac{2\pi}{\hbar} \gamma^2 C^2 \left(\frac{\hbar}{2\rho V v}\right)^3 \sum_{k_2} k_1 k_2 k_3 \, \cancel{N_{k_3}} (1+N_{k_2})(1+N_{k_1}) \, \delta(\hbar v k_3 - \hbar v k_2 - \hbar v k_3)$$

↳ only one sum because k_1 is fixed by momentum cons.: $\vec{k}_1 + \vec{k}_2 = \vec{k}_3$

$$\propto \underbrace{D(\omega)}_{\propto \omega^2} \underbrace{\omega^3}_{k_1 k_2 k_3} \propto \omega^5$$

Compare to $\frac{1}{\tau_{defect}} \propto \omega^4$. At low ω, phonon-phonon scattering is weaker than phonon-defect scattering.

Sound: Phonons with low ω ⇒ Phonon-defect dominates physical (transport) properties!

Heat: Phonons with high ω ⇒ Phonon-phonon dominates physics!

Photon-photon interactions are similar ⇒ non-linear optics.

Thermal expansion] Nov. 25

Equation of state for phonons

$$dU = \underbrace{-PdV}_{work} + \underbrace{TdS}_{Heat} \Rightarrow S = \int dS = \int \left(\frac{dU}{T}\right)_V = \boxed{\int_0^T \frac{1}{T'}\left(\frac{\partial U}{\partial T'}\right)_V dT'} \quad (S=0 \text{ at } T=0)$$

$$F = U - TS \Rightarrow dF = dU - TdS - SdT = -PdV - SdT$$

$$\Rightarrow \boxed{P = -\left(\frac{\partial F}{\partial V}\right)_T}$$

(4)

write $U = \sum_{k} \hbar\omega_{\vec k} N_{\vec k}(T)$

$$\Rightarrow TS = T\int_0^T \frac{1}{T'} \sum_k \hbar\omega_k \frac{\partial N_k(T')}{\partial T'}\, dT'$$

$$N_k(T') = \frac{1}{e^{\frac{\hbar\omega_k}{kT'}}-1} \Rightarrow \frac{\partial N_k}{\partial T'} = \frac{+\frac{\hbar\omega_k}{kT'^2}}{\left(e^{\frac{\hbar\omega_k}{kT'}}-1\right)^2}\, e^{\frac{\hbar\omega_k}{kT'}}$$

$$\frac{1}{T'}\hbar\omega_k \frac{\partial N_k}{\partial T'}\, dT' = \frac{k_B}{T'}\left(\frac{\hbar\omega_k}{kT'}\right)^2 \frac{e^{\frac{\hbar\omega_k}{kT'}}}{\left(e^{\frac{\hbar\omega_k}{kT'}}-1\right)^2}\, dT' = \frac{k_B}{\cancel{T'}}\, x^2 \frac{e^x}{(e^x-1)^2}\,\frac{(-\cancel{T'})\,dx}{\cancel{x}} = k_B x \frac{d}{dx}\left(\frac{1}{e^x-1}\right)dx$$

$$x = \left(\frac{\hbar\omega_k}{kT'}\right),\quad dx = -\frac{\hbar\omega}{kT'^2}\, dT' = \frac{-1}{T'}\, x\, dT' \Rightarrow dT' = -\frac{T'\,dx}{x}$$

$$TS = \sum_k k_BT\int_0^{\frac{\hbar\omega_k}{kT}} \underbrace{x}_{u}\ \underbrace{\frac{d\left(\frac{1}{e^x-1}\right)}{dx}\, dx}_{dv} = \sum_k k_BT\left[\frac{x}{e^x-1}\Big|_0^{\frac{\hbar\omega_k}{kT}} - \int_0^{\frac{\hbar\omega_k}{k_BT}} dx\,\frac{1}{e^x-1}\right]$$

$$= \underbrace{\sum_k \frac{\hbar\omega_k}{e^x-1}}_{U} - \sum_k k_BT\left[\underbrace{\frac{x}{e^x-1}\Big|_{x\to0}}_{=1} + \underbrace{\int_0^{\frac{\hbar\omega_k}{k_BT}} dx\,\frac{1}{e^x-1}}_{-\ln(1-e^{-x})\big|_0^{\frac{\hbar\omega_k}{k_BT}}}\right]$$

$$TS = U - k_BT\sum_k\left[1 + \underbrace{\lim_{x\to0}\ln(1-e^{-x})}_{\text{CANCELS SINGULARITY AT } k=0!} - \ln\left(1-e^{-\frac{\hbar\omega_k}{k_BT}}\right)\right]$$

$$TS = U - k_BT\sum_k(1) + k_BT\sum_{k\neq0}\ln\left(1-e^{-\frac{\hbar\omega_k}{k_BT}}\right) \Rightarrow \boxed{TS = U - k_BT N_{atoms} + k_BT\sum_{k\neq0}\int_{\frac{\hbar\omega_k}{k_BT}}^{\infty} \frac{dx}{e^x-1}}$$

$$P = -\frac{\partial}{\partial V}(U-TS) = \underbrace{0}_{\frac{\partial N_{atom}}{\partial V}=0} + k_BT\frac{\partial}{\partial V}\sum_k\int_{\frac{\hbar\omega_k}{kT}}^{\infty}\frac{dx}{e^x-1} = -\cancel{k_BT}\sum_k \frac{\partial(\hbar\omega_k)}{\partial V}\frac{1}{\cancel{k_BT}}\, N_k$$

$$= -\hbar\sum_k\left(\frac{\partial\omega_k}{\partial V}\right)N_k = -\int\frac{\partial E}{\partial V}\, D(E)\, f(E)\, dE$$

Grüneisen: $\gamma(\omega) = \frac{V}{\omega}\frac{\partial\omega}{\partial V} \Rightarrow$ (Because $\varepsilon = \frac{\Delta V}{V}$)

$$\boxed{P = -\frac{1}{V}\int \gamma(E)\, E\, f(E)\, D(E)\, dE}$$

Eqn of state

Compute thermal expansion coefficient β:

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{-\left(\frac{\partial P}{\partial T}\right)_V}{\underbrace{V\left(\frac{\partial P}{\partial V}\right)_T}_{\to B}}$$

$\to B$ (Bulk modulus), relates hydrostatic stress to strain. $B = \frac{1}{3}(c_{11} + 2c_{12})$ for isotropic

(Because: $dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT$

$dP = 0 \Rightarrow -\left(\frac{\partial P}{\partial V}\right)_T dV = \left(\frac{\partial P}{\partial T}\right)_V dT$

$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{-\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial V}\right)_T}$)

But:

$$-\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{V}\int \gamma(E)\, \underbrace{E\frac{\partial f}{\partial T} D(E)}_{c_V(E)}\, dE$$

Motivates the definition of average γ:

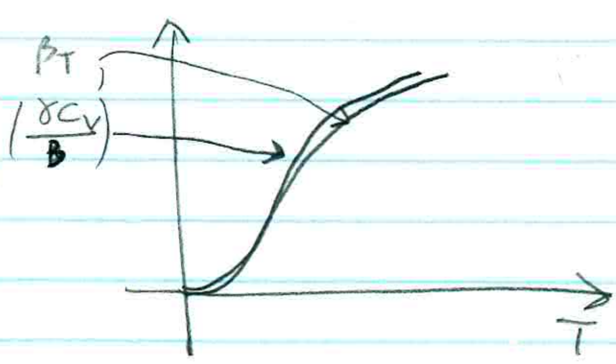
$$\gamma = \frac{\int \gamma(E)\, c_V(E)\, dE}{\int c_V(E)\, dE} = \frac{-V\left(\frac{\partial P}{\partial T}\right)_V}{\int c_V(E)\, dE} = \frac{-\left(\frac{\partial P}{\partial T}\right)_V}{\underbrace{\left[\frac{1}{V}\int c_V(E)\, dE\right]}_{\equiv C_V = \frac{1}{V}\left(\frac{\partial U}{\partial T}\right)_V}} = -\frac{1}{C_V}\left(\frac{\partial P}{\partial T}\right)_V$$

$$\Rightarrow \quad \boxed{\beta = \frac{\gamma C_V}{B}}$$

If $V = \ell^3$, find linear coeff. of thermal expansion α_T:

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{\ell^3}\left(\frac{\partial(\ell^3)}{\partial T}\right)_P = \frac{3\ell^2}{\ell^3}\left(\frac{\partial \ell}{\partial T}\right)_P$$

$$= 3\underbrace{\frac{1}{\ell}\left(\frac{\partial \ell}{\partial T}\right)_P}_{\alpha_T} = 3\alpha_T$$



$$\Rightarrow \boxed{\alpha_T = \frac{\beta}{3} = \frac{\gamma C_V}{3B}}$$