Chpt. 25 - Anharmonic Effects

Equation of State / Thermal Expansion:

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

$$F = U - TS$$

$$T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Why? $T \gg \Theta_D$

- Corrections Dulong & Petit
- Width phonon peaks (lifetime)
- Thermal expansion (harmonic crystal. size (~~temp.~~))
- Thermal conductivity

†

$$\rightarrow P = -\frac{\partial}{\partial V}\Big[\underbrace{U - T\int_0^T \frac{dT'}{T'}\frac{\partial}{\partial T'}U(T';V)}_{F}\Big]$$

$$U = U^{eq} + \frac{1}{2}\sum_{k,s}\hbar\omega_s(k) + \sum_{k,s}\frac{\hbar\omega_s(k)}{e^{\beta\hbar\omega_s(k)}-1}$$

$$\rightarrow P = -\frac{\partial}{\partial V}\Big[U^{eq} + \frac{1}{2}\sum_{k,s}\hbar\omega_s(k) + \sum_{k,s}\frac{\hbar\omega_s(k)}{e^{\beta\hbar\omega_s(k)}-1}$$
$$- T\int_0^T\frac{dT'}{T'}\sum_{k,s}\hbar\omega_s(k)\frac{-1}{(e^{\beta\hbar\omega_s(k)}-1)^2}e^{\beta\hbar\omega_s(k)}\frac{-\hbar\omega_s(k)}{T'^2}$$

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† Cubic unstable, but do perturbation many times

Claim:

$$P = -\frac{\partial}{\partial V}\Big[U^{eq} + \sum\frac{1}{2}\hbar\omega_s\Big] + \sum_{ks}\left(\frac{-\partial}{\partial V}(\hbar\omega_s(k))\right)\frac{1}{e^{\beta\hbar\omega_s(k)}-1}$$

0 inharmonic

$$\beta = \frac{1}{T}; \quad d\beta = -\frac{1}{T^2}dT; \quad \frac{\partial}{\partial\beta} = -T^2\frac{\partial}{\partial T}$$

$$\frac{dT}{T}\frac{\partial}{\partial T} = \frac{1}{T}\left(-T^2 d\beta\,\frac{1}{-T^2}\frac{\partial}{\partial\beta}\right) = \frac{1}{T}\frac{\partial}{\partial\beta}$$

In the harmonic approximation $\omega_s(k)$ does not depend on volume:

$$U^{eq} + \frac{1}{2}\varepsilon^2 \sum_{RR'} R\, D(R-R')\, R' + \frac{1}{2}\sum_{R,R'} \bar{u}(R) D(R-R') \bar{u}(R')$$

$$u(R) = \varepsilon R + \bar{u}(\bar{R})$$

Dynamics don't change.

Implications:

(1) $P(V, \cancel{T})$

(2) $\left(\frac{\partial V}{\partial T}\right)_P = -\frac{(\partial P/\partial T)_V}{(\partial P/\partial V)_T} = 0$ pressure required to maintain a given volume

$\rightarrow V =$ const. indep. T at fixed P.

(3) $\alpha =$ thermal expansion coefficient $= 0$

$$= \frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{3B}\left(\frac{\partial P}{\partial T}\right)_V, \quad B = -V\left(\frac{\partial P}{\partial V}\right).$$

Grüneisen Parameter:

Phonon frequencies do depend on volume.

$$\left(\frac{1}{l}\frac{\partial l}{\partial T}\right)_P = \alpha = \frac{1}{3B}\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{3B}\sum_{k,s}\left(\frac{-\partial}{\partial V}(\hbar\omega_s(k))\right)\frac{\partial}{\partial T}n_s(k)$$

$$n_s(k) = \frac{1}{e^{\beta\hbar\omega_s(k)}-1}$$

$$C_V = \sum_{k,s}\frac{\hbar\omega_s(k)}{V}\frac{\partial}{\partial T}n_s(k)$$

Define: $C_{Vs}(k) = \dfrac{\hbar\omega_s(k)}{V}\dfrac{\partial}{\partial T}n_s(k)$

$$\rightarrow \alpha = \frac{1}{3B}\sum_{k,s}\frac{V}{\hbar\omega_s(k)}\left(\frac{-\partial}{\partial V}(\hbar\omega_s(k))\right)C_{Vs}(k)$$

$$C_V = \sum_{k,s} C_{Vs}(k)$$

Define: $\gamma_{ks} = \dfrac{-V}{\omega_s(k)}\dfrac{\partial\omega_s(k)}{\partial V} = -\dfrac{\partial \ln(\omega_s(k))}{\partial \ln V}$

$$\gamma = \frac{\sum_{k,s}\gamma_{ks}C_{Vs}(k)}{\sum_{k,s}C_{Vs}(k)} = \text{Grüneisen Parameter}$$

$$\alpha = \frac{\gamma C_V}{3B} \quad \text{(observable)}$$

B is weakly T dependent. → For insulators,

$\alpha \sim T^3$ as $T \rightarrow 0$

$\alpha \sim$ const. for $T \gg \Theta_D$

$\Rightarrow$ γ approaches difference constants as $T \to 0$ and $T \gg \Theta_D$.

In a metal we also have the electron contribution. For free electrons,

$$P = \frac{2}{3}\frac{U}{V} \longrightarrow \left(\frac{\partial P^{el}}{\partial T}\right)_V = \frac{2}{3} C_V^{el}$$

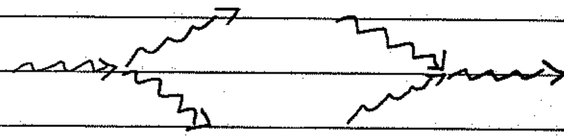
$$\alpha = \frac{1}{3B}\left(\gamma C_V^{ion} + \frac{2}{3} C_V^{el}\right)$$

$\Rightarrow \alpha \propto T$ at low temperatures.

Lattice thermal conductivity:

Sources: (1) imperfections
(2) sample sides
(3) anharmonic effects

Weak anharmonicity → Boltzmann equation

Processes:  3rd order

 4th order

Conservation laws:

$$\sum \hbar\omega_s(k)\, n_{ks} = \sum \hbar\omega_s(k)\, n'_{ks} \qquad \text{energy}$$
$$\sum k\, n_{ks} = \sum k\, n'_{ks} + K \qquad \text{crystal momentum}$$

"Drude" theory:

Local equilibrium: $u(x) = u^{eq}[T(x)]$

$$j = \langle c_x\, u(x_0 - l\cos\theta)\rangle_\theta = \int_0^\pi c\cdot\cos\theta\, u(x_0 - l\cos\theta)\, \frac{2\pi \sin\theta\, d\theta}{4\pi}$$

$$= \frac{1}{2}\int_{-1}^{1} \mu\, d\mu\, c\, u(x_0 - l\mu)$$

$$\approx -\frac{1}{2}\frac{\partial u}{\partial x}\, c\, l \int_{-1}^{1} \mu^2 d\mu$$

$$= -\frac{1}{3}\, c\, l\, \frac{\partial u}{\partial x}$$

$$= -\frac{1}{3}\, c\, l\, \frac{\partial u}{\partial T}\frac{\partial T}{\partial x}$$

$$j = \kappa\left(\frac{-\partial T}{\partial x}\right)$$

$$\kappa = \frac{1}{3} c\, l\, c_v \leftarrow$$
$$= \frac{1}{3} c_v\, c^2 \tau$$
$$= c_v\,(\text{Diff. coeff.})$$

same as for els.

($T \gg \Theta_D$) At high temperatures, $n_s(k) \approx \frac{k_B T}{\hbar \omega_s(k)}$

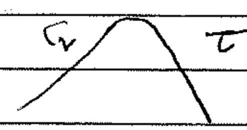
More phonons $\rightarrow$ more scattering.
$C_v \sim$ constant at high T.
$\Big\}$ $K \sim \frac{1}{T^x}$, $1 < x < 2$

($T \ll \Theta_D$) At low temperatures or for that matter all temperatures one needs umklapp processes to degrade the thermal current. These processes involve high energy phonons $\rightarrow$ $\tau \sim e^{T_0/T}$

$\frac{1}{\tau} \sim e^{-T_0/T}$

very low $\frac{1}{\tau}$ indep. T $K \sim T^3$

$\frac{1}{\tau} \sim e^{-T_0/T}$



Second sound:

For sound need: (1) collisions conserve $N, E, \vec{P}$
(2) $\omega \ll \frac{1}{\tau}$

In a crystal, (1)′ number not conserved
(2)′ crystal momentum not conserved

(1)′ OK since $n(T)$ only ← wave in temp.
(2)′ OK if $\underset{\text{umklapp}}{\frac{1}{\tau_u}} \ll \omega \ll \underset{\text{normal}}{\frac{1}{\tau_N}}$

Seen in solid He^4 and NaF.

new HW: Chpt. 23, prob. 2
Chpt. 24, prob. 2
Chpt. 25, prob. 2 or 1