Quantum statistics

Heat capacity, diatomic gas, phonons, and photons

Quantum statistics

- Let’s continue to calculate the exact heat capacity coming from **vibrational modes**.
- A **diatomic molecule** has **one** vibrational mode with stiffness $K \equiv m\omega^2$, where ω is the frequency of oscillations. First, let’s look at the single particle ***classical*** partition function for this mode, it is

$$H(p,q) = \frac{p^2}{2m} + \frac{m\omega^2 q^2}{2}$$

$$Z^c_{\text{vib}} = \int \frac{\mathrm{d}p\,\mathrm{d}q}{h} \exp\left[-\beta\left(\frac{p^2}{2m} + \frac{m\omega^2 q^2}{2}\right)\right]$$

$$= \frac{1}{h}\sqrt{\left(\frac{2\pi m}{\beta}\right)\left(\frac{2\pi}{\beta m\omega^2}\right)} = \frac{2\pi}{h\beta\omega} = \frac{k_B T}{\hbar\omega}$$

$$\int_{-\infty}^{\infty} e^{-a(x+b)^2} dx = \sqrt{\frac{\pi}{a}}$$

- The corresponding energy stored in this mode in **classical limit** is,

$$\langle \mathcal{H}_{\text{vib}} \rangle^c = -\frac{\partial \ln Z}{\partial \beta} = \frac{\partial \ln(\beta\hbar\omega)}{\partial \beta} = \frac{1}{\beta} = k_B T$$

result of equipartition theorem, two quadratic terms result in two $k_B T/2$)

- **Quantization:** quantum oscillator with quantized energy levels

$$\mathcal{H}^q_{\text{vib}} = \hbar\omega\left(n + \frac{1}{2}\right) \qquad n = 0,\ 1,\ 2\ \cdots$$

Q: What is the partition function?

Quantum statistics

- The **quantum partition function** is a summation over all discrete energy levels

$$\mathcal{H}_{\text{vib}}^{q}=\hbar\omega\left(n+\frac{1}{2}\right)\qquad Z_{\text{vib}}^{q}=\sum_{n=0}^{\infty}\mathrm{e}^{-\beta\hbar\omega(n+1/2)}=\frac{\mathrm{e}^{-\beta\hbar\omega/2}}{1-\mathrm{e}^{-\beta\hbar\omega}}$$

$$\sum_{n=0}^{\infty}x^{n}=\frac{1}{1-x}$$

$$e^{x}=1+x+\frac{x^{2}}{2}+\frac{x^{3}}{6}+\cdots+\frac{x^{n}}{n!}+\cdots;$$

$$e^{-x}=1-\frac{x}{1!}+\frac{x^{2}}{2!}-\frac{x^{3}}{3!}+\ldots$$

- The high-temperature limit (guess)?

$$\lim_{\beta\to 0}Z_{\text{vib}}^{q}=\frac{\left(\mathrm{e}^{-\beta\hbar\omega/2}\right)}{\left(1-\mathrm{e}^{-\beta\hbar\omega}\right)}\frac{\mathrm{e}^{\beta\hbar\hbar\omega/2}}{\mathrm{e}^{\beta\hbar\hbar\omega/2}}=\frac{1}{e^{\beta\hbar\omega/2}-e^{-\beta\hbar\omega/2}}$$

$$\approx\frac{1}{1+\frac{\beta\hbar\omega\omega}{2}-\left(1-\frac{\beta\hbar\omega}{2}\right)}=\frac{1}{\beta\hbar\omega}=\frac{k_{B}T}{\hbar\omega}$$

- **Quantum (low temperature):** The expectation value of vibrational energy is

$$E_{\text{vib}}^{q}=-\frac{\partial\ln Z}{\partial\beta}=\frac{\hbar\omega}{2}+\frac{\partial}{\partial\beta}\ln\left(1-\mathrm{e}^{-\beta\hbar\omega}\right)=\frac{\hbar\omega}{2}+\hbar\omega\frac{\mathrm{e}^{-\beta\hbar\omega}}{1-\mathrm{e}^{-\beta\hbar\omega}}$$

- The 1st term is due to ***quantum fluctuations*** that are present even in the zero-temperature ground state. The 2nd term describes the additional energy due to thermal fluctuations. (Our final goal is the heat capacity)

Quantum statistics

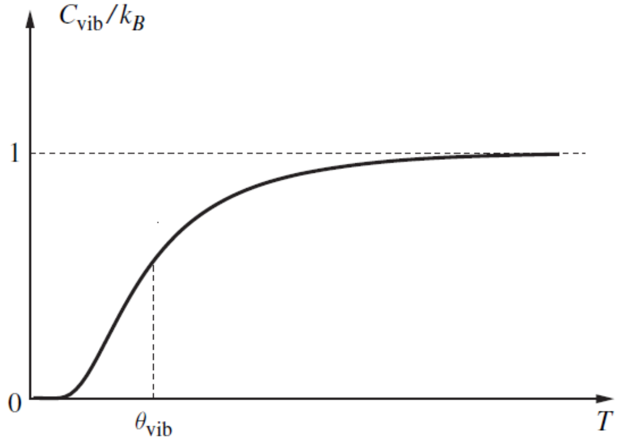
- ❑ The resulting heat capacity,

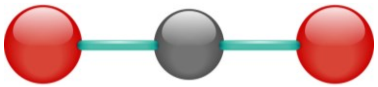
$$E_{\mathrm{vib}}^{q} = \frac{\hbar\omega}{2} + \hbar\omega \frac{\mathrm{e}^{-\beta\hbar\omega}}{1-\mathrm{e}^{-\beta\hbar\omega}}$$

$$C_{\mathrm{vib}}^{q} = \frac{\mathrm{d}E_{\mathrm{vib}}^{q}}{\mathrm{d}T} = k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\mathrm{e}^{-\beta\hbar\omega}}{\left(1-\mathrm{e}^{-\beta\hbar\omega}\right)^2},$$

Characteristic T for the quanta of vibrational energy, ~ 10^3 to 10^4 K

$$\theta_{\mathrm{vib}} = \hbar\omega / k_B$$

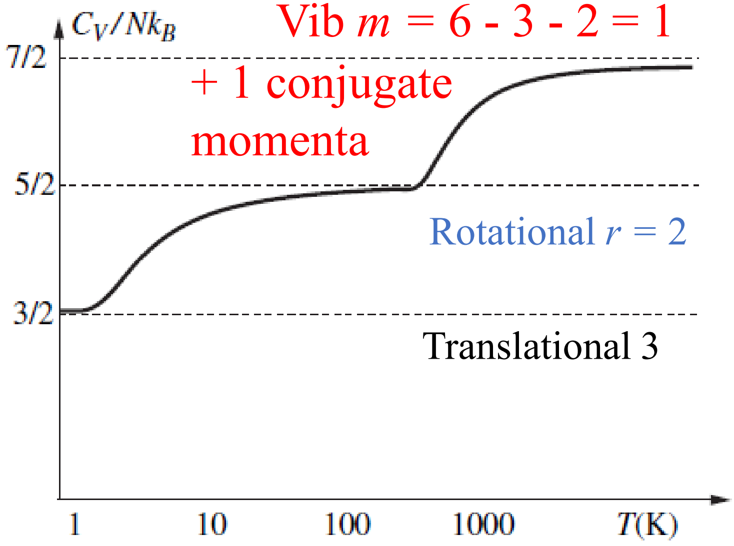




- ✓ total normal modes: $3n$
- ✓ translation modes (zero K_s): 3
- ✓ rotation modes (zero K_s): r
  $r = 2$ for liner molecule,
- ✓ $m = 3n - 3 - r$.

$$\langle \mathcal{H}_1 \rangle = \frac{6n-3-r}{2} k_B T. \qquad C_V = \frac{6n-3-r}{2} k_B$$

$n = 2$, $C_V = (7/2)k_B$



Vib m = 6 - 3 - 2 = 1

+ 1 conjugate momenta

Rotational r = 2

Translational 3

Quantum statistics

- ☐ **Rotational modes.** Hamiltonian?

$$\mathcal{H}_{\text{rot}} = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) \equiv \frac{\vec{L}^2}{2I},$$

$\vec{L}$ is angular momentum

Classical partition function for rotations (continuous), (guess?)

$$\int_0^\pi \sin x dx = 2$$

$$Z_{\text{rot}}^c = \frac{1}{h^2}\int_0^\pi \mathrm{d}\theta \int_0^{2\pi}\mathrm{d}\phi \int_{-\infty}^{\infty}\mathrm{d}p_\theta \mathrm{d}p_\phi \exp\left[-\frac{\beta}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right)\right]$$

$$= \left(\frac{2\pi I}{\beta}\right)\left(\frac{4\pi}{h^2}\right) = \frac{2Ik_BT}{\hbar^2},$$

$$\int_{-\infty}^{\infty} e^{-a(x+b)^2}dx = \sqrt{\frac{\pi}{a}}.$$

Integral: first do exponential terms (const θ, ϕ), then do θ, ϕ

$$\langle E_{\text{rot}}\rangle^c = -\frac{\partial \ln Z}{\partial\beta} = \frac{\partial}{\partial\beta}\ln\left(\frac{\beta\hbar^2}{2I}\right) = k_BT,$$

Equipartition theorem, two rotation modes give two $k_BT/2$

Quantum statistics

- **Quantum partition function (with degeneracy)**

$$\mathcal{H}_{\text{rot}} = \vec{L}^2 / 2I, \qquad \vec{L}^2 = \hbar^2 \ell(\ell+1) \text{ with } \ell = 0,\ 1,\ 2, \cdots$$

For each l, we can have different quantum states of $L_z = -\ell, \cdots, +\ell$, so degeneracy $2\ell+1$

$$Z_{\text{rot}}^{q} = \sum_{\ell=0}^{\infty} \exp\left[-\frac{\beta\hbar^2 \ell(\ell+1)}{2I}\right](2\ell+1) = \sum_{\ell=0}^{\infty} \exp\left[-\frac{\theta_{\text{rot}} \ell(\ell+1)}{T}\right](2\ell+1),$$

$\theta_{rot} = \hbar^2 / (2Ik_B)$ Characteristic temperature

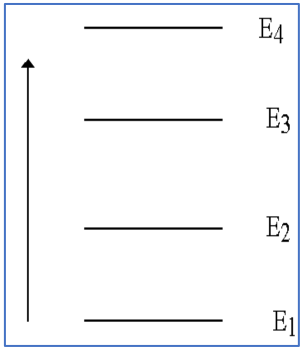
- The sum cannot be analytically evaluated. (look at its high/low temperature limit)
- High-temperature limits: $T \gg \theta_{rot}$, the sum can be replaced by the integral

$$\lim_{T\to\infty} Z_{\text{rot}}^{q} = \int_0^{\infty} \mathrm{d}x (2x+1) \exp\left[-\frac{\theta_{\text{rot}} x(x+1)}{T}\right]$$

$$= \int_0^{\infty} \mathrm{d}y e^{-\theta_{\text{rot}} y/T} = \frac{T}{\theta_{\text{rot}}} = Z_{\text{rot}}^{c},$$

$$y = x(x+1)$$
$$dy = dx(2x+1)$$

$$\int_0^{\infty} e^{-ax} dx = \frac{1}{a}$$



gap

$\theta_{rot} = \hbar^2 / (2Ik_B)$

$T \gg \theta_{rot}$

Continuous

Quantum statistics

- **Low-temperature limit:** $T \ll \theta_{rot}$, thermal energy too low to excite high energy levels. Only the first few (e. g., 2) terms dominate

$$Z_{\text{rot}}^{q} = \sum_{\ell=0}^{\infty} \exp\left[-\frac{\theta_{\text{rot}}\ell(\ell+1)}{T}\right](2\ell+1), \qquad \lim_{T\to 0} Z_{\text{rot}}^{q} = 1 + 3\mathrm{e}^{-2\theta_{\text{rot}}/T} + \mathcal{O}\left(\mathrm{e}^{-6\theta_{\text{rot}}/T}\right)$$

- Leading to an energy

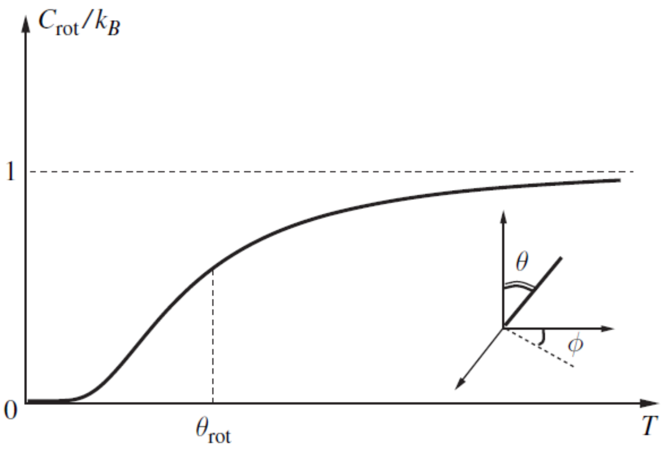
$$E_{\text{rot}}^{q} = -\frac{\partial \ln Z}{\partial \beta} \approx -\frac{\partial}{\partial \beta}\ln\left[1+3\mathrm{e}^{-2\theta_{\text{rot}}/T}\right]$$

$$= \frac{6k_B\theta e^{-2\theta/T}}{1+3e^{-2\theta/T}} \approx \frac{6k_B\theta e^{-2\theta/T}}{1+0} \approx 6k_B\theta_{\text{rot}}\mathrm{e}^{-2\theta_{\text{rot}}/T}.$$

- Heat capacity vanishes at low temperature as

$$C_{\text{rot}} = \frac{\mathrm{d}E_{\text{rot}}^{q}}{\mathrm{d}T} = 3k_B\left(\frac{2\theta_{\text{rot}}}{T}\right)^2 \mathrm{e}^{-2\theta_{\text{rot}}/T} + \cdots$$

Typical values of θ_{rot} are between 1 to 10 K



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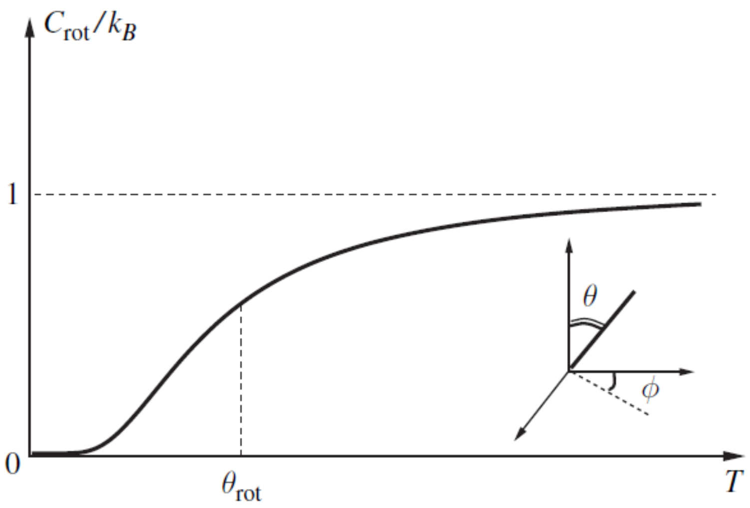
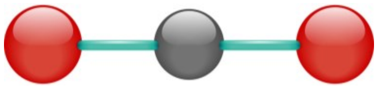
- ☐ The resulting heat capacity for rotation,

$$C_{\text{rot}} = \frac{\mathrm{d}E^q_{\text{rot}}}{\mathrm{d}T} = 3k_B\left(\frac{2\theta_{\text{rot}}}{T}\right)^2 \mathrm{e}^{-2\theta_{\text{rot}}/T} + \cdots$$

Typical values of θ_{rot} are between 1 to 10 K





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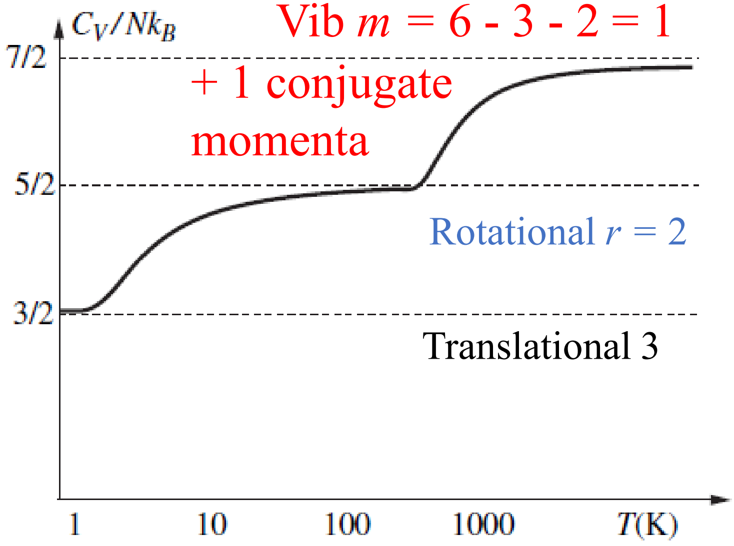

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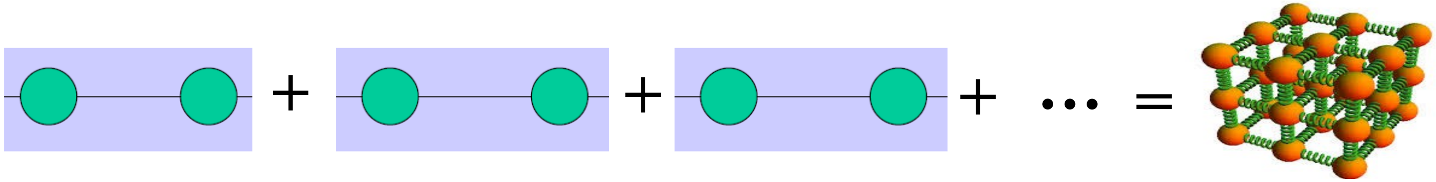
Quantum statistics

- ☐ **Solid crystal:** Bind many polyatomic molecules in 3 dimensions



- ☐ A crystal can be considered as one huge molecule consisted of N atoms. Potential sums over all N atoms:

$$\mathcal{V} = \mathcal{V}^* + \frac{1}{2}\sum_{\vec{r},\vec{r}'} \frac{\partial^2 \mathcal{V}}{\partial q_{\vec{r},\alpha}\partial q_{\vec{r}',\beta}} u_\alpha(\vec{r}) u_\beta\left(\vec{r}'\right) + O\left(u^3\right). \qquad \frac{\partial^2 \mathcal{V}}{\partial q_{\vec{r},\alpha}\partial q_{\vec{r}',\beta}} = K_{\alpha\beta}\left(\vec{r} - \vec{r}'\right).$$

Periodic structure exerts constraints: $\vec{r} \equiv [\ell\hat{a} + m\hat{b} + n\hat{c}]$, with $\{\ell, m, n\}$ a triplet of integers

- ☐ **Normal modes.** A diatomic molecule is an isolated quantum oscillator. For solid, we will find the normal modes using the following procedure.
  - ✓ Different from a diatomic molecule: crystal has the *translational symmetry*, i. e., periodic structure, one dimensional (1D), $r_x \in [0, Na]$, N number of atoms.
  - ✓ For such periodic structure: The deformation $u_i(\vec{r})$ could be expanded using a *Fourier basis*.

$$u_\alpha(\vec{r}) = \sum_{\vec{k}}{}' \frac{\mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{r}}}{\sqrt{N}} \tilde{u}_\alpha(\vec{k}).$$

Quantum statistics

$$u_\alpha(\vec{r}) = \sum_{\vec{k}}{}' \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{N}} \tilde{u}_\alpha(\vec{k})$$

- ❑ Using the *Fourier basis,* Hamiltonian can be diagonalized to:

$$\mathcal{H} = \mathcal{V}^* + \sum_{\vec{k},\alpha} \left[\frac{1}{2m} \left| \tilde{p}_\alpha(\vec{k}) \right|^2 + \frac{\tilde{K}(\vec{k})}{2} \left| \tilde{u}_\alpha(\vec{k}) \right|^2 \right]$$

$$\tilde{p}_\alpha(\vec{k})$$

Conjugate momentum

- ❑ This Hamiltonian describes *3N* **independent harmonic oscillators** of frequencies (Each oscillator is labeled by its Fourier vector $\vec{k}$)

$$\omega_\alpha(\vec{k}) = \sqrt{\tilde{K}(\vec{k}) / m}.$$

- ❑ Quantizing each harmonic mode separately gives the allowed values of the Hamiltonian as

$$\mathcal{H}^q = \mathcal{V}^* + \sum_{\vec{k},\alpha} \hbar\omega_\alpha(\vec{k}) \left(n_{\vec{k},\alpha} + \frac{1}{2} \right)$$

Integers $\{n_{\vec{k},\alpha}\}$ describe the quantum microstate of the oscillators.

Quantum statistics

- Since the **oscillators are independent (why?)**, their partition function

$$Z^q = \sum_{\{n_{\vec{k},\alpha}\}} \mathrm{e}^{-\beta\mathcal{H}^q} = \sum_{\{n_{\vec{k},\alpha}\}} \exp\left[-\beta\left(\mathcal{V}^* + \sum_{\vec{k},\alpha} \hbar\omega_\alpha(\vec{k})\left(n_{\vec{k},\alpha} + \frac{1}{2}\right)\right)\right] \qquad \mathcal{H}^q = \mathcal{V}^* + \sum_{\vec{k},\alpha} \hbar\omega_\alpha(\vec{k})\left(n_{\vec{k},\alpha} + \frac{1}{2}\right)$$

$$= \mathrm{e}^{-\beta E_0} \prod_{\vec{k},\alpha} \sum_{n_{\vec{k},\alpha}} \exp\left[-\beta\hbar\omega_\alpha(\vec{k}) n_{\vec{k},\alpha}\right] = \mathrm{e}^{-\beta E_0} \prod_{\vec{k},\alpha} \left[\frac{1}{1-\mathrm{e}^{-\beta\hbar\omega_\alpha(\vec{k})}}\right]$$

It is the product of single oscillator partition functions such as $Z^q_{\mathrm{vib}} = \dfrac{\mathrm{e}^{-\beta\hbar\omega/2}}{1-\mathrm{e}^{-\beta\hbar\omega}}$

- The internal energy is

$$E = -\frac{\partial \ln Z^q}{\partial\beta} = -\frac{\partial}{\partial\beta} \ln\left\{\mathrm{e}^{-\beta E_0} \prod_{\vec{k},\alpha} \left[\frac{1}{1-\mathrm{e}^{-\beta\hbar\omega_\alpha(\vec{k})}}\right]\right\} = -\frac{\partial}{\partial\beta}\left\{-\beta E_0 + \sum_{\vec{k},\alpha} \ln\left[\frac{1}{1-\mathrm{e}^{-\beta\hbar\omega_\alpha(\vec{k})}}\right]\right\}$$

$$= E_0 + \frac{\partial}{\partial\beta}\left\{\sum_{\vec{k},\alpha} \ln\left[1-\mathrm{e}^{-\beta\hbar\omega_\alpha(\vec{k})}\right]\right\} = E_0 + \sum_{\vec{k},\alpha} \frac{1}{\mathrm{e}^{\beta\hbar\omega_\alpha(\vec{k})}-1} \hbar\omega_\alpha(\vec{k})$$

$$E = \left\langle \mathcal{H}^q \right\rangle = \left\langle \mathcal{V}^* + \sum_{\vec{k},\alpha} \hbar\omega_\alpha(\vec{k})\left(n_{\vec{k},\alpha} + \frac{1}{2}\right)\right\rangle = E_0 + \sum_{\vec{k},\alpha} \left\langle n_{\vec{k},\alpha} \right\rangle \hbar\omega_\alpha(\vec{k})$$

$\langle n_\alpha(\vec{k})\rangle$ is the **occupation number** of oscillators with a Fourier vector $\vec{k}$ and index α

Quantum statistics

- **Occupation number:** $Z^q = \mathrm{e}^{-\beta E_0} \prod_{\vec{k},\alpha} \sum_{n_{\vec{k},\alpha}} \exp\left[-\beta\hbar\omega_\alpha(\vec{k}) n_{\vec{k},\alpha}\right]$

For the oscillators with fixed $\vec{k}$ and α, the Boltzmann weight for n number of such oscillators is:

$\exp\left[-\beta\hbar\omega_\alpha(\vec{k})n\right]$

$$\text{Probability of } n_\alpha(\vec{k}) = \frac{\text{Boltzmann weight}}{\text{Sum of Boltzmann weight}} = \frac{\exp\left[-\beta\hbar\omega_\alpha(\vec{k})n\right]}{\sum_{n=0}^{\infty}\exp\left[-\beta\hbar\omega_\alpha(\vec{k})n\right]}$$

$$\left\langle n_\alpha(\vec{k})\right\rangle = \sum_{n=0}^{\infty}[n][\text{Probability of } n] = \frac{\sum_{n=0}^{\infty} n \times \exp[-\beta\hbar\omega n]}{\sum_{n=0}^{\infty}\exp[-\beta\hbar\omega n]} = -\frac{\partial}{\partial(\beta\hbar\omega)}\ln\left(\sum_{n=0}^{\infty}\exp[-\beta\hbar\omega n]\right)$$

$$-\frac{\partial}{\partial(\beta\hbar\omega)}\ln\left(\sum_{n=0}^{\infty}\mathrm{e}^{-\beta\hbar\omega n}\right) = \frac{-1}{\sum_{n=0}^{\infty}\mathrm{e}^{-\beta\hbar\omega n}}\left[\frac{\partial}{\partial(\beta\hbar\omega)}\sum_{n=0}^{\infty}\mathrm{e}^{-\beta\hbar\omega n}\right] = \frac{\sum_{n=0}^{\infty} n\mathrm{e}^{-\beta\hbar\omega n}}{\sum_{n=0}^{\infty}\mathrm{e}^{-\beta\hbar\omega n}}$$

$$\sum_n x^n = \frac{1}{1-x}$$

$$\left\langle n_\alpha(\vec{k})\right\rangle = -\frac{\partial}{\partial\left(\beta\hbar\omega_\alpha(\vec{k})\right)}\ln\left(\frac{1}{1-\exp\left[-\beta\hbar\omega_\alpha(\vec{k})\right]}\right)$$

Quantum statistics

- **Occupation number:**

$$\left\langle n_\alpha(\vec{k})\right\rangle = -\frac{\partial}{\partial\left(\beta\hbar\omega_\alpha(\vec{k})\right)}\ln\left(\frac{1}{1-\exp\left[-\beta\hbar\omega_\alpha(\vec{k})\right]}\right) = \frac{\exp\left[-\beta\hbar\omega_\alpha(\vec{k})\right]}{1-\exp\left[-\beta\hbar\omega_\alpha(\vec{k})\right]} = \frac{1}{\exp\left[\beta\hbar\omega_\alpha(\vec{k})\right]\text{-}1}$$

This is one special case of a general occupation number of bosons (quantum statistics):

$$\left\langle n_{\vec{k}}\right\rangle_\eta = \frac{1}{z^{-1}e^{\beta\mathcal{E}(\vec{k})}-\eta}$$

with $\eta = -1$ for fermions,
and $\eta = +1$ for bosons

$z = \exp(\beta\mu)$

Harmonic oscillators ⇒ quasi-particles ⇒ phonons: one kind of bosons

Particle number is not conserved, chemical potential $\mu = 0$.

Since $\mu = 0$, we do not use $\langle N\rangle = \frac{\partial}{\partial(\beta\mu)}\ln\mathcal{Q}$ to calculate the *occupation number*.

Quantum statistics

Lattice vibrations

Harmonic potential

independent normal modes (classic waves)

Quantum mechanics

Harmonic oscillators $(n_k + \frac{1}{2})\hbar\omega$

Quantum of lattice waves,
in analogy to photons

Phonons

Phonons do not interact with each other, so we call phonon gas. (Why?)

They are independent normal modes

Team Discussion: Dispersion

$$E = E_0 + \sum_{\vec{k},\alpha} \left\langle n_{\vec{k},\alpha} \right\rangle \hbar\omega_\alpha(\vec{k}) \qquad \left\langle n_\alpha(\vec{k}) \right\rangle = \frac{1}{\exp\left[\beta\hbar\omega_\alpha(\vec{k})\right] - 1}$$

The energy $\varepsilon = \hbar\omega_\alpha(\vec{k})$ dispersion, i.e., as a function of $\vec{k}$ is unknown.
We need to consider some specific models to describe the dispersion relation.

☐ Can you guess some simple models for the dispersion?

Quantum statistics

- ☐ **Einstein Model:** Simplest, no dispersion. All the oscillators have the same ω_E.

$$\langle n_\alpha \rangle = \frac{1}{\exp[\beta\hbar\omega_E]\text{-}1} \qquad E(T) = E_0 + \sum_{\vec{k},\alpha} \hbar\omega_E \langle n_\alpha \rangle = E_0 + \sum_{\vec{k},\alpha} \frac{\hbar\omega_E}{\mathrm{e}^{\beta\hbar\omega_E}-1} = E_0 + \frac{3N\hbar\omega_E}{\mathrm{e}^{\beta\hbar\omega_E}-1}$$

$$C = \frac{\mathrm{d}E}{\mathrm{d}T} = 3Nk_B\left(\frac{T_E}{T}\right)^2 \frac{\mathrm{e}^{-T_E/T}}{\left(1-\mathrm{e}^{-T_E/T}\right)^2},$$

Characteristic temperature $T_E = \hbar\omega_E / k_B$

- ☐ However, the experimentally heat capacity decays to zero much more slowly, as T^3. Need a better model with dispersion relation. Q: Propose your model?

- ☐ **Debye model:** simplest dispersion, linear dispersion relation $\omega(\vec{k}) = vk$, where $v = \sqrt{B/m}$ is the speed of sound in the crystal.

$$E(T) = E_0 + \sum_{\vec{k},\alpha} \hbar\omega_\alpha(\vec{k})\left\langle n_\alpha(\vec{k})\right\rangle = E_0 + \sum_{\vec{k},\alpha} \hbar\omega_\alpha(\vec{k}) \frac{1}{\mathrm{e}^{\beta\hbar\omega_\alpha(\vec{k})}-1} = E_0 + \sum_{\vec{k},\alpha} \frac{\hbar vk}{\mathrm{e}^{\beta\hbar vk}-1}$$

Only one problem left over: Sum over *k* vectors. Allowed *k* vectors?

Quantum statistics

- ❑ **Periodic boundary conditions:** for a crystal with size of $L_x \times L_y \times L_z$, the allowed **smallest *k* vectors** are?

$$\Delta\vec{k} = \left(\frac{2\pi}{L_x}, \frac{2\pi}{L_y}, \frac{2\pi}{L_z}\right)$$

The number of modes in a volume element d^3k is

$$\mathrm{d}\mathcal{N} = \frac{\mathrm{d}k_x}{2\pi / L_x} \frac{\mathrm{d}k_y}{2\pi / L_y} \frac{\mathrm{d}k_z}{2\pi / L_z} = \frac{V}{(2\pi)^3} \mathrm{d}^3\vec{k} \equiv \rho \mathrm{d}^3\vec{k}$$

ρ: density of states

Any sum over allowed wavevectors can be replaced by an integral as

$$E(T) = E_0 + \sum_{\vec{k},\alpha} \frac{\hbar\nu k}{\mathrm{e}^{\beta\hbar\nu k} - 1} \quad \Rightarrow \quad E = E_0 + \int d\mathcal{N} \frac{\hbar\nu k}{\mathrm{e}^{\beta\hbar\nu k} - 1} = E_0 + \int^{B.Z.} \rho \mathrm{d}^3\vec{k} \frac{\hbar\nu k}{\mathrm{e}^{\beta\hbar\nu k} - 1}$$

$$= E_0 + \int^{B.Z.} \frac{3V}{(2\pi)^3} \mathrm{d}^3\vec{k} \frac{\hbar\nu k}{\mathrm{e}^{\beta\hbar\nu k} - 1}$$

where the integral is over the Brillouin zone (depends on the specific crystal structure), and the factor of 3 comes from the three polarizations (two transversal, one longitudinal).

Quantum statistics

- The integral dependents on the shape of the Brillouin zone, so it is not possible to give a simple closed form expression for the energy. However, we can examine its high- and low-T limits. (Q: Can you guess the high temperature limit?)

- **High-*T* limit.** Define a characteristic *Debye temperature:* $T_D = \dfrac{\hbar v k_{\max}}{k_B} \approx \dfrac{\hbar v}{k_B} \cdot \dfrac{\pi}{a}$

Here, a is the lattice constant.

$$E = E_0 + \int^{\text{B.Z.}} \frac{3V}{(2\pi)^3} \mathrm{d}^3\vec{k} \, \frac{\hbar v k}{e^{\beta \hbar v k} - 1}$$

$$= E_0 + k_B T \int^{\text{B.Z.}} \frac{3V}{(2\pi)^3} \mathrm{d}^3\vec{k} = E_0 + 3N k_B T$$

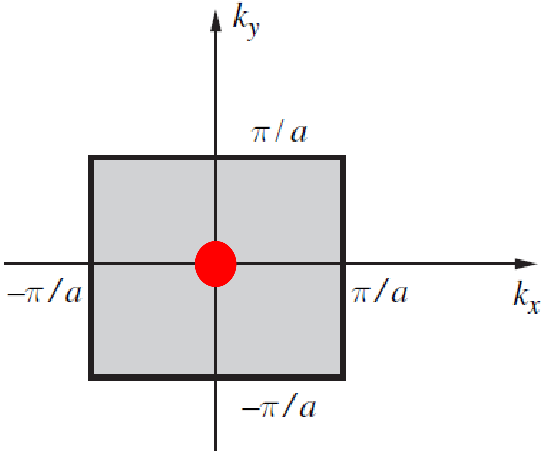
$$\frac{\hbar v k}{\exp(\hbar v k / k_B T) - 1} \approx \frac{\hbar v k}{1 + (\hbar v k / k_B T) - 1} = k_B T$$

For $T \gg T_D$, the integrand is just $k_B T$.

Classical energy and heat capacity are recovered: $C = 3N k_B$

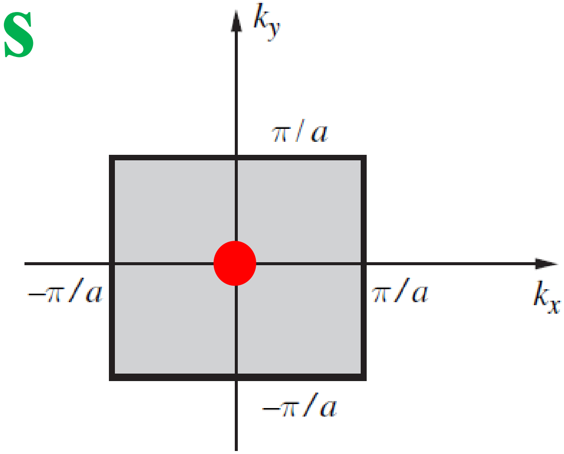
The total number of modes is $3N = 3V \int^{\text{B.Z.}} \mathrm{d}^3\vec{k} / (2\pi)^3$

- **Low-*T* limit.** For $T \ll T_D \sim \pi/a$, the $\exp(\hbar v k / k_B T)$ is very large at the Brillouin zone edge ($k \sim \pi/a \gg T$). The most important contribution to the integral comes from small k, so the integral over Brillouin zone can be replaced by integral from zero to infinite.



Quantum statistics

- **Low-*T* limit.** For $T \ll T_D \sim \pi/a$, the $\exp(\hbar v k/k_B T)$ is very large at the Brillouin zone edge ($k \sim \pi/a \gg T$). The most important contribution to the integral comes from small k, so the integral over Brillouin zone can be replaced by integral from zero to infinite.



$$E(T) = E_0 + \int^{\text{B.Z.}} \frac{3V}{(2\pi)^3}\,\mathrm{d}^3\vec{k}\,\frac{\hbar v k}{\mathrm{e}^{\beta\hbar v k}-1} \underset{T\ll T_D}{\approx} E_0 + \int_0^{\infty} \frac{3V}{(2\pi)^3}\,\mathrm{d}^3\vec{k}\,\frac{\hbar v k}{\mathrm{e}^{\beta\hbar v k}-1}$$

$$= E_0 + \frac{3V}{8\pi^3}\left(\frac{k_B T}{\hbar v}\right)^3 4\pi k_B T \int_0^{\infty} \mathrm{d}x\,\frac{x^3}{\mathrm{e}^x - 1}$$

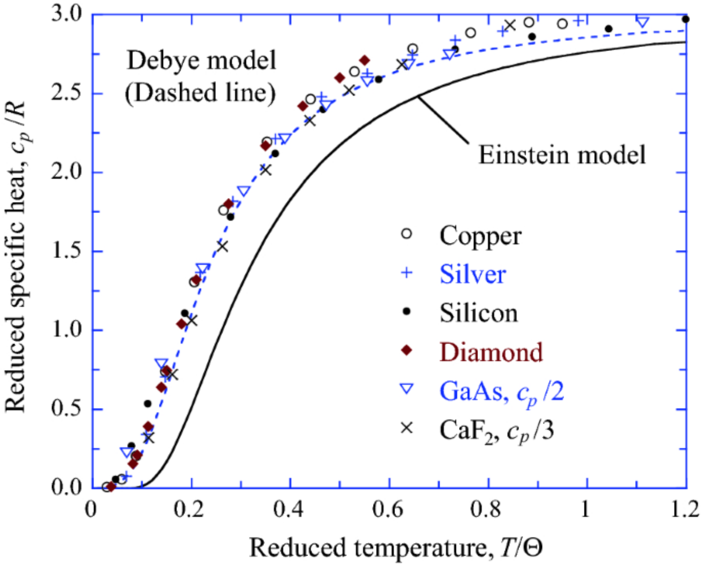
$$x = \beta\hbar v\,|\vec{k}| = \beta\hbar v k,$$

$$\mathrm{d}^3\vec{k} = 4\pi k^2\,\mathrm{d}k = 4\pi x^2\,\mathrm{d}x/(\beta\hbar v)^3$$

$$= E_0 + \frac{\pi^2}{10} V \left(\frac{k_B T}{\hbar v}\right)^3 k_B T$$

$$= E_0 + \frac{\pi^2 V k_B^{\,4}}{10(\hbar v)^3} T^4$$

$$C = \frac{\mathrm{d}E}{\mathrm{d}T} = \frac{2\pi^2 V k_B^4}{5(\hbar v)^3} T^3$$



$$\int_0^{\infty} \frac{x^3}{e^x - 1}\,\mathrm{d}x = \frac{\pi^4}{15}$$

Quantum statistics

❑ **Density of states in energy basis:** $\varepsilon(\vec{k}) = ck$ $\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$

In the momentum space, periodic boundary conditions, the smallest momentums are $\Delta k_x = \frac{2\pi}{L_x}$, ($n_x = 1$), $\Delta k_y = \frac{2\pi}{L_y}$, ($n_y = 1$), $\Delta k_z = \frac{2\pi}{L_z}$, ($n_z = 1$),
where L_x, L_y and L_z are the lengths in *xyz* space and $L_x \times L_y \times L_z = V$

Then, the **momentum density of states** is $\rho(\vec{k}) = \frac{1}{\Delta k_x}\frac{1}{\Delta k_x}\frac{1}{\Delta k_x} = \frac{L_x}{2\pi}\frac{L_y}{2\pi}\frac{L_z}{2\pi} = \frac{V}{(2\pi)^3}$

In a small volume $d^3\vec{k}$, the number of states $\rho(\vec{k})d^3\vec{k} = \frac{V}{(2\pi)^3}d^3\vec{k} = \frac{V}{(2\pi)^3}4\pi k^2 dk$

Change to energy basis: $|k| = \varepsilon/c$, then d$k = 1/c\, d\varepsilon$,
$\rho(\vec{k})d^3\vec{k} = \frac{V}{(2\pi)^3}4\pi k^2 dk = \frac{V}{(2\pi c)^3}4\pi\varepsilon^2 d\varepsilon = \rho(\varepsilon)d\varepsilon$,
Therefore, the **energy density of states** $\rho\,(\varepsilon) = \frac{V}{(2\pi c)^3}4\pi\varepsilon^2 = \frac{V\varepsilon^2}{2\pi^2 c^3}$

For $\omega(\vec{k}) = vk$, **the frequency density of states** $\rho\,(\omega) = \frac{V}{(2\pi v)^3}4\pi\omega^2 = \frac{V\omega^2}{2\pi^2 v^3}$

Quantum statistics

- ❑ **Debye frequency, vector, and temperature.**

For phonons, $\rho\,(\omega) = 3\,\frac{V\omega^2}{2\pi^2 v^3}$, where the factor 3 is due to the polarization.

$$3N = \int_0^{\omega_D} \rho(\omega)d\omega = \int_0^{\omega_D} \frac{3V}{2\pi^2}\frac{\omega^2}{v^3}d\omega = \frac{V}{2\pi^2}\frac{\omega_D^3}{v^3}$$

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

Debye frequency

$$\omega(\vec{k}) = vk$$

$$k_D = \left(6\pi^2\frac{N}{V}\right)^{1/3} \approx \left(\frac{1.9\pi^3}{V/N}\right)^{1/3} \approx \frac{1.24\pi}{a}$$

Debye vector

$$T_D = \frac{\hbar v k_D}{k_B}$$

Debye temperature

- ❑ **Different dimensions:** *N* atoms and *N* primitive cells

$$N_{states,1D} = \int_0^{\omega_D} \rho_{1D}(\omega)d\omega = 1_p\cdot\frac{L}{2\pi}\int_0^{\omega_D} 2\frac{1}{v}d\omega \;= N$$

$$N_{states,2D} = \int_0^{\omega_D} \rho_{2D}(\omega)d\omega = 2_p\left(\frac{L}{2\pi}\right)^2\int_0^{\omega_D} 2\pi\frac{\omega}{v^2}d\omega = 2N$$

$$N_{states,3D} = \int_0^{\omega_D} \rho_{3D}(\omega)d\omega = 3_p\left(\frac{L}{2\pi}\right)^3\int_0^{\omega_D} 4\pi\frac{\omega^2}{v^3}d\omega = 3N$$

For example, 2D

$$E - E_0 = \int^{B.Z.} \rho d^2\vec{k}\,\frac{\hbar v k}{e^{\beta\hbar v k}-1}$$

$$= 2_p\left(\frac{L}{2\pi}\right)^2\int_0^{\omega_D}\frac{2\pi\omega}{v^2}\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}d\omega$$

Next week

Various Ensembles and Fermi gas