

At low temperature, quantum mechanical effects occur; e.g., (a) failure of classical heat capacities of gases and solids; (b) ultraviolet catastrophe in black-body radiation; (c) reformulate SM with QM.

6.1 Dilute polyatomic gases

\mathcal{H}_1 for each molecule of n atoms

$$\mathcal{H}_1 = \sum_{i=1}^n \frac{\vec{p}_i^2}{2m} + \mathcal{V}(\vec{q}_1, \dots, \vec{q}_N)$$

- * the potential energy \mathcal{V} contains all the info. on molecular bonds
- * If masses are different, rescaling the coordinates \vec{q}_i by $\sqrt{m_i/m}$ (and momenta \vec{p}_i by $\sqrt{m/m_i}$), where m_i is the mass of the i th atom.

Ignore the interactions between molecules, partition func. of a dilute gas

$$Z(N) = \frac{Z_1^N}{N!} = \frac{1}{N!} \left\{ \int \prod_{i=1}^n \frac{d^3 \vec{p}_i d^3 \vec{q}_i}{h^3} \exp \left[-\beta \sum_{i=1}^n \frac{\vec{p}_i^2}{2m} - \beta \mathcal{V}(\vec{q}_1, \dots, \vec{q}_N) \right] \right\}^N$$

- * The chemical bonds within molecules are strong (unit order \sim eV)
- * Corresponding dissociation T ($\sim 10^4 K$) \gg accessible T
 \Rightarrow molecules keep well-defined shapes with small deformations

Contribution of deformations to one-particle partition func Z_1

- (a) Minimizing potential \mathcal{V} to find equilibrium positions $(\vec{q}_1^*, \dots, \vec{q}_n^*)$
- (b) Energy cost of small deformations about equilibrium $(\vec{q}_i = \vec{q}_i^* + \vec{u}_i)$

$$\mathcal{V} = \mathcal{V}^* + \sum_{i=1}^n \sum_{\alpha=1}^3 \frac{\partial \mathcal{V}}{\partial q_{i,\alpha}} u_{i,\alpha} + \frac{1}{2!} \sum_{i,j=1}^n \sum_{\alpha,\beta=1}^3 \frac{\partial^2 \mathcal{V}}{\partial q_{i,\alpha} \partial q_{j,\beta}} u_{i,\alpha} u_{j,\beta} + \mathcal{O}(u^3)$$

- * $i, j = 1, \dots, n$ identify the atoms, and $\alpha, \beta = 1, 2, 3$ labels particular component.
 Expansion is around a stable equilibrium configuration, 1st derivative = 0
 Matrix of 2nd derivatives is positive-definite (with non-negative eigenvalues)
- (c) Normal modes of molecule: diagonalizing $3n \times 3n$ matrix $\partial^2 \mathcal{V} / \partial q_{i,\alpha} \partial q_{j,\beta}$
- * $3n$ eigenvalues $\{k_s\}$ indicate the stiffness of each mode.
- * the original deformation $\{\vec{u}_i\}$ \Rightarrow amplitudes $\{\vec{u}_s\}$ of eigenmodes
 corresponding conjugate momenta $\{\tilde{p}_s = m \dot{u}_s\}$
- * Transformation from $\{\vec{u}_i\}$ to $\{\vec{u}_s\}$ is unitary. (preserve length of a vector).

$$\sum_i \vec{p}_i^2 = \sum_s \tilde{p}_s^2$$

$$\mathcal{H}_1 = \mathcal{V}^* + \sum_{s=1}^{3n} \left[\frac{1}{2m} \tilde{p}_s^2 + \frac{k_s}{2} \tilde{u}_s^2 \right]$$

- * Canonical transformation preserves the measure of integration in phase space, $\prod_{i,\alpha} du_{i,\alpha} dp_{i,\alpha} = \prod_s d\tilde{u}_s d\tilde{p}_s$

Quadratic part of the resulting deformation \mathcal{H}_1

average energy of each molecule = expectation value of above \mathcal{H}

Equipartition theorem : each quadratic degree of freedom classically contributes a factor of $\frac{1}{2}k_B T$ to energy

$$\text{Average energy : } \mathcal{H}_1 = U^* + \sum_{S=1}^{3n} \left[\frac{1}{2m} \vec{P}_S^2 + \frac{k_S}{2} \vec{U}_S^2 \right] \Rightarrow \langle \mathcal{H}_1 \rangle = U^* + \frac{3n+m}{2} k_B T$$

* m is the number of such modes with non-zero k_S . (finite stiffness)

(a) Translational symmetry :

$$U(\vec{q}_1 + \vec{c}, \dots, \vec{q}_n + \vec{c}) = U(\vec{q}_1, \dots, \vec{q}_n)$$

\Rightarrow no energy stores in center of mass coordinate $\vec{Q} = \sum_{\alpha} \vec{q}_{\alpha} / n$; $U(\vec{Q}) = U(\vec{Q} + \vec{c})$

\Rightarrow corresponding 3 values of $K_{\text{trans}} = 0$

(b) Rotation symmetry :

no potential energy $\Rightarrow K_{\text{rot}} = 0$ for the corresponding stiffness.

Single atom	$r=0$
rod-shaped	$r=2$
normal	$r=3$

Symmetries of the potential

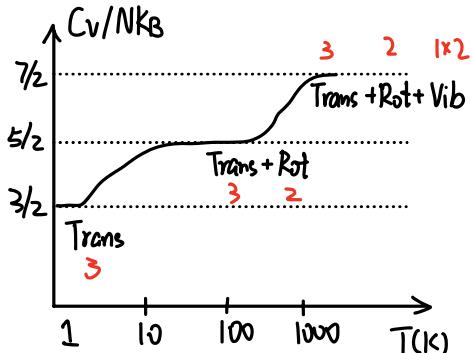
\Rightarrow some eigenvalues to be 0.

Vibrational normal modes
(non-zero stiffness)

$$m = 3n - 3 - r \Rightarrow \langle \mathcal{H}_1 \rangle = \frac{3n+m}{2} k_B T = \frac{6n-3-r}{2} k_B T$$

$$\Rightarrow C_V = \frac{6n-3-r}{2} k_B ; C_P = C_V + k_B = \frac{6n-1-r}{2} k_B \quad (T \text{ independent})$$

$\gamma = C_P/C_V$ measured in adiabatic processes



e.g. O₂ (quantized energy)

Monatomic	He	$n=1$	$r=0$	$\gamma = 5/3$
Diatomlic	O ₂ or CO	$n=2$	$r=2$	$\gamma = 9/7$
Linear triatomic	O=C=O	$n=3$	$r=2$	$\gamma = 15/13$
Planar triatomic	H ⁻ O-H	$n=3$	$r=3$	$\gamma = 14/12 = 7/6$
Tetra atomic	NH ₃	$n=4$	$r=3$	$\gamma = 20/18 = 10/9$

Vibrational modes: a diatomic molecule has 1 vib mode with stiffness $K = mw^2$
 ω is the freq. of oscillations

Classical Partition func. for
 a diatomic molecule

$$Z_{\text{vib}}^c = \int \frac{dp dq}{h} \exp\left[-\beta\left(\frac{p^2}{2m} + \frac{mw^2 q^2}{2}\right)\right]$$

$$= \frac{1}{h} \sqrt{\frac{2\pi m}{\beta}} \cdot \frac{2\pi}{\beta m w^2} = \frac{k_B T}{\hbar \omega} \quad \text{w.r.t. } \hbar = \frac{h}{2\pi}$$

$$\langle H_{\text{vib}} \rangle^c = -\frac{\partial \ln Z}{\partial \beta} = \frac{\partial \ln(\beta \hbar \omega)}{\partial \beta} = \frac{1}{\beta} = k_B T = \frac{k_B T/2}{\text{kinetic}} + \frac{k_B T/2}{\text{potential energy}}$$

Quantum mechanics:

Assume prob. of each distance level \propto boltzmann weight

$$\mathcal{H}_{\text{vib}}^q = \hbar \omega \left(n + \frac{1}{2}\right) \quad \text{quantized harmonic oscillator}$$

$$(n = 0, 1, 2, \dots)$$

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

$$\lim_{\beta \rightarrow 0} Z_{\text{vib}}^q = \frac{1}{\beta \hbar \omega} \xrightarrow{\text{high T}} Z_{\text{vib}}^c \quad \left. \begin{array}{l} \text{h is chosen as the measure of} \\ \text{classical phase space} \end{array} \right\}$$

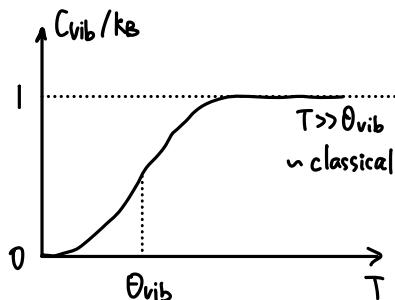
$$E_{\text{vib}}^q = -\frac{\partial \ln Z}{\partial \beta} = \frac{\hbar \omega}{2} + \frac{\partial}{\partial \beta} \ln(1 - e^{-\beta \hbar \omega}) = \frac{\hbar \omega}{2} + \frac{\hbar \omega e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}}$$

① ②

①: quantum fluctuations; present even in zero-temperature ground state.

②: thermal fluctuations

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



characteristic temperature
 associated with quanta of
 vibrational energy

$$\Theta_{\text{vib}} = \frac{\hbar \omega}{k_B} \quad T > \Theta_{\text{vib}} : C_{\text{vib}}^q \rightarrow k_B \quad (\text{classical})$$

$$T < \Theta_{\text{vib}} : C_{\text{vib}}^q \rightarrow 0, \text{ as } \exp(-\Theta_{\text{vib}}/T)$$

i.e., $\Theta_{\text{vib}} \sim 10^3 \text{ to } 10^4 \text{ K}$

Rotational modes: account for low-temperature anomaly in heat capacity

Classically, the orientation of a diatomic molecule is specified by two angles θ and ϕ

$$\mathcal{L} = \frac{I}{2}(\dot{\theta}^2 + \sin^2\theta \dot{\phi}^2) \quad (\text{Lagrangian: } \mathcal{L} = T - V, \text{ only kinetic energy exists})$$

$$P_\theta = \frac{\partial \mathcal{L}}{\partial \dot{\theta}} = I\dot{\theta}; \quad P_\phi = \frac{\partial \mathcal{L}}{\partial \dot{\phi}} = I\sin^2\theta \dot{\phi} \quad (I: \text{moment of inertia})$$

$$P: \text{conjugated momenta}$$

$$\mathfrak{H}_{\text{rot}} = \frac{1}{2I}(P_\theta^2 + \frac{P_\phi^2}{\sin^2\theta}) \equiv \frac{\vec{L}^2}{2I} \quad (\vec{L}: \text{angular momentum})$$

Classical partition func.

$$\begin{aligned} Z_{\text{rot}}^C &= \frac{1}{h^2} \int_0^\pi d\theta \int_0^{2\pi} d\phi \int_{-\infty}^{+\infty} dp_\theta dp_\phi \exp\left[-\frac{\beta}{2I}\left(P_\theta^2 + \frac{P_\phi^2}{\sin^2\theta}\right)\right] \\ &= \frac{2\pi I}{\beta h^2} \int_0^\pi d\theta \int_0^{2\pi} d\phi \sin\theta = \frac{4\pi^2 \cdot 2I}{\beta h^2} = \frac{2I k_B T}{\hbar^2} \\ \langle E_{\text{rot}} \rangle^C &= -\frac{\partial \ln Z}{\partial \beta} = \frac{\partial}{\partial \beta} \ln\left(\frac{\beta \hbar^2}{2I}\right) = k_B T \end{aligned}$$

Quantum mechanics:

$$\vec{L}^2 = \hbar^2 l(l+1) \quad (\text{quantized angular momentum})$$

$$(l=0, 1, 2, \dots)$$

with a degeneracy of $2l+1$ ($\vec{L}_z = -l, \dots, +l$)

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

$$\Theta_{\text{rot}} = \frac{\hbar^2}{2I k_B}$$

(a) $T \gg \Theta_{\text{rot}}$: terms vary slowly, integral approximates the sum.

$$\lim_{T \rightarrow \infty} Z_{\text{rot}}^q = \int_0^{\infty} dx (2x+1) \exp\left[-\frac{\Theta_{\text{rot}} x(x+1)}{T}\right] = \int_0^{\infty} dy e^{-\Theta_{\text{rot}} y/T}$$

$$= T/\Theta_{\text{rot}} = Z_{\text{rot}}^C$$

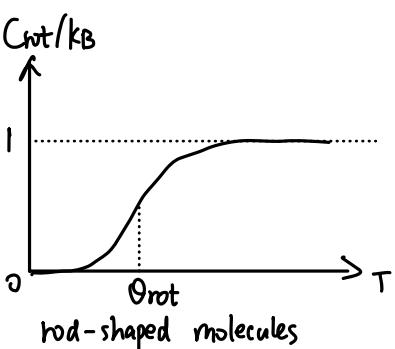
(b) $T \ll \Theta_{\text{rot}}$, first few terms dominate the sum

$$\lim_{T \rightarrow 0} Z_{\text{rot}}^q = 1 + 3e^{-2\Theta_{\text{rot}}/T} + \mathcal{O}(e^{-6\Theta_{\text{rot}}/T})$$

$$E_{\text{rot}}^q = -\frac{\partial \ln Z}{\partial \beta} \approx -\frac{\partial}{\partial \beta} \ln(1 + 3e^{-2\Theta_{\text{rot}}/T}) \approx 6k_B \Theta_{\text{rot}} e^{-2\Theta_{\text{rot}}/T}$$

$$C_{\text{rot}} = \frac{dE_{\text{rot}}^q}{dT} = 3k_B \left(\frac{2\Theta_{\text{rot}}}{T}\right)^2 e^{-2\Theta_{\text{rot}}/T} + \dots$$

$$\Theta_{\text{rot}} \sim 1 \text{ to } 10 \text{ K}$$



At very low T ,

- only kinetic energy of center of mass contributes to heat capacity
- behaves as monatomic particle

Heat capacity vanishes in even lower T due to quantum statistics (in context of identical particles)

b.2 vibration of a solid

Attractive interactions \Rightarrow condensation from gas to liquid \Rightarrow freezing from liquid to solid

Thermodynamic perspective, solid \sim polyatomic gases with $n = N \gg 1$ atoms

(a) ground state configuration $\xrightarrow{\text{minimizing the potential } \mathcal{V}}$ periodic arrangement of the solid of atoms (lattices)

Three basis vectors

\hat{a} , \hat{b} and \hat{c}

locations of atoms in a simple crystal:

$$\vec{q}^*(l, m, n) = [l\hat{a} + m\hat{b} + n\hat{c}] \equiv \vec{r}; \{l, m, n\} \text{ in a triplet of integers}$$

(b) small deformations at finite temperature, $\vec{q}_{\vec{r}} = \vec{r} + \vec{u}(\vec{r})$

$$\mathcal{V} = \mathcal{V}^* + \frac{1}{2} \sum_{\substack{(\vec{r}, \vec{r}'), \\ \alpha, \beta}} \frac{\partial^2 \mathcal{V}}{\partial q_{\vec{r}, \alpha} \partial q_{\vec{r}', \beta}} U_{\alpha}(\vec{r}) U_{\beta}(\vec{r}') + \mathcal{O}(u^3)$$

(c) translational symmetry \rightarrow simplify normal modes

Matrix of 2nd derivatives only depend on the relative separation of 2 points.

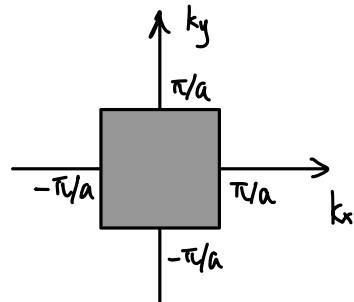
$$\frac{\partial^2 \mathcal{V}}{\partial q_{\vec{r}, \alpha} \partial q_{\vec{r}', \beta}} = K_{\alpha\beta}(\vec{r} - \vec{r}')$$

Fourier basis to partly diagonalize the matrix

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

* The sum is restricted to wavevectors \vec{k} inside the Brillouin zone,
 ⇔ no additional info outside interval as $(k_x + 2\pi m/a)(na) = k_x(na) + 2\pi nm$

$$\Rightarrow \mathcal{V} = \mathcal{V}^* + \frac{1}{2N} \sum_{\substack{(\vec{r}, \vec{r}'), \\ (\vec{k}, \vec{k}'), \\ \alpha, \beta}} K_{\alpha\beta}(\vec{r} - \vec{r}') e^{i\vec{k} \cdot \vec{r}} \tilde{U}_{\alpha}(\vec{k}) e^{i\vec{k}' \cdot \vec{r}'} \tilde{U}_{\beta}(\vec{k}')$$



$$\begin{aligned} \vec{p} &= \vec{r} - \vec{r}' \quad \text{and} \quad \vec{R} = \frac{\vec{r} + \vec{r}'}{2} \\ \Rightarrow \vec{r} &= \vec{R} + \frac{\vec{p}}{2} \quad \text{and} \quad \vec{r}' = \vec{R} - \frac{\vec{p}}{2} \end{aligned}$$

$$\Rightarrow \mathcal{V} = \mathcal{V}^* + \frac{1}{2N} \sum_{\substack{(\vec{k}, \vec{k}'), \\ \alpha, \beta}} \left(\sum_{\vec{R}} e^{i(\vec{k} + \vec{k}') \cdot \vec{R}} \right) \left(\sum_{\vec{p}} K_{\alpha\beta}(\vec{p}) e^{i(\vec{k} - \vec{k}') \cdot \vec{p}/2} \tilde{U}_{\alpha}(\vec{k}) \tilde{U}_{\beta}(\vec{k}') \right)$$

e.g., $(\vec{k} + \vec{k}')$ is not integer or $(\vec{k} + \vec{k}') \cdot \vec{R}$ is not integer multiple of 2π
 the sum over \vec{R} is zero

$$\Rightarrow = N \delta_{\vec{k} + \vec{k}', \vec{0}}$$

$$\Rightarrow \mathcal{V} = \mathcal{V}^* + \frac{1}{2} \sum_{\vec{k}, \alpha, \beta} \left[\sum_{\vec{p}} K_{\alpha\beta}(\vec{p}) e^{i\vec{k} \cdot \vec{p}} \right] U_{\alpha}(\vec{k}) U_{\beta}(-\vec{k})$$

$$(1) \tilde{K}_{\alpha\beta}(\vec{k}) = \sum_{\vec{p}} K_{\alpha\beta}(\vec{p}) \exp(i\vec{k} \cdot \vec{p})$$

$$(2) \tilde{U}_{\beta}(\vec{k})^* = \tilde{U}_{\beta}(-\vec{k}) \text{ complex conjugate}$$

$$* \text{real } U_{\alpha}(\vec{r}) \rightarrow \sum \tilde{U}_{\alpha}(\vec{k}) e^{i\vec{k} \cdot \vec{r}} \langle \tilde{U}_{\alpha}(\vec{k}) e^{i\vec{k} \cdot \vec{r}} | \tilde{U}_{\alpha}(-\vec{k}) e^{-i\vec{k} \cdot \vec{r}} \rangle$$

Potential energy of deformation

$$\Rightarrow \mathcal{V} = \mathcal{V}^* + \frac{1}{2} \sum_{\vec{k}, \alpha, \beta} \tilde{K}_{\alpha\beta}(\vec{k}) \tilde{U}_{\alpha}(\vec{k}) \tilde{U}_{\beta}(\vec{k})^*$$

Decouple different Fourier modes at quadratic order

diagonalize $3N \times 3N$ matrix of 2nd derivatives \rightarrow 3×3 matrix $\tilde{K}_{\alpha\beta}(\vec{k})$ separately for each \vec{k}

* Point group symmetry decides $\tilde{K}_{\alpha\beta}(\vec{k})$

Assume $\tilde{K}_{\alpha\beta}(\vec{k}) = \delta_{\alpha\beta} \tilde{K}(\vec{k})$
(diagonal)

Kinetic energy of deformation

$$\sum_{i=1}^N \frac{m}{2} \dot{\vec{q}}_i^2 = \sum_{\vec{k}, \alpha} \frac{m}{2} \dot{\vec{U}}_{\alpha}(\vec{k}) \dot{\vec{U}}_{\alpha}(\vec{k})^* = \sum_{\vec{k}, \alpha} \frac{1}{2m} \tilde{P}_{\alpha}(\vec{k}) \tilde{P}_{\alpha}(\vec{k})^*$$

where $\tilde{P}_{\alpha}(\vec{k}) = \frac{\partial \mathcal{L}}{\partial \dot{\vec{U}}_{\alpha}(\vec{k})} = m \dot{\vec{U}}_{\alpha}(\vec{k})$ momentum conjugate to $\vec{U}_{\alpha}(\vec{k})$

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

($3N$ independent harmonic oscillators of freq. $(\omega_{\alpha}(\vec{k}) = \sqrt{\tilde{K}(\vec{k})/m})$)

Classical treatment

each harmonic oscillator of non-zero stiffness $\Rightarrow k_B T$

at most, six of $3N$ oscillators are 0. \Rightarrow no potential of trans. and rots.

$E = (3N+6) k_B T \approx 3N k_B T$ (non-extensive corrections of order $1/N$)

$\rightarrow C_V = 3k_B / \text{per atom}$ (temperature-independent)

Quantum treatment

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

(independent oscillators)

* $\{n_{\vec{k}, \alpha}\}$: quantum microstates of the oscillators

Partition func.

$$\begin{aligned} Z^Q &= \sum_{\{n_{\vec{k}, \alpha}\}} e^{-\beta \mathcal{H}^Q} = e^{-\beta E_0} \prod_{\vec{k}, \alpha} \sum_{n_{\vec{k}, \alpha}} e^{-\beta \hbar \omega_{\alpha}(\vec{k}) n_{\vec{k}, \alpha}} = e^{-\beta E_0} \prod_{\vec{k}, \alpha} \left[\frac{1}{1 - e^{-\beta \hbar \omega_{\alpha}(\vec{k})}} \right] \\ &\left\{ * \sum_{\{n_{\vec{k}, \alpha}\}} \prod_{\vec{k}, \alpha} e^{-\beta \hbar \omega_{\alpha}(\vec{k}) (n_{\vec{k}, \alpha} + \frac{1}{2})} = e^{-\beta E_0} \prod_{\vec{k}, \alpha} \sum_{n_{\vec{k}, \alpha}=0}^{\infty} e^{-\beta \hbar \omega_{\alpha}(\vec{k}) n_{\vec{k}, \alpha}} \right\} \end{aligned}$$

* similar to product of single oscillator partition funcs in section 6.1

* $E_0 = \mathcal{V}^* \oplus$ all ground state energies of all oscillators

Internal energy

$$E(T) = \langle \mathcal{H}^Q \rangle = E_0 + \sum_{\vec{k}, \alpha} \hbar \omega_{\alpha}(\vec{k}) \langle n_{\alpha}(\vec{k}) \rangle \quad \left\{ \langle E \rangle = - \frac{\partial \ln Z}{\partial \beta} \right\}$$

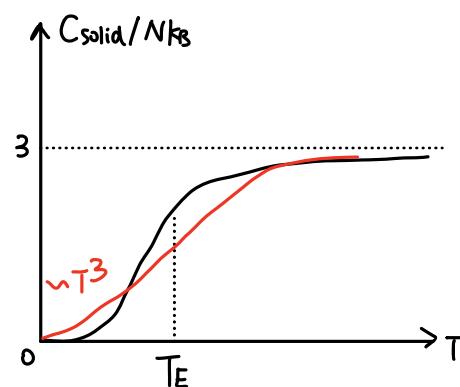
Average occupancy numbers

$$\begin{aligned} \langle n_{\alpha}(\vec{k}) \rangle &= \frac{\sum_{n=0}^{\infty} n e^{-\beta \hbar \omega_{\alpha}(\vec{k}) n}}{\sum_{n=0}^{\infty} e^{-\beta \hbar \omega_{\alpha}(\vec{k}) n}} = - \frac{\partial}{\partial (\beta \hbar \omega_{\alpha}(\vec{k}))} \ln \left(\frac{1}{1 - e^{-\beta \hbar \omega_{\alpha}(\vec{k})}} \right) \\ &= \frac{e^{-\beta \hbar \omega_{\alpha}(\vec{k})}}{1 - e^{-\beta \hbar \omega_{\alpha}(\vec{k})}} = \frac{1}{e^{\beta \hbar \omega_{\alpha}(\vec{k})} - 1} \end{aligned}$$

Adopt Einstein model

1) all oscillators with the same ω_E

2) all atoms are pinned to their ideal locus by springs of stiffness $\vec{K} = \frac{\partial^2 V}{\partial q^2} = m\omega_E^2$



$$E = E_0 + 3N \frac{\hbar \omega_E e^{-\beta \hbar \omega_E}}{1 - e^{-\beta \hbar \omega_E}} \propto E_1$$

$$C = \frac{dE}{dT} = 3N k_B \left(\frac{T_E}{T}\right)^2 \frac{e^{-T_E/T}}{(1-e^{-T_E/T})^2} \propto C_1 \quad (\text{single oscillator in Sec. 6.1})$$

characteristic temperature : $T_E = \hbar \omega_E / k_B$

* $C \rightarrow 0$ (Einstein model) $\propto e^{-1/T}$ Exponentially
 $C \rightarrow 0$ (real measurement) $\propto T^3$ slowly

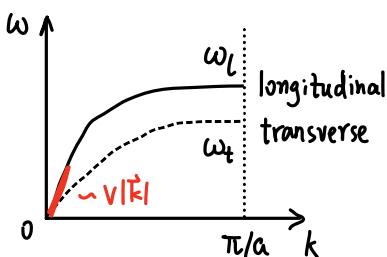
Debye model

* the modes with $\vec{K}=0$:
 pure translations of the
 lattice (0 stiffness)

At low T , the main contribution to heat capacity :

the oscillation of lowest freq. that are the most easily excited.
 ⇒ 1) lowest energy mode
 2) smallest wave vectors $k = |\vec{k}|$
 3) longest wavelengths $\lambda = 2\pi/k$

- 1) Continuity $\Rightarrow \lim_{\vec{k} \rightarrow 0} \tilde{K}(\vec{k}) = 0$
- 2) Ignore considerations of crystal symmetry



dispersion relation in $\omega(\vec{k}) = v k$
 low-energy phonons to $\langle \partial \vec{r}^q \rangle$

the expansion of $\tilde{K}(\vec{k})$ at small wavevectors :

$$\tilde{K}(\vec{k}) = Bk^2 + \mathcal{O}(k^4), \quad \omega(\vec{k}) = \sqrt{\frac{\tilde{K}(\vec{k})}{m}} = \sqrt{\frac{Bk^2}{m}} = Vk$$

* Real space $K(\vec{r} - \vec{r}') = K(\vec{r}' - \vec{r}) \Rightarrow \tilde{K}(\vec{k}) = \tilde{K}(-\vec{k})$

⇒ odd terms are absent

* speed of sound in the crystal $V = \sqrt{B/m}$

(In real materials, $K_{\alpha\beta}$ is not proportional to $\delta_{\alpha\beta}$, and different polarizations of sound have different velocities.)

Phonon : quanta of vibrational modes

$$\langle \partial \vec{r}^q \rangle = E_0 + \sum_{\vec{k}, \alpha} \frac{\hbar v k}{e^{\beta \hbar v k} - 1}$$

Periodic boundary conditions
 in box $L_x \times L_y \times L_z$

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

large size limit \Rightarrow densely packed

Number of modes in a volume element $d^3 \vec{k}$: $dN = \frac{dk_x}{2\pi/L_x} \cdot \frac{dk_y}{2\pi/L_y} \cdot \frac{dk_z}{2\pi/L_z} = \frac{V}{(2\pi)^3} d^3 \vec{k} \equiv \rho d^3 \vec{k}$

* Density of state ρ

$$\lim_{V \rightarrow \infty} \sum_{\vec{k}} f(\vec{k}) = \int d^3 k \rho f(\vec{k}) \Rightarrow E = \langle \mathcal{H}^0 \rangle = E_0 + \sum_{\vec{k}, \alpha} \frac{\hbar v k}{e^{\beta \hbar v k} - 1} = E_0 + 3V \int_{B.Z.} \frac{d^3 k}{(2\pi)^3} \frac{\hbar v k}{e^{\beta \hbar v k} - 1}$$

$\{ B.Z. \equiv \text{Brillouin zone} \}$

* 3 comes from the same sound velocity for 3 polarizations

Characteristic Debye temperature $T > T_D$ (High T), all modes behave classically

$$T_D = \frac{\hbar v k_{max}}{k_B} \asymp \frac{\hbar v}{k_B} \cdot \frac{\pi}{\alpha}$$

$$E = E_0 + 3V \int_{B.Z.} \frac{d^3 k}{(2\pi)^3} \frac{\hbar v k}{e^{\beta \hbar v k} - 1} \rightarrow E(T) = E_0 + 3N k_B T$$

$\sim 3N$ $\sim k_B T$

high-freq modes at the edge of the zone

let $x = \beta \hbar v |\vec{k}|$ & spherical sym.

$$\begin{aligned} d^3 k &= 4\pi |\vec{k}|^2 d|\vec{k}| \\ &= 4\pi \frac{x^2}{(\beta \hbar v)^2} \frac{dx}{\beta \hbar v} \\ &= 4\pi x^2 dx / (\beta \hbar v)^3 \end{aligned}$$

$T \ll T_D$ (Low T), $e^{\beta \hbar v k} \rightarrow \infty$

Most important contribution: small k

Small error $\int_{B.Z.} \rightarrow \int_0^\infty$

$$\begin{aligned} \lim_{T \ll T_D} E(T) &\asymp E_0 + \frac{3V}{8\pi^3} \left(\frac{k_B T}{\hbar v} \right)^3 4\pi \int_0^\infty dx \frac{x^2 \cdot \hbar v x / \beta \hbar v}{e^x - 1} \\ &= E_0 + \frac{3V}{8\pi^3} \left(\frac{k_B T}{\hbar v} \right)^3 4\pi k_B T \int_0^\infty dx \frac{x^3}{e^x - 1} \\ &= E_0 + \frac{3V}{8\pi^3} \left(\frac{k_B T}{\hbar v} \right)^3 4\pi k_B T \cdot \frac{\pi^4}{15} = E_0 + \frac{\pi^2}{10} V \left(\frac{k_B T}{\hbar v} \right)^3 k_B T \end{aligned}$$

* Complex Analysis by Mathematica (online) (V = Nα³)

$$\int dz \frac{z^3}{e^z - 1} = -3z^2 \text{Li}_2(e^{-z}) - 6z \text{Li}_3(e^{-z}) - 6 \text{Li}_4(e^{-z}) + z^3 \log(1 - e^{-z}) + C$$

$$\star \int_0^\infty dx \frac{x^3}{e^x - 1} = \int_0^\infty dx x^3 (e^{-x} + e^{-2x} + \dots) = 3! \sum_{n=1}^\infty \frac{1}{n^4} = 6 \zeta(4) = \frac{\pi^4}{15}$$

$$A = \int_0^\infty x^m e^{-nx} dx = \frac{1}{n^{m+1}} \int_0^\infty u^m e^{-u} du = \frac{m!}{n^{m+1}}$$

$$\int_0^\infty \frac{x^n}{e^x - 1} dx = n! \cdot \zeta(n+1)$$

Riemann Ζ (zeta)

$$\int_0^\infty \frac{x^n}{e^x + 1} dx = n! \cdot \eta(n+1)$$

Dirichlet η (eta)

(Debye) heat capacity

$$C = \frac{dE}{dT} = k_B V \frac{2\pi^2}{5} \left(\frac{k_B T}{\hbar v} \right)^3 \propto N k_B \left(\frac{T}{T_D} \right)^3 \quad (V = N\alpha^3)$$

$T \ll T_D$, only a fraction of phonon modes can be thermally excited
low freq phonons $\hbar w(\vec{k}) \ll k_B T$ with $|\vec{k}| < k^*(T) \asymp k_B T / \hbar v$

In d dimensions, the number of modes is $\sim V [k^*(T)]^d \asymp V (k_B T / \hbar v)^d$

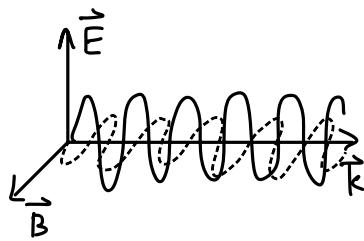
each excited mode can be treated classically. contributes $\sim k_B T$ (kin. + pot.)

$\Rightarrow E \sim V (k_B T / \hbar v)^d k_B T$, $C \sim V (k_B T / \hbar v)^d k_B$ vanishes as $T \downarrow$

6.3 Black-body radiation

Vibrations of a solid medium \Rightarrow phonon; liquid and gas states \Rightarrow longitudinal sound modes (section 3.8, 3.9)

Fluctuation of electromagnetic (EM) fields, photons



as $\nabla \cdot \vec{E} = 0$ in free space,

$\vec{E} \perp \vec{k}$ (transverse modes)

Normal modes of this field are EM waves { wavevector \vec{k}
two polarizations α

Hamiltonian for the EM field (photon)

$$\mathcal{H} = \frac{1}{2} \sum_{\vec{k}, \alpha} \left[|\hat{P}_{\vec{k}, \alpha}|^2 + \omega_{\alpha}(\vec{k}) |\hat{U}_{\alpha}(\vec{k})|^2 \right] \quad (\text{ignore mass } m)$$

with $\omega_{\alpha}(\vec{k}) = ck$, c is speed of light

$\vec{k} = 2\pi(n_x, n_y, n_z)/L$ but no Brillouin zone for \vec{k} in photon.

\Rightarrow ultraviolet catastrophe in a classical treatment:

no limit to wavevector ($k_B T$ per mode \Rightarrow infinite energy in high-freq modes)

(low freqs. are cut off by the finite size of the box)

$$|\mathcal{H}|^2 = \sum_{\vec{k}, \alpha} \hbar c k \left(n_{\alpha}(\vec{k}) + \frac{1}{2} \right) \quad \text{with } n_{\alpha}(\vec{k}) = 0, 1, 2, \dots$$

\sim similar to phonons

$$E = \langle |\mathcal{H}|^2 \rangle = \sum_{\vec{k}, \alpha} \hbar c k \left(\frac{1}{2} + \frac{e^{-\beta \hbar c k}}{1 - e^{-\beta \hbar c k}} \right) = V E_0 + \underbrace{\frac{2V}{(2\pi L)^3} \int d^3 \vec{k} \frac{\hbar c k}{e^{\beta \hbar c k} - 1}}_{\text{infinite zero-point energy}} \quad \text{2 polarizations } \propto$$

$$\frac{E^*}{V} = \frac{\hbar c}{\pi^2} \left(\frac{k_B T}{\hbar c} \right)^4 \int_0^\infty \frac{dx}{e^x - 1} x^3 = \frac{\pi^2}{15} \left(\frac{k_B T}{\hbar c} \right)^3 k_B T$$

Partition func.: $Z = \prod_{\{n_{\alpha}(\vec{k})\}} \prod_{\vec{k}, \alpha} \exp \left[-\beta \hbar \omega(\vec{k}) \left(n_{\alpha}(\vec{k}) + \frac{1}{2} \right) \right] = \prod_{\vec{k}, \alpha} \frac{e^{-\beta \hbar c k / 2}}{1 - e^{-\beta \hbar c k}}$

Free energy: $F = -k_B T \ln Z = k_B T \sum_{\vec{k}, \alpha} \left[\frac{\beta \hbar c k}{2} + \ln(1 - e^{-\beta \hbar c k}) \right]$
 $= 2V \int \frac{d^3 \vec{k}}{(2\pi L)^3} \left[\frac{\hbar c k}{2} + k_B T \ln(1 - e^{-\beta \hbar c k}) \right]$

Pressure: $P = -\frac{\partial F}{\partial V} \Big|_T = -\int \frac{d^3 \vec{k}}{(2\pi L)^3} \left[\hbar c k + 2k_B T \ln(1 - e^{-\beta \hbar c k}) \right]$
 $= P_0 - \frac{k_B T}{\pi^2} \int_0^\infty dk k^2 \ln(1 - e^{-\beta \hbar c k})$

$$* \int_0^\infty dk k^2 \ln(1 - e^{-\beta \hbar c k}) = \int_0^\infty \ln(1 - e^{-\beta \hbar c k}) dk \frac{k^3}{3} = \frac{k^3}{3} \ln(1 - e^{-\beta \hbar c k}) \Big|_0^\infty - \int_0^\infty dk \frac{k^3}{3} \frac{\beta \hbar c e^{-\beta \hbar c k}}{1 - e^{-\beta \hbar c k}}$$

$$\lim_{k \rightarrow +\infty} k^3 \ln(1 - e^{-\beta \hbar c k}) = \lim_{k \rightarrow +\infty} \frac{\ln(1 - e^{-\beta \hbar c k})}{k^{-3}} = \lim_{k \rightarrow +\infty} \frac{\beta \hbar c / (e^{\beta \hbar c k} - 1)}{-3k^{-2}} = -\frac{\beta \hbar c}{3} \lim_{k \rightarrow +\infty} \frac{k^2}{e^{\beta \hbar c k} - 1} = 0$$

$$= P_0 + \frac{k_B T}{\pi^2} \int_0^\infty dk \frac{k^3}{3} \frac{\beta \hbar c e^{-\beta \hbar c k}}{1 - e^{-\beta \hbar c k}}$$

$$\underline{\underline{x = \beta \hbar c k}} \quad P_0 + \frac{1}{3} \frac{k_B T}{\pi^2} \left(\frac{k_B T}{\hbar c} \right)^3 \int_0^\infty \frac{x^3}{e^x - 1} dx$$

Differences in this pressure

Casimir force between conducting plates

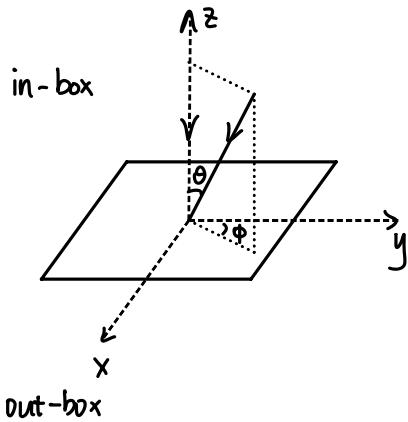
Quantum fluctuations in confined space

infinite zero-point pressure

$$= P_0 + \frac{1}{3} \frac{\pi^2}{15} \left(\frac{k_B T}{\hbar c} \right)^3 k_B T$$

$$= P_0 + \frac{1}{3} \frac{E}{V}$$

dispersion relation
 $E \propto l^p l^s \Rightarrow P = (s/d)(E/V)$
 d: dimension



Stefan - Boltzmann law
for black-body radiation

$$\text{let } E(T)/V = \int dk \epsilon(k, T)$$

Flux of emitted radiation in interval $[k, k+dk] \equiv I(k, T)dk$

If a hole is opened in the container wall,
The escape energy flux per unit area and per unit time

$$\phi = \langle C_{\perp} \rangle \frac{E}{V}$$

Photon speed c , the average of the component of velocity perpendicular to hole

$$\langle C_{\perp} \rangle = c \times \frac{1}{4\pi} \int_0^{\pi/2} 2\pi \sin\theta d\theta \cos\theta = \frac{c}{4}$$

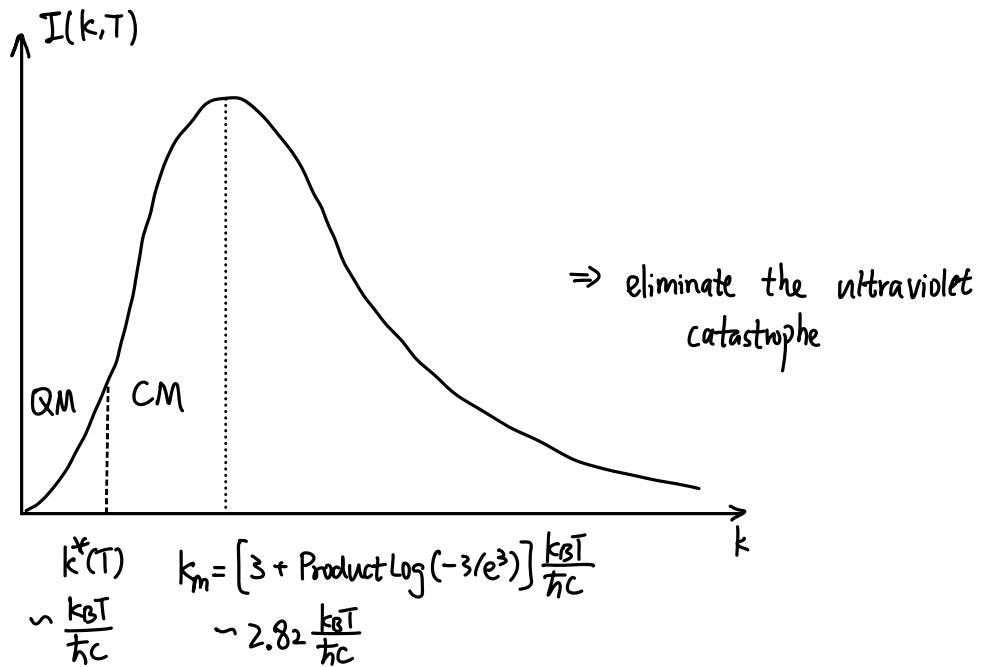
$$* \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta = 4\pi, \quad \int_0^{2\pi} d\phi \int_0^{\frac{\pi}{2}} \cos\theta (\sin\theta d\theta) = \int_0^{\pi/2} 2\pi \sin\theta d\theta \cos\theta$$

$$\phi = \frac{c}{4} \frac{E^*}{V} = \frac{\pi^2}{60} \frac{k_B T^4}{\hbar^3 c^2} \Rightarrow \phi = \sigma T^4, \quad \sigma = \frac{\pi^2}{60} \frac{k_B^4}{\hbar^3 c^2} \approx 5.67 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$$

Stefan Constant

$$\epsilon(k, T) = \frac{\hbar c}{\pi^2} \frac{k^3}{e^{\beta \hbar c k} - 1}, \quad \epsilon(k, T) \text{ energy density in wavevector } \vec{k}$$

$$I(k, T) = \frac{c}{4} \epsilon(k, T) = \frac{\hbar c^2}{4\pi^2} \frac{k^3}{e^{\beta \hbar c k} - 1} \sim \begin{cases} \frac{1}{4\pi} c k_B T k^2 & k \ll k^*(T) \\ \frac{1}{4\pi^2} \hbar c^2 k^3 e^{-\beta \hbar c k} & k \gg k^*(T) \end{cases}$$



6.4 Quantum microstates

Justify assumption: Microstates of a quantum systems in discrete energy levels
 inherent prob. with uncertainty in QM $\xrightarrow{\text{unrelated}}$ prob. in SM

$\{\vec{p}_i, \vec{q}_i\}$ in $6N-d$ phase space (CM) \Rightarrow In an infinite-dimensional Hilbert space, unit vector $|\psi\rangle$
 components $\langle n|\psi\rangle$; orthonormal basis vectors $|n\rangle$

$$|\psi\rangle = \sum_n \langle n|\psi\rangle |n\rangle$$

e.g., position coordinates $|\vec{q}_i\rangle$ $\langle \{\vec{q}_i\} |\psi\rangle \equiv \psi(\vec{q}_1, \dots, \vec{q}_N)$ wave func.
 Normalization $\langle \psi | \psi \rangle = \sum_n \langle \psi | n \rangle \langle n | \psi \rangle = 1$ where $\langle \psi | n \rangle \equiv \langle n | \psi \rangle^*$
 e.g., $\langle \psi | \psi \rangle = \int \prod_{i=1}^N d\vec{q}_i |\psi(\vec{q}_1, \dots, \vec{q}_N)|^2 = 1$

Observation $\mathcal{O}(\{\vec{p}_i, \vec{q}_i\})$ (CM) \Rightarrow Hermitian matrices (operators) in Hilbert space

$$\{P_j, q_k\} = \sum_{\alpha=1}^{3N} \left(\frac{\partial P_j}{\partial q_{j\alpha}} \frac{\partial q_k}{\partial p_\alpha} - \frac{\partial P_j}{\partial p_\alpha} \frac{\partial q_k}{\partial q_{j\alpha}} \right) \Rightarrow [P_j, q_k] = P_j q_k - q_k P_j = \frac{\hbar}{i} \delta_{j,k}$$

$$= -\delta_{j,k} \quad (\text{CM}) \quad (\text{Coordinate basis}) \quad |\vec{q}_i\rangle : \quad P_j = \frac{\hbar}{i} \frac{\partial}{\partial q_j}$$

operator \mathcal{O} is determined for a particular microstates (CM) \Rightarrow operator \mathcal{O} is a random variable

$$\langle \mathcal{O} \rangle \equiv \langle \psi | \mathcal{O} | \psi \rangle \equiv \sum_{m,n} \langle \psi | m \rangle \langle m | \mathcal{O} | n \rangle \langle n | \psi \rangle$$

e.g., $\langle U(\vec{q}) \rangle = \int \prod_{i=1}^N d^3 \vec{q}_i \psi^*(\vec{q}_1, \dots, \vec{q}_N) U(\vec{q}) \psi(\vec{q}_1, \dots, \vec{q}_N)$

$$\langle K(\vec{p}) \rangle = \int \prod_{i=1}^N d^3 \vec{q}_i \psi^*(\vec{q}_1, \dots, \vec{q}_N) K\left(\frac{\hbar}{i} \frac{\partial}{\partial \vec{q}_i}\right) \psi(\vec{q}_1, \dots, \vec{q}_N)$$

Expectation value $\langle \mathcal{O} \rangle$ is real in all states (\mathcal{O} must be Hermitian)
 $\mathcal{O}^+ = \mathcal{O}$, where $\langle m | \mathcal{O}^+ | n \rangle = \langle n | \mathcal{O} | m \rangle^*$

* replace \vec{p}, \vec{q} in classical operator $\mathcal{O}(\{\vec{p}_i, \vec{q}_i\})$ by corresponding matrices
 proper symmetrization \rightarrow hermiticity

Hamilton's equations of motion based on $\mathcal{H}(\{\vec{p}_i, \vec{q}_i\})$ (CM) $\Rightarrow i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \mathcal{H} |\psi(t)\rangle \xrightarrow[\mathcal{H}]{\text{diagonalize}} \mathcal{H} |n\rangle = E_n |n\rangle$ (energy eigenstates)

$$* \langle m | i\hbar \frac{\partial}{\partial t} \sum_n \langle n | \psi(t) \rangle | n \rangle = \langle m | \mathcal{H} \sum_n \langle n | \psi(t) \rangle | n \rangle \xrightarrow{\langle m | n \rangle = \delta_{mn}} i\hbar \frac{\partial}{\partial t} \langle n | \psi(t) \rangle = \epsilon_n \langle n | \psi(t) \rangle$$

$$\Rightarrow \langle n | \psi(t) \rangle = \exp(-\frac{i\epsilon_n t}{\hbar}) \langle n | \psi(0) \rangle \xrightarrow[\text{operator } U]{\text{time evolution}} |\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle$$

* $i\hbar \frac{\partial}{\partial t} U(t, t_0) = \mathcal{H} U(t, t_0)$ with boundary condition $U(t_0, t_0) = 1$

(\mathcal{H} independent of t) $U(t, t_0) = \exp\left[-\frac{i}{\hbar} \mathcal{H}(t-t_0)\right]$

6.5 Quantum macrostates

An ensemble of a large number N , of microstates $\mu_\alpha \Rightarrow$ macrostates (CM)

($P_\alpha = \frac{1}{N}$ for an unbiased estimation in absence of information)

Ensemble average (CM)

$$\overline{\langle \mathcal{O}(\{\vec{p}_i, \vec{q}_i\}) \rangle}_t = \sum_{\alpha} P_\alpha \langle \mathcal{O}(\mu_\alpha(t)) \rangle = \int \prod_{i=1}^N d^3 \vec{p}_i d^3 \vec{q}_i \langle \mathcal{O}(\{\vec{p}_i, \vec{q}_i\}) \rangle P(\{\vec{p}_i, \vec{q}_i\}, t)$$

$$\text{where phase space density } \rho(\{\vec{p}_i, \vec{q}_i\}, t) = \sum_{\alpha} P_\alpha \prod_{i=1}^N \delta^3(\vec{q}_i - \vec{q}_i(t)_\alpha) \delta^3(\vec{p}_i - \vec{p}_i(t)_\alpha)$$

Ensemble average (QM)

w.r.t. possible states $\{|\psi_\alpha\rangle\}$

with prob. $\{P_\alpha\}$

$$\begin{aligned} \overline{\langle \mathcal{O} \rangle} &= \sum_{\alpha} P_\alpha \langle \Psi_\alpha | \mathcal{O} | \Psi_\alpha \rangle = \sum_{\alpha, m, n} P_\alpha \langle \Psi_\alpha | m \rangle \langle n | \Psi_\alpha \rangle \langle m | \mathcal{O} | n \rangle \\ &= \sum_{m, n} \langle n | \rho | m \rangle \langle m | \mathcal{O} | n \rangle = \text{tr}(\rho \mathcal{O}) \end{aligned}$$

where basis $\{|n\rangle\}$ and density matrix

$$\langle n | \rho(t) | m \rangle \equiv \sum_{\alpha} P_\alpha \langle n | \Psi_\alpha(t) \rangle \langle \Psi_\alpha(t) | m \rangle \xrightarrow[\text{basis}]{\text{slip}} \rho(t) = \sum_{\alpha} P_\alpha |\Psi_\alpha(t)\rangle \langle \Psi_\alpha(t)|$$

Properties of Density matrix

* ρ corresponds to pure state $\Leftrightarrow \text{tr}(\rho^2) = 1$
mixed state $\Leftrightarrow \text{tr}(\rho^2) < 1$

idempotent $\rho^2 = \rho$ (projection matrix)

Normalization: Each $|\Psi_\alpha\rangle$ is normalized to unity

$$\langle 1 \rangle = \text{tr}(\rho) = \sum_n \langle n | \rho | n \rangle = \sum_{\alpha, n} P_\alpha |\langle n | \Psi_\alpha \rangle|^2 = \sum_{\alpha} P_\alpha = 1$$

Hermiticity: $\langle m | \rho^+ | n \rangle = \langle n | \rho | m \rangle^* = \sum_{\alpha} P_\alpha \langle \Psi_\alpha | m \rangle \langle n | \Psi_\alpha \rangle = \langle n | \rho | m \rangle \Rightarrow \rho^+ = \rho$

$$\Rightarrow \overline{\langle \mathcal{O} \rangle} = \text{tr}(\rho \mathcal{O}) = \text{real number}$$

Positivity: For any $|\Phi\rangle$

$$\langle \Phi | \rho | \Phi \rangle = \sum_{\alpha} P_\alpha \langle \Phi | \Psi_\alpha \rangle \langle \Psi_\alpha | \Phi \rangle = \sum_{\alpha} P_\alpha |\langle \Phi | \Psi_\alpha \rangle|^2 \geq 0$$

ρ is semi-positive definite \Rightarrow non-negative eigenvalues

Liouville's theorem (CM) $\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} - \{H, \rho\} = 0$

Evolution of QM density matrix $i\hbar \frac{\partial}{\partial t} \langle n | \rho(t) | m \rangle = i\hbar \frac{\partial}{\partial t} \sum_{\alpha} P_\alpha \langle n | \Psi_\alpha(t) \rangle \langle \Psi_\alpha(t) | m \rangle$

$$= i\hbar \sum_{\alpha} P_\alpha \left[\langle n | \frac{\partial}{\partial t} |\Psi_\alpha(t)\rangle \langle \Psi_\alpha(t) | m \rangle + \langle n | \Psi_\alpha(t) \rangle \frac{\partial}{\partial t} \langle \Psi_\alpha(t) | m \rangle \right]$$

$$= i\hbar \sum_{\alpha} P_\alpha \left[\langle n | \underbrace{\frac{1}{i\hbar} \hat{H}}_{\text{red}} |\Psi_\alpha(t)\rangle \langle \Psi_\alpha(t) | m \rangle + \langle n | \Psi_\alpha(t) \rangle \left(-\frac{1}{i\hbar} \right) \langle \Psi_\alpha(t) | \hat{H} | m \rangle \right]$$

$$= \sum_{\alpha} P_\alpha [\langle n | \hat{H} | \Psi_\alpha(t) \rangle \langle \Psi_\alpha(t) | m \rangle - \langle n | \Psi_\alpha(t) \rangle \langle \Psi_\alpha(t) | \hat{H} | m \rangle]$$

$$= \langle n | \hat{H} \hat{\rho} - \hat{\rho} \hat{H} | m \rangle = \langle n | [\hat{H}, \hat{\rho}] | m \rangle$$

in the basis of energy eigenstates

tensorial density (independent of the choice of basis)

$$i\hbar \frac{\partial}{\partial t} \hat{g} = [\hat{H}, \hat{g}]$$

$$\rho = \rho(\mathcal{H})$$

$$\text{or } \rho = \rho(\mathcal{H}, \mathcal{L}_\alpha)$$

Equilibrium requires time independent averages $\Rightarrow \frac{\partial \rho}{\partial t} = 0 \Rightarrow \begin{cases} CM: \langle \mathcal{H}, \rho \rangle = 0 \\ QM: [\hat{H}, \hat{\rho}] = 0 \end{cases} \Rightarrow$ if conserved quantity \mathcal{L}_α fulfills $[\hat{H}, \mathcal{L}_\alpha] = 0$

(Section 3.2)

QM Microcanonical ensemble $\rho(E) = \frac{\delta(\mathcal{H}-E)}{\Omega(E)}$ $\Rightarrow \langle n | \rho | m \rangle = \sum_\alpha p_\alpha \langle n | \mathbb{I}_\alpha \rangle \langle \mathbb{I}_\alpha | m \rangle = \begin{cases} \frac{1}{\Omega} & \text{if } \varepsilon_n = E \text{ and } m = n \\ 0 & \text{if } \varepsilon_n \neq E \text{ or } m \neq n \end{cases}$

Condition 1: $\mathcal{H}(n) = E$ (CM)
 $\varepsilon_n = E$ (QM)

Classical assumption
of equal a priori
equilibrium prob.

\Leftrightarrow
Only eigenstates of the correct energy can appear in GM states (for $p_\alpha = 1/\Omega$) has same amplitude
 $\frac{1}{|\langle n | \mathbb{I}_\alpha \rangle|^2} = 1/\Omega$

Condition 2: $m = n$

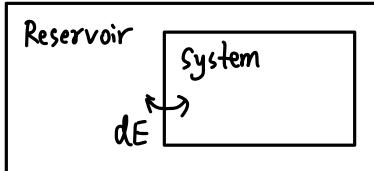
None

Ω eigenstates of E are combined in a typical microstates with independent random phases.

$$\left\{ \begin{array}{l} \text{tr}(\rho) = 1 \Rightarrow \Omega(E) = \sum_n \delta(E - \varepsilon_n) \text{ degeneracy} \\ \text{number of eigenstates of } \mathcal{H} \text{ with } E \end{array} \right\}$$

QM Canonical Ensemble

(at fixed $T = 1/k_B \beta$)



$$\rho(\beta) = \frac{\exp(-\beta \mathcal{H})}{Z(\beta)} \Rightarrow (\text{tr}(\rho) = 1) \quad Z = \text{tr}(e^{-\beta \mathcal{H}}) = \sum_n e^{-\beta \varepsilon_n}$$

Sum over the discrete energy levels of \mathcal{H}

QM Grand Canonical Ensemble Fock space \Leftarrow QM microstates with indefinite particle number

$$\rho(\beta, \mu) = \frac{e^{-\beta \mathcal{H} + \beta \mu N}}{\Omega} \Rightarrow \Omega(\beta, \mu) = \text{tr}(e^{-\beta \mathcal{H} + \beta \mu N}) = \sum_{N=0}^{\infty} e^{\beta \mu N} Z_N(\beta)$$

Example. A single particle in a QM canonical ensemble in a box of volume V

$$\hat{H}_1 = \frac{\vec{P}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2 \quad \text{and} \quad \hat{H}_1|\vec{k}\rangle = E(\vec{k})|\vec{k}\rangle$$

Eigen-funcs with Eigen-energies $\langle \vec{x} | \vec{k} \rangle = \frac{e^{i\vec{k} \cdot \vec{x}}}{\sqrt{V}}$ with $E(\vec{k}) = \frac{\hbar^2 k^2}{2m}$

Periodic boundary conditions in a box of size L

$\vec{k} = \frac{2\pi}{L}(l_x, l_y, l_z)$ w.r.t. $l_x, l_y, l_z \in \mathbb{Z}$

The space of QM microstates
 { infinite number in one-particle }
 Hilbert space

>> 6-dimensional CM phase space ($\{\vec{p}_i, \vec{q}_i\}$)

QM Partition func

$$Z_1 = \text{tr}(e^{-\beta \hat{H}}) = \sum_{\vec{k}} \exp\left(-\frac{\beta \hbar^2 k^2}{2m}\right) \xrightarrow{L \rightarrow \infty} V \int \frac{d^3 \vec{k}}{(2\pi L)^3} \exp\left(-\frac{\beta \hbar^2 k^2}{2m}\right)$$

$$= \frac{V}{(2\pi L)^3} \left(\frac{2m\pi k_B T}{\hbar^2}\right)^{3/2} = \frac{V}{\lambda^3}$$

Justification the use of $d^3 \vec{p} d^3 \vec{q} / h^3$ as the correct dimensionless measure of phase space.

Elements of density matrix in a coordinate representation

↓

Diagonal $\langle \vec{x} | \rho | \vec{x} \rangle = \frac{1}{V}$

Off diagonal no classical analog

Particle (wave packet with λ)

as $T \rightarrow \infty, \lambda \rightarrow 0, \text{ CM}$

$T \rightarrow 0, \lambda$ diverges, QM
 ($\lambda \sim \text{size of box } L$)

$$\begin{aligned} \langle \vec{x}' | \rho | \vec{x} \rangle &= \sum_{\vec{k}} \langle \vec{x}' | \vec{k} \rangle \frac{e^{-\beta E(\vec{k})}}{Z_1} \langle \vec{k} | \vec{x} \rangle \\ &\xrightarrow{L \rightarrow \infty} \frac{\lambda^3}{V} \int \frac{V d^3 \vec{k}}{(2\pi)^3} \frac{e^{-i\vec{k}(\vec{x}-\vec{x}')}}{V} \exp\left(-\frac{\beta \hbar^2 k^2}{2m}\right) \\ &\ast \exp\left(-\frac{\beta \hbar^2 k^2}{2m}\right) \xrightarrow{\substack{\text{I.F.T.} \\ k \rightarrow x-x'}} \frac{\exp\left[-\frac{m(x-x')^2}{2\hbar^2 \beta}\right]}{(\hbar^2 \beta/m)^{1/2}} \xrightarrow{3d} \frac{\exp\left[-\frac{m(\vec{x}-\vec{x}')^2}{2\hbar^2 \beta}\right]}{(\hbar^2 \beta/m)^{3/2}} \\ &= \frac{(\hbar^2 \beta / 2\pi m)^{3/2}}{V} \frac{1}{(2\pi)^3} \frac{1}{(\hbar^2 \beta/m)^{3/2}} (2\pi)^{3/2} \exp\left[-\frac{m(\vec{x}-\vec{x}')^2}{2\hbar^2 \beta}\right] \\ &= \frac{1}{V} \exp\left[-\frac{m(\vec{x}-\vec{x}')^2}{2\hbar^2 \beta}\right] \quad \text{Coefficient in I.F.T.} \\ &= \frac{1}{V} \exp\left[-\frac{\pi(\vec{x}-\vec{x}')^2}{\lambda^2}\right] \quad \text{yields to} \end{aligned}$$

Diffusion Eqn. (free particle) $\left(\rho(\beta) = \frac{e^{-\beta \hat{H}}}{Z_1} \right) \Rightarrow$

$$\frac{\partial}{\partial \beta} Z\rho = -\Im Z\rho = \frac{\hbar^2}{2m} \nabla^2 Z\rho$$

w.r.t. initial condition $\rho(\beta=0)=1$ $\langle \vec{x}' | \rho(\beta=0) | \vec{x} \rangle = \frac{\delta^3(\vec{x}-\vec{x}')}{V}$ (QM Mcan. En.) = $\frac{\delta^3(\vec{x}-\vec{x}')}{V}$

$$\frac{1}{|\langle \vec{n} | \vec{z} \rangle|^2} = 1/V$$