Lattice Vibrations – Phonons

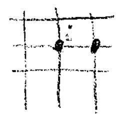
$\{x_i\}_{i=1}^{3N}$ potential energy: $\phi(x_i) = \phi_0 + \sum_i \underbrace{\frac{\partial \phi}{\partial x_i}}_{=0}(x_i - \bar{x}_i) + \frac{1}{2}\sum \frac{\partial^2 \phi}{\partial x_i \partial x_j}(x_i - \bar{x}_i)(x_j - \bar{x}_j) + \dots$

but $\bar{x}_j$ is the equilibrium position

$u_i \equiv x_i - \bar{x}_i$ displacements

$i = 1, 2, \dots, N$

$$\phi(u_i) = \phi_0 + \frac{1}{2}\sum_{i,j} \alpha_{ij} u_i u_j \quad , \text{where} \quad \alpha_{ij} = \left.\frac{\partial^2 \phi}{\partial x_i \partial x_j}\right|_{x_i = \bar{x}_j}$$



$N = N_x N_y N_z$

$k_x = \frac{2\pi}{N_x a} n_x$

$$\mathcal{H}(u_i, \dot{u}_i) = \sum_{i=1}^{3N} \frac{1}{2} m \dot{u}_i^2 + \sum_{i,j} \frac{1}{2} \alpha_{ij} u_i u_j$$

normal coordinates: q_i (then diagonalization)

$n_x = 0, 1, 2, \dots, N_x - 1$

$u(x,t) \propto e^{i(kx - \omega t)}$

$$\mathcal{H}(q_i, \dot{q}_i) = \sum_{i=1}^{3N}\left(\frac{1}{2} m \dot{q}_i^2 + \frac{1}{2} m \omega_i^2 q_i^2\right)$$

$\frac{\partial^2 u}{\partial x^2} - \frac{1}{c^2}\frac{\partial^2 u}{\partial t^2} = 0$

$$\Rightarrow \mathcal{H} = \sum_{\bar{k}, s} \hbar \omega_{\bar{k}, s}\left(n_{\bar{k}, s} + \frac{1}{2}\right) \qquad n_{\bar{k}s} = 0, 1, 2, \dots$$

$k = \frac{2\pi}{L} n$

wave equation

$\omega_{\bar{k}, tr} = k c_{tr}$

$\omega_{\bar{k}, long} = k c_l$

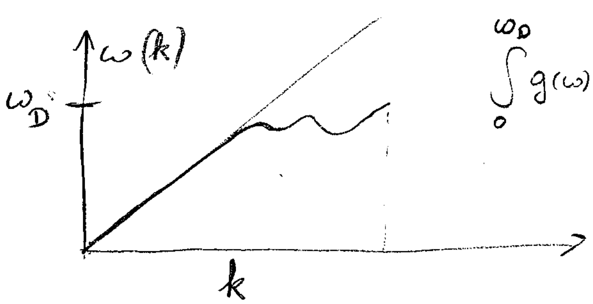
$$\sum_{\bar{k}, s} \frac{V}{(2\pi)^3} \Delta k_x \Delta k_y \Delta k_z = \sum_s \int \frac{V}{(2\pi)^3} 4\pi k^2 dk$$

$$= \int \frac{V}{(2\pi)^3} 4\pi \left[2\frac{\omega^2}{c_{tr}^3} + \frac{\omega^2}{c_l^3}\right] d\omega$$

$$g(\omega) = \frac{V\omega^2}{2\pi^2}\left(\frac{2}{c_{tr}^3} + \frac{1}{c_l^3}\right) = \frac{3}{2}\frac{V\omega^2}{\pi^2 c^3}$$

"effective" sound velocity

$$\frac{2}{c_{tr}^3} + \frac{1}{c_l^3} \equiv \frac{3}{c^3}$$



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

Debye interpolation

Black body radiation "photon gas"

$$E = \int_0^\infty g(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\, d\omega \quad + \cancel{E_0}$$

$$g(\omega) = \frac{V\omega^2}{\pi^2 c^3}$$

(2 transverse modes)

$$\frac{\hbar\omega}{kT} \equiv x$$

$$E = V \frac{(kT)^4}{\pi^2 c^3 \hbar^3} \underbrace{\int_0^\infty \frac{x^3\, dx}{e^x - 1}}_{\frac{\pi^4}{15}}$$

$$= \frac{\pi^2}{15} V \frac{(kT)^4}{c^3 \hbar^3}$$

$$C_V \propto T^3$$

lattice vibration "phonon gas"

$$E = \int_0^{\omega_D} g(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\, d\omega \quad + E_0$$

$$g(\omega) = \frac{3}{2} \frac{V\omega^2}{\pi^2 c^3}$$ (2 tr + 1 long mode)

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

$$\omega_D = \left(6\pi^2 \frac{N}{V}\right)^{1/3} c$$ finite number of modes

$$E = V \frac{(kT)^4}{\pi^2 c^3 \hbar^3} \frac{3}{2} \int_0^{\frac{\hbar\omega_D}{kT}} \frac{x^3\, dx}{e^x - 1} \quad + E_0$$

$\frac{\hbar\omega_D}{kT} \gg 1$ low-temperature limit

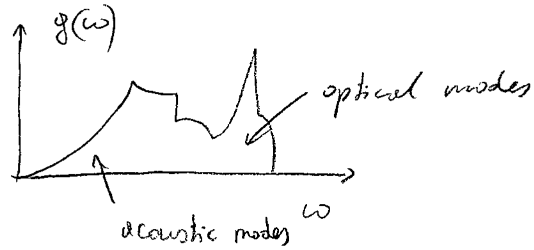
$$E \simeq \frac{\pi^2}{10} V \frac{(kT)^4}{c^3 \hbar^3} \quad + E_0$$

$$C_V \sim T^3$$

Comparison of photon gas and phonon gas at low temperatures

(123a) – Bosons; $\mu = 0$; quasi particles

$\omega_{max} = \omega_D$



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

(2 tr. + 1 long for each $\bar{k}$ vector

$$\frac{V\omega_D^3}{2\pi^2 c^3} = 3N$$

$$\boxed{\omega_D = \left(\frac{6\pi^2 N}{V}\right)^{1/3} c}$$ Debye frequency

the corresponding minimum wavelength:

$$\lambda_{min} = \frac{2\pi}{k_{max}} \sim \frac{2\pi}{\omega_D/c} = \frac{2\pi}{\left(\frac{6\pi^2 N}{V}\right)^{1/3}} \sim a$$ ~ lattice constant $a \propto \left(\frac{V}{N}\right)^{1/3}$

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

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

$$F = \underbrace{\left[\phi_0 + \sum_{i=1}^{3N}\frac{\hbar\omega_i}{2}\right]}_{} + kT\sum_{\bar{k},s} \ln\left(1 - e^{-\beta\hbar\omega_{\bar{k},s}}\right)$$

binding energy $\longrightarrow E_0$

$$= E_0 + kT\int_0^{\omega_D} g(\omega)\ln\left(1 - e^{-\beta\hbar\omega}\right)d\omega$$

$$-S = +\left(\frac{\partial F}{\partial T}\right) = \frac{F - E_0}{T} + kT\int_0^{\omega_D} g(\omega)\frac{-e^{-\beta\hbar\omega}\frac{\hbar\omega}{kT^2}}{1 - e^{-\beta\hbar\omega}}\, d\omega$$

$$E = F + TS = E_0 + \int_0^{\omega_D} g(\omega)\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\, d\omega$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \int_0^{\omega_D} g(\omega)\frac{\hbar\omega\,\frac{\hbar\omega}{kT^2}\,e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2}d\omega = \frac{9N}{\omega_D^3}\frac{\hbar^2}{kT^2}\int_0^{\omega_D}\frac{\omega^4 e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2}d\omega$$

$\left[\beta\hbar\omega = \frac{\hbar\omega}{kT} \equiv x\right]$

$\omega = \frac{kT}{\hbar}x$

$$= \frac{9N}{\omega_D^3\hbar^3}k^4T^3\int_0^{x_D}\frac{x^4 e^x}{\left(e^x - 1\right)^2}dx$$

$$= 9Nk\left(\frac{kT}{\omega_D \hbar}\right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x-1)^2}\,dx \qquad x_D = \frac{\hbar\omega_D}{kT} = \frac{\Theta_D}{T}$$

$$\Theta_D \equiv \frac{\hbar\omega_D}{k}$$

$$= 9Nk\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x-1)^2}\,dx \qquad \boxed{\Theta_D = \frac{\hbar c}{k}\left(\frac{6\pi^2 N}{V}\right)^{1/3}}$$

Thus, $\boxed{C_V = 3Nk\,D(x_D)}$,

where $D(x_D) = \frac{3}{x_D^3}\int_0^{x_D} \frac{x^4 e^x}{(e^x-1)^2}\,dx$ <u>Debye function</u>

$$\int_0^{x_D} \frac{x^4 e^x\,dx}{(e^x-1)^2} = -\frac{x_D^4}{e^{x_D}-1} + 4\int_0^{x_D} \frac{x^3\,dx}{e^x-1}$$

$$D(x_D) = -\frac{3x_D}{e^{x_D}-1} + \frac{12}{x_D^3}\int_0^{x_D} \frac{x^3\,dx}{e^x-1} \qquad x_D = \frac{\Theta_D}{T}$$

<u>High Temperature limit:</u> $T \gg \Theta_D$ $\qquad x_D \ll 1$

$$D(x_D) \simeq 1 - \frac{x_D^2}{20} + \dots$$

$$C_V \simeq 3Nk - \frac{3}{20}Nk\left(\frac{\Theta_D}{T}\right)^2 \longrightarrow 3Nk$$

Dulong-Petit
high temperature
specific heat of solids
(classical behavior,
reflects equipartition
for 3N harm. oscillators)

Low-temperature limit $T \ll \Theta_D$

$$D(x_D) \simeq \frac{12}{x_D^3} \underbrace{\int_0^\infty \frac{x^3\,dx}{e^x-1}}_{\Gamma(4)\zeta(4) = 6\cdot\frac{\pi^4}{90} = \frac{\pi^4}{15}} + o(e^{-x_0}) \simeq \frac{4}{5}\frac{\pi^4}{x_D^3} = \frac{4\pi^4}{5}\left(\frac{T}{\Theta_D}\right)^3$$

$$\boxed{C \simeq 3Nk\,\frac{4\pi^4}{5}\left(\frac{T}{\Theta_D}\right)^3 = \frac{12\pi^4}{5}\,Nk\left(\frac{T}{\Theta_D}\right)^3}$$

note same behavior as of photon gas $\sim T^3$

Specific Heat of Metals: $(N_{el} \propto N)$
must include both electronic and lattice contributions (phonons)

$$C = C_{el} + C_{phonon} \simeq \frac{\pi^2}{2} N_{el} k\left(\frac{T}{T_F}\right) + \frac{12\pi^4}{5} Nk\left(\frac{T}{\Theta_D}\right)^3$$

Note:
low temperatures: phonon gas as lattice vibration, harmonic appr. is o.k.
collective excitations "ideal" Bose gas

typical Θ_D: $\Theta_D = \frac{\hbar c}{k}\left(6\pi^2\frac{N}{V}\right)^{1/3}$

INTERACTING SYSTEMS

Cluster Expansion for interacting classical gas

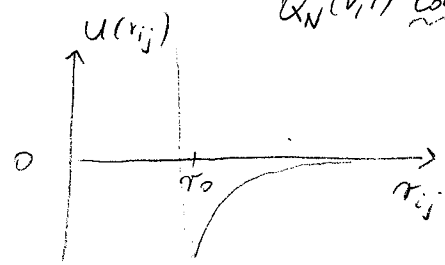
$$\mathcal{H} = \sum_i \frac{\bar{p}_i^2}{2m} + \sum_{i<j} U(\bar{x}_i - \bar{x}_j) \qquad \left(+ \sum_{i<j<k} V(\bar{x}_i, \bar{x}_j, \bar{x}_k)\right)$$

two-body interaction

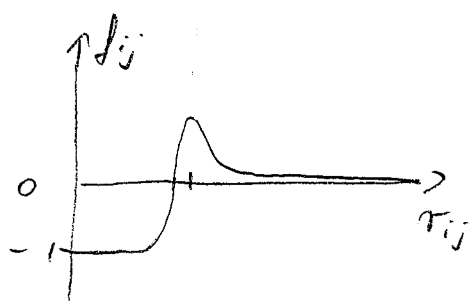
$$Z_N = \int \frac{dp^{3N} dx^{3N}}{N!\, h^{3N}} e^{-\beta\mathcal{H}(p,x)} = \frac{1}{N!\, h^{3N}} \int dp^{3N} e^{-\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m}} \times$$

$$\times \int dx^{3N} e^{-\beta \sum_{i<j} U(\bar{x}_i - \bar{x}_j)} =$$

$$= \frac{1}{N!} \frac{1}{\lambda^{3N}} \underbrace{\int dx^{3N} e^{-\beta \sum_{i<j} U(\bar{x}_i - \bar{x}_j)}}_{Q_N(V,T) \text{ configurational integral}}$$



$$r_{ij} = |\bar{x}_i - \bar{x}_j|$$



$$\boxed{f_{ij} = e^{-\beta U(r_{ij})} - 1}$$ Mayer function

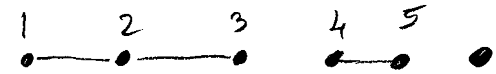
$$\int d^{3N}x\, e^{-\beta U(r_{ij})} = \int d^{3N}x \left(e^{-\beta U(r_{ij})} - 1 + 1\right) = \int d^{3N}x\, (f_{ij} + 1)$$

$$Q_N(V,T) = \int d^{3N}x\, e^{-\beta \sum_{i<j} U(r_{ij})} = \int d^{3N}x \prod_{i<j} e^{-\beta U(r_{ij})} = \int d^3x \prod_{i<j} (1 + f_{ij})$$

$$Q_N(V,T) = \int d^{3N}x \left(1 + \sum_{i<j} f_{ij} + \sum_{i<j,\, k<l} f_{ij} f_{kl} + \dots\right)$$

e.g.

$N=6 \qquad \underbrace{\int d^3x_1\, d^3x_2 \ldots d^3x_6}_{d^{3N}x} \; f_{12} f_{23} f_{45}$



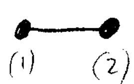
— disconnected portions of graphs are the building block
the corresponding integrals can be carried out independently
and then multiplied by each other

i.e. $\left[\int f_{12} f_{23}\, d^3x_1\, d^3x_2\, d^3x_3\right]\left[\int f_{45}\, d^3x_4\, d^3x_5\right]\left[\int d^3x_6\right]$

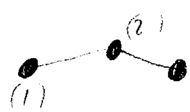
One must focus on different <u>connected</u> subgraphs
→ cluster integral
(topologically different clusters/connected graphs)

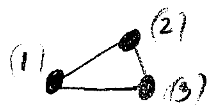
$$\boxed{b_\ell(V,T) = \frac{1}{\ell!\,V} \times (\text{sum of } \ell\text{-particle clusters})}$$

$\ell=1$  $\quad 1 \quad = b_1$

$\ell=2$  $\quad \frac{1}{2}\int f(r)\, d^3x \quad = b_2$

$\bar{x} = \bar{x}_1 - \bar{x}_2$
$\bar{y} = \bar{x}_1 - \bar{x}_3$
$\bar{R} = \frac{\bar{x}_1+\bar{x}_2+\bar{x}_3}{3}$

$\ell=3$ (3×) 

(1×) 

$$\frac{1}{6V}\left[3V\int f(r_{12}) f(r_{23})\, d^3r_{12}\, d^3r_{23} + \int f(r_{12}) f(r_{13}) f(r_{23})\, d^3r_{12}\, d^3r_{13}\, d^3R\right]$$

$$= \frac{1}{6V}\left[3V(2b_2)^2 + V\iint f(x)\, f(y)\, f(|\bar{y}-\bar{x}|)\, d^3x\, d^3y\right]$$

⋮

$$= 2b_2^2 + \frac{1}{6}\iint f(x) f(y) f(|\bar{y}-\bar{x}|)\, d^3x\, d^3y$$

Note:

3 ×  $= \int f(r_{12}) f(r_{23})\, d^3x_1\, d^3x_2\, d^3x_3 + \int f(r_{12}) f(r_{13})\, d^3x_1\, d^3x_2\, d^3x_3$
$+ \int f(r_{13}) f(r_{23})\, d^3x_1\, d^3x_2\, d^3x_3 = 3V\int f(x) f(y)\, d^3x\, d^3y$

$\boxed{Q_N(V,T) = \text{sum of all distinct } N\text{-particle graphs}}$

given $\sum_{l=1}^{N} l m_l = N$ m_l is the number of l-particle clusters

$m_1 = 1 \quad m_2 = 2 \quad m_3 = 1$

e.g. $N = 8$

$\sum_{l=1}^{N} m_l$ = total # of clusters

Contributions to $Q_N(V,T)$

$\Downarrow$

combinatorial prefactor (i) $\dfrac{N!}{(1!)^{m_1}(2!)^{m_2}\cdots} = \dfrac{N!}{\prod_{l=1}^{N}(l!)^{m_l}}$ assigning N particles to $\sum_l m_l$ clusters

(ii) cluster integral contribution $\prod_{l=1}^{N} \dfrac{[\text{sum of the values of all possible } l\text{-particle clusters}]^{m_l}}{m_l!}$

$$= \prod_{l=1}^{N} \left(b_l \, l! \, V\right)^{m_l} \frac{1}{m_l!}$$

(summation restricted to $\sum_l m_l l = N$)

$$Q_N(T,V) = \sum_{\{m_l\}}{}' \frac{N!}{\prod_{l=1}^{N}(l!)^{m_l}} \cdot \prod_{l=1}^{N} \frac{(b_l \, l! \, V)^{m_l}}{m_l!} =$$

$$= N! \sum_{\{m_l\}}{}' \prod_{l=1}^{N} \frac{(b_l V)^{m_l}}{m_l!}$$