$$C_V = \left.\frac{\partial E}{\partial T}\right)_V$$ classically $\bar{E} = \frac{3}{2}NkT$ $C_V = \frac{3}{2}NK$

for ideal gas or PIB w/ no interactions

For FD gas situation is very different. Only electrons near fermi surface contribute to specific heat.

Those $e^-$ near fermi surface behave like classical particles w/ MB distribution so we estimate their energy using equipartition. Each $e^-$ contributes $\frac{3}{2}k$ to the heat capacity

$$N_{eff} \approx \underbrace{g(\mu)}_{\text{\# of states at energy } \epsilon=\mu}\ \underbrace{kT}_{\text{width of decaying region}}$$

$$C_V \approx N_{eff}\frac{3}{2}k \approx \frac{3}{2}k_B^2\, g(\mu)\, T$$

$$\approx \frac{3}{2}\frac{Nk_B^2}{\mu}T$$

$$C_V \propto T$$

This is different from the Einstein result. We will show that w/ phonons contributions

$$C_V = C_V^{(e)} + C_V^{(lattice)} = \gamma T + AT^3$$

---

# Black Body Radiation

Photons ~~are~~ in thermal equilibrium inside a body of volume $V$ whose walls are maintained at temperature $T$

Photons absorbed & Reemitted by walls

For Photons (special case of BE)

$$\bar{n}_s = \frac{1}{e^{\beta\epsilon_s}-1}$$

How do we specify state of each photon?
all photons satisfy wave eq.

$$\nabla^2 \mathcal{E} = \frac{1}{c^2}\frac{\partial^2 \mathcal{E}}{\partial t^2}$$ Solutions are plane waves of the form

$$\mathcal{E} = Ae^{i(\vec{k}\cdot\vec{r}-\omega t)} = \mathcal{E}_0(r)e^{-i\omega t}$$

$\mathcal{E}$ = electric field

$|\vec{k}| = \frac{\omega}{c}$, $\epsilon = \hbar\omega$, $|\vec{p}| = \hbar|\vec{k}| = \frac{\hbar\omega}{c}$ Since $\vec{\nabla}\cdot\vec{E} = 0$ $\vec{k}\cdot\vec{E} = 0$

There are only two Components of $\vec{\varepsilon} \perp$ to $k$

2 possible photons corresponding to the two polarization directions of the $\vec{\varepsilon}$ field.

Photons in a Box are just like particle in a box

assume $L \gg \lambda = \frac{2\pi}{k}$ From Continuous Boundary Conditions

longest wavelength of significance

just like PIB there are $\frac{d^3k}{(2\pi)^3}$ ~~photon~~ states/unit volume ~~of k space~~

$f(k)\, d^3k$ = the mean # of photons per unit volume w/ one specified direction of polarization where wave vector lies between $k$ & $k+dk$

$$f(k)\, d^3k = \underbrace{\frac{1}{e^{\beta\hbar\omega}-1}}_{\text{\# of photons in each state}} \underbrace{\frac{d^3k}{(2\pi)^3}}_{\text{\# of states/unit volume}}$$

If we want to find the mean # of photons [per unit volume] w/ ~~energy~~ freq between $\omega$ & $\omega + d\omega$

$$\underbrace{2}_{\text{2 polarizations}} f(k)\left(4\pi k^2\, dk\right) = \frac{8\pi}{(2\pi c)^3}\frac{\omega^2\, d\omega}{e^{\beta\hbar\omega}-1} \qquad k = \frac{\omega}{c}$$

let $\bar{u}(\omega; T)\, d\omega$ denote the mean energy/unit volume (this is just the energy density) w/ both polarizations & freq between $\omega$ & $\omega + d\omega$

$$\hbar\omega\left(2 f(k)\, 4\pi k^2\, dk\right) = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3\, d\omega}{e^{\beta\hbar\omega}-1}$$

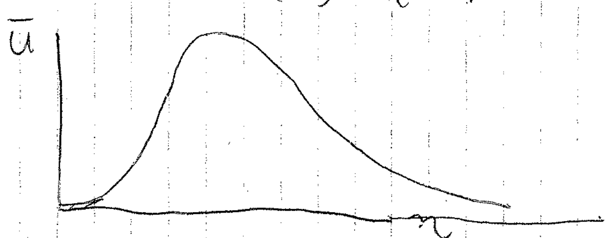
$$\eta \equiv \beta\hbar\omega = \frac{\hbar\omega}{kT}$$

$$\bar{u} = \frac{\hbar}{\pi^2 c^3}\left(\frac{kT}{\hbar}\right)^{4}\frac{\eta^3\, d\eta}{e^{\eta}-1}$$

Comes from where? $d^3k$ & $\hbar\omega$ i.e. # of particles is prop to volume of space in k space each particle has energy ~kT

what happens in 2D?

" " " 11 D?



For total energy density (no freq dep)

$$\bar{u}_0(T) = \frac{\hbar}{\pi^2 c^3}\left(\frac{kT}{\hbar}\right)^4 \underbrace{\int \frac{\eta^3\, d\eta}{e^{\eta}-1}}_{\text{Const}} = \boxed{\frac{\pi^2}{15}\frac{(kT)^4}{(c\hbar)^3}}$$

Stefan-Boltzmann Law

# Phonon Modes

Recall Einstein model for determines $C_V$ at low T

all atoms vibrate at the same frequency

$$\bar{E} = 3N_a\hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega}-1}\right)$$

$$C_{V\,T\to 0} = 3R\left(\frac{\Theta_E}{T}\right)^2 e^{-\Theta_E/T} \quad \text{exponential decay}$$

Once we let particles interact with one another you get Collective Vibrational modes

Each of these modes can be thought of as a quasi particle called a "Phonon" Then we can treat system as an ideal gas of quasi particles

Phonons obey BE statistics

---

$$\xi_{i\alpha} \equiv X_{i\alpha} - X_{i\alpha}^{(0)} \qquad \alpha = \overset{x}{1}, \overset{y}{2}, \overset{z}{3} \quad i = 1, \ldots N$$

$$K = \frac{1}{2}\sum_i \sum_\alpha m_i \dot{X}_{i\alpha}^2 = \frac{1}{2}\sum_i\sum_\alpha m_i \dot{\xi}_{i\alpha}^2$$

What about the potential energy? Usually we are perturbing systems that are in equilibrium

$$V = V_0 + \frac{1}{2}\sum_{i\alpha, j\gamma}\left[\frac{\partial^2 V}{\partial X_{i\alpha}\partial X_{j\gamma}}\right]\xi_{i\alpha}\xi_{j\gamma}$$

$$A_{i\alpha, j\gamma}$$

$$\mathcal{H} = V_0 + \sum_i \frac{P_i^2}{2m} + \frac{1}{2}\sum_{\substack{ij\\ \alpha\gamma}} \xi_{i\alpha}\left[\frac{\partial^2 V}{\partial \xi_{i\alpha}\partial\xi_{j\gamma}}\right]_0 \xi_{j\gamma}$$

Write $\underline{P} = \begin{pmatrix} P_{1x} \\ P_{1y} \\ P_{1z} \\ \vdots \\ P_{Nz} \end{pmatrix}$, $\underline{X} = \begin{pmatrix} \xi_{1x} \\ \xi_{1y} \\ \xi_{1z} \\ \vdots \\ \xi_{Nz} \end{pmatrix}$, $\underline{\underline{A}} = \begin{pmatrix} \frac{\partial^2 V}{\partial \xi_{1x} \partial \xi_{1x}} & \frac{\partial^2 V}{\partial \xi_{1x} \partial \xi_{1y}} & \cdots & \frac{\partial^2 V}{\partial \xi_{1x} \partial \xi_{N}} \\ \vdots & & & \\ \frac{\partial^2 V}{\partial \xi_{Nz} \partial \xi_{1x}} & \cdots & & \frac{\partial^2 V}{\partial \xi_{Nz} \partial \xi_{Nz}} \end{pmatrix}$

$$\mathcal{H} = \frac{P^T P}{2m} + \frac{1}{2} \underline{X}^T \underline{A} \, \underline{X}$$

So this reduces to an Eigenvalue problem & obtain an orthonormal basis

* A: real symmetric matrix Can be diagonalized by an orthogonal matrix $\mathcal{O}$

* All Eigenvalues of A must be positive otherwise equilibrium positions are not stable

These Eigenvalues are the "Normal Modes".

write Eigenvalues as $m\omega_r^2 \quad r = 1, \ldots, 3N$

$$A = m \, \mathcal{O}^T \begin{pmatrix} \omega_1^2 & & \\ & \ddots & \\ & & \omega_{3N}^2 \end{pmatrix} \mathcal{O}$$

define $\underline{\tilde{P}} = \mathcal{O} \underline{P}$, $\underline{\tilde{q}} = \mathcal{O} \underline{X}$

then $\underline{\tilde{P}}, \underline{\tilde{q}}$ are also Canonical momenta Coordinates

$$\mathcal{H} = V_0 + \frac{\underline{\tilde{P}}^T \underline{\tilde{P}}}{2m} + \frac{1}{2} m \, \underline{\tilde{q}}^T \begin{pmatrix} \omega_1^2 & & \\ & \ddots & \\ & & \omega_{3N}^2 \end{pmatrix} \underline{\tilde{q}}$$

$$= V_0 + \sum_{r=1}^{3N} \left( \frac{\tilde{P}_r^2}{2m} + \frac{\tilde{q}_r^2 \, m \omega_r^2}{2} \right)$$

notice that there are no cross terms so we're back to solving things we already know how to do since this is just the Hamiltonian of a Harmonic oscilator

Gone from a Hamiltonian for N interacting atoms to 3N non interacting H.O.

$$E = V_0 + \sum_{r=1}^{3N} \left(n_r + \tfrac{1}{2}\right)\hbar\omega_r$$

each particle has its own $n_r$

Zero pt. energy $\sum_r \frac{1}{2}\hbar\omega_r$

$$-N\eta \equiv V_0 + \sum_{r=1}^{3N} \frac{1}{2}\hbar\omega_r$$ lowest energy of atoms

$$Z = \sum_{n_1}\sum_{n_2}\sum_{n_3}\cdots e^{-\beta[-N\eta + n_1\hbar\omega_1 + n_2\hbar\omega_2 + \cdots n_{3N}\hbar\omega_{3N}}$$

$$= e^{\beta N\eta}\left(\frac{1}{1-e^{-\beta\hbar\omega_1}}\right)\cdots\left(\frac{1}{1-e^{-\beta\hbar\omega_{3N}}}\right)$$

$$\ln Z = \beta N\eta - \sum_{r=1}^{3N} \ln\left(1-e^{-\beta\hbar\omega}\right)$$

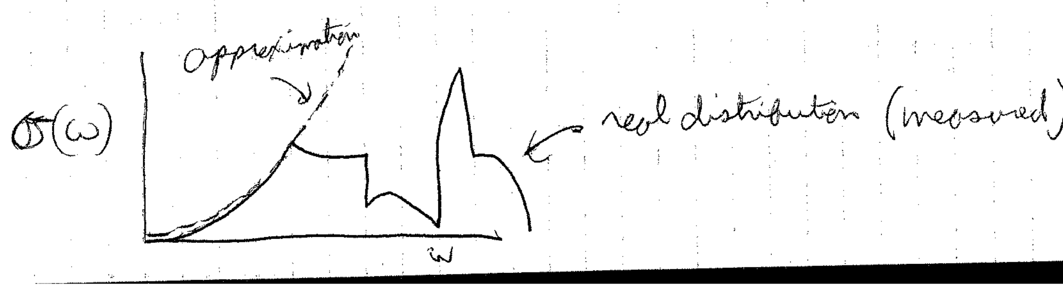
Continuum Limit

$$\underbrace{\sigma(\omega)\,d\omega}_{\text{this is the hard part}} \equiv$$ # of normal modes w/ freq in range between $\omega$ & $\omega + d\omega$

$$\ln Z = \beta N\eta - \int_0^\infty \ln\left(1-e^{-\beta\hbar\omega}\right)\sigma(\omega)\,d\omega$$

$$\bar{E} = -\frac{\partial \ln Z}{\partial\beta} = -N\eta + \int_0^\infty \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\,\sigma(\omega)\,d\omega$$

$$C_V = \left.\frac{\partial\bar{E}}{\partial T}\right)_V = k\int_0^\infty \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega}-1\right)^2}(\beta\hbar\omega)^2\,\sigma(\omega)\,d\omega$$



<u>Two limits</u> $\underbrace{\text{High } T}_{\text{easy}}$ & $\underbrace{\text{Low } T}_{\text{Hard need Debye approx}}$

High T limit

let $\omega_{max}$ represent the highest freq mode

if $\beta\hbar\omega_{max} << 1$ then $\beta\hbar\omega << 1$ for all $\omega$

$$e^{\beta\hbar\omega} = 1 + \beta\hbar\omega + \cdots$$

$$C_v = k \underbrace{\int_0^\infty \sigma(\omega)\, d\omega}_{\text{total \# of modes } 3N} = 3Nk$$

## Low T limit

For low T you excite low frequencies or long wavelength modes. Consequently whole system can be treated as continuum elastic medium since relative difference in displacement are small from site to site
if $\lambda >> a$ (lattice spacing) this approx is exact at $\lambda < a$ this approx is completely wrong since a real solid can't have modes at $\lambda < a$
So for low T we are in the $\lambda >> a$ limit & we can simplify the problem by looking at excitations in an elastic medium
$U(r,t) \equiv$ displacement of a point in this medium

U must satisfy a wave equation w/ effective velocity $C_s \equiv$ Speed of Sound
$\omega = C_s|\vec{k}|$ We've already solved such problems (maxwell eq)
# of possible modes w/ freq between $\omega$ & $\omega + d\omega$

$$\sigma_c(\omega)\,d\omega = \frac{3V}{(2\pi)^3}\left(4\pi k^2 dk\right) = 3\,\frac{V}{2\pi^2 c_s^3}\,\omega^2 d\omega$$

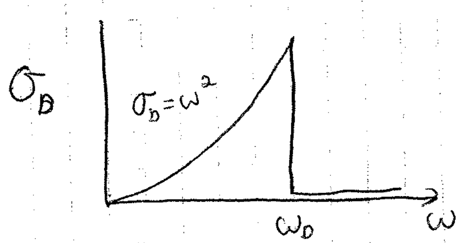
2 transverse + 1 longitudinal

use $\sigma_c(\omega)$ at all $\omega$ up to $\omega_{3N}$

$$\sigma_D(\omega) = \begin{cases} \sigma_c(\omega) & \text{for } \omega < \omega_D \\ 0 & \text{for } \omega > \omega_D \end{cases}$$

where $\omega_D$ is chosen so that

$$\int_0^\infty \sigma_D(\omega)\,d\omega = 3N$$




$$\frac{3V}{2\pi^2 c_s^3}\int_0^{\omega_D} \omega^2 d\omega = \frac{V}{2\pi^2 c_s^3}\,\omega_D^3 = 3N$$

$$\omega_D = \underbrace{c_s}_{\text{sound velocity}}\left(6\pi^2 \underbrace{\frac{N}{V}}_{\text{density}}\right)^{1/3}$$

$c_s \sim 10^5$ cm/sec

$a \sim 10^{-8}$ cm

$\omega_D \sim 10^{14}\ \text{sec}^{-1}$ (infrared)

$$C_V = k\int_0^{\omega_D} \frac{e^{\beta\hbar\omega}(\beta\hbar\omega)^2}{(e^{\beta\hbar\omega}-1)^2}\,\frac{3V}{2\pi^2 c_s^3}\,\omega^2 d\omega \qquad V = 6\pi^2 N\left(\frac{c_s}{\omega_D}\right)^3$$

$$C_V = 3Nk\, f_D\!\left(\frac{\Theta_D}{T}\right) \qquad \Theta_D = \frac{\hbar\omega}{k}$$

$$f_D\!\left(\frac{\Theta_D}{T}\right) \equiv \frac{3}{\left(\frac{\Theta_D}{T}\right)^3}\int_0^{\Theta_D/T} \frac{e^x}{(e^x-1)^2}\,x^4 dx$$

at high $T$ $f_D \to 1$

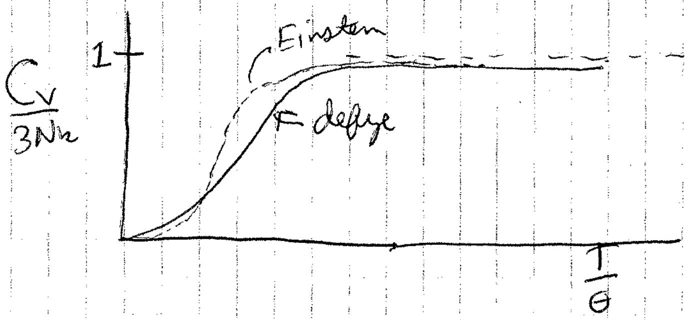
at low $T$ only oscillators of low freq are excited

$\frac{\Theta_D}{T} \to \infty$ & the integral becomes easy to solve

it turns out $\int_0^\infty \frac{e^x}{(e^x-1)^2} x^4 \, dx = \frac{4\pi^4}{15}$

$$f_D = \frac{4\pi^4}{5} \frac{1}{\left(\frac{\Theta_D}{T}\right)^3} \qquad C_v = \frac{12\pi^4}{5} Nk \frac{T}{\Theta_D}^3$$

$$C_v = \frac{2\pi^2}{5} Vk \left(\frac{kT}{C_s \hbar}\right)^3$$




| Solid | $\Theta_D$ from specific heat (°K) | $\Theta_D$ elastic const (°K) |
|---|---|---|
| NaCl | 308 | 320 |
| KCl | 230 | 246 |
| Ag | 225 | 216 |
| Zn | 308 | 305 |