①

Recap:

Quantum harmonic oscillator $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$

$$Z = \frac{e^{-\beta\frac{\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} \Rightarrow E = \frac{\hbar\omega}{2} + \underbrace{\frac{\hbar\omega\, e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}}_{\omega \text{ such that } \hbar\omega \leq k_B T \text{ contribute}}$$

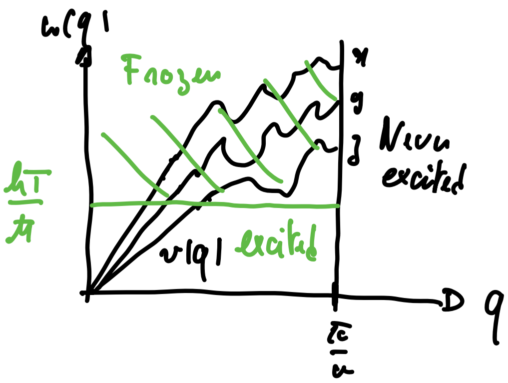
$$\Rightarrow \boxed{C^{vib}_{1,QM} = \frac{\hbar^2\omega^2}{k_B T^2} \frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2}}$$

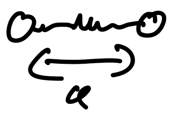
Solid

. Collective set of harmonic oscillators parametrized by wave vector $\vec{q}$ & polarization α.

$\Rightarrow \omega(\vec{q}, \alpha)$ & $E_{\vec{q},\alpha} = \hbar\omega(\vec{q},\alpha)\left(n_{\vec{q}\alpha} + \frac{1}{2}\right)$

. By symmetry $\vec{q} \to -\vec{q} \Rightarrow \omega(\vec{q}, \alpha) \simeq v_\alpha |\vec{q}|$ as $\vec{q} \to 0$





$q_{max} = \frac{2\pi}{a}$

* All the $T \to 0$ physics is controlled by $\omega(q) = v|\vec{q}|$

$\omega(\vec{q}) = v_\alpha |q| = v|q|$ for simplicity

$$E = \sum_{\substack{|q| < q_{max} \\ \text{polarization } \alpha}} \left(\frac{\hbar\omega(q)}{2} + \frac{\hbar\omega(q)\, e^{-\beta\hbar\omega(q)}}{1 - e^{-\beta\hbar\omega(q)}}\right) = E_0 + 3\sum_{\vec{q}} \frac{\hbar v|\vec{q}|}{e^{\beta\hbar v|\vec{q}|} - 1}$$

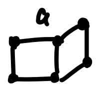
$$\boxed{\sum_{q_x, q_y, q_z} = \frac{V}{(2\pi)^3} \underbrace{\sum_{q_x} \overbrace{\frac{2\pi}{L}}^{dq_x} \sum_{q_y} \overbrace{\frac{2\pi}{L}}^{dq_y} \sum_{q_z} \overbrace{\frac{2\pi}{L}}^{dq_z}}_{\int dq_x \int dq_y \int dq_z} = \frac{V}{(2\pi)^3} \int d^3 q}$$

$$E(T) = E_0 + 3\frac{V}{(2\pi)^3}\int^{q_{max}} 4\pi q^2 dq \cdot k_B T \cdot \frac{\overbrace{\beta\hbar v q}^{x}}{e^{\underbrace{\beta\hbar v q}_{x}}-1} \quad ; \quad q = \frac{x k_B T}{v\hbar} \quad ; \quad dq = dx\,\frac{k_B T}{v\hbar}$$

$$= E_0 + 3\,\frac{V k_B T}{2\pi^2}\left(\frac{k_B T}{v\hbar}\right)^3 \int_0^{x_{max}} dx\, \frac{x^3}{e^x-1} \qquad x_{max} \propto \frac{q_{max}}{T} \xrightarrow[T\to 0]{} \infty$$

as $T \to 0 \simeq \int_0^\infty dx\, \frac{x^3}{e^x-1} = \frac{\pi^4}{15}$

$$E_{tot} = E_0 + \frac{V\pi^2}{10} k_B T \left(\frac{k_B T}{\hbar v}\right)^3 \quad ; \quad V = N a^3$$



$$\boxed{C_V = \frac{2\pi^2}{5} N k \left(\frac{k_B T a}{\hbar v}\right)^3 \Rightarrow \frac{C_V}{Nk} = \frac{2\pi^2}{5}\left(\frac{T}{\Theta_D}\right)^3 \qquad \Theta_D = \frac{\hbar v}{a k_B}} \sim 10^2 K$$

Debye temperature (1912)

5.3) Black body radiation

Electromagnetic field

Without sources $\vec\nabla\cdot\vec E = \vec\nabla\cdot\vec B = 0 \Rightarrow$ only two polarizations. ($\vec\nabla\cdot\vec E = 0 \Leftrightarrow \vec q\cdot\vec E_q = 0$)

Energy $u = \frac{\epsilon_0 \vec E^2}{2} + \frac{\vec B^2}{2\mu_0}$

Expand on normal modes $\Rightarrow$ sum of harmonic oscillators with frequencies $\omega(\vec q,\alpha) = c|\vec q|$

Same computation as for the solid!

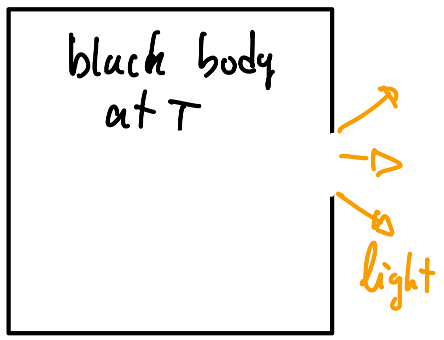
Energy & radiation energy

$$E = \sum_{\vec q,\alpha}\left[\hbar\omega(\vec q)\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar c|q|}-1}\right)\right]$$

from the computation we did for the vibrational degree of freedom of the diatomic gas.

$$E = V\left[\mathcal{E}_0 + \int_0^\infty dq\, \underbrace{\frac{q^2}{\pi^2}\, kT\, \frac{\beta\hbar c q}{e^{\beta\hbar c q}-1}}_{\frac{E(q)}{V}\ \text{density of energy in mode } q}\right]$$

$$E = V\left[\mathcal{E}_0 + kT\left(\frac{k_BT}{\hbar c}\right)^3\frac{\pi^4}{15}\right]$$

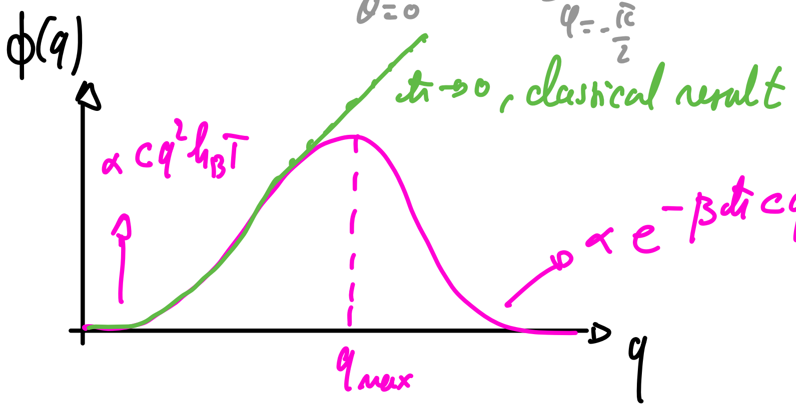


Radiated energy : $\langle v_x\rangle \times E(q)$

$$I(q) = \frac{\hbar c^2}{4\pi^2}\,\frac{q^3}{e^{\beta\hbar c q}-1}$$

Planck's law
1900

$$\langle v_x\rangle = \frac{1}{4\pi}\int_{\theta=0}^{\pi} d\theta \sin\theta \int_{\varphi=-\frac{\pi}{2}}^{\frac{\pi}{2}} d\varphi\, \overbrace{c\sin\theta\cos\varphi}^{v_x} = \frac{c}{4\pi}\cdot\frac{\pi}{2}\cdot 2 = \frac{c}{4}$$



$\propto e^{-\beta\hbar c q} \Rightarrow$ suggested the quantization

Total flux $= \frac{c}{4}\frac{E}{V} = \sigma T^4$ Stefan's law

↳ $\sigma = 5.67 \times 10^{-8}\ W.m^{-2}.K^{-1}$

Radiation pressure

$$Z = \prod_{\vec q,\alpha}\frac{e^{-\beta\hbar c q/2}}{1-e^{-\beta\hbar c q}} \Rightarrow F = k_BT\sum_{\vec q,\alpha}\left[\frac{\beta\hbar c q}{2} + \ln\left(1-e^{-\beta\hbar c q}\right)\right]$$

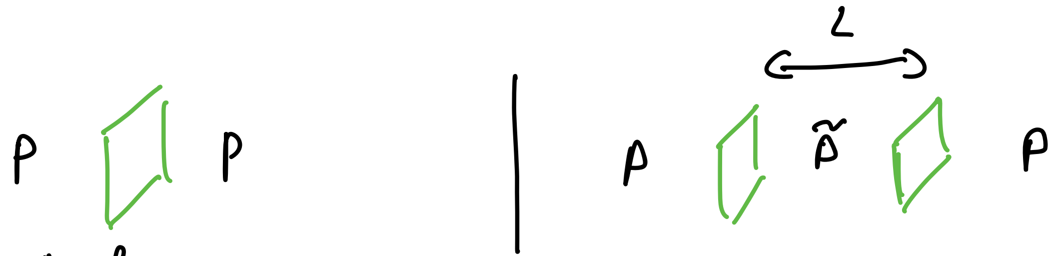
$$\simeq \frac{2V}{(2\pi)^3}\int d^3q\left[\frac{\hbar c q}{2} + k_BT\ln\left(1-e^{-\beta\hbar c q}\right)\right]$$

$$P = -\frac{\partial F}{\partial V} = P_0 - \frac{k_B T}{\pi^2}\int_0^\infty dq\, q^2 \ln\left(1 - e^{-\beta\hbar c q}\right)$$

IBP

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

$$= P_0 + \underbrace{\frac{E}{3V}}_{\delta P}$$



No force

$\tilde{P}$ has no mode such that $q_x < \frac{2\pi}{L}$

$\Rightarrow$ different energy $\Rightarrow$ Casimir force between the plates.

2018 Les Houches lecture notes by Kardar.

Chapter 6: Quantum statistical mechanics

6.1) Density matrix

Microstates: Classical $(\vec{q}, \vec{p}) \longrightarrow |\Psi\rangle$ unit vector in a Hilbert space $\mathcal{H}$.

* Vector product $\langle \Psi_1 | \Psi_2 \rangle$

* $|n\rangle$ a basis of $\mathcal{H}$ $\quad \langle n|\Psi\rangle$ component of $|\Psi\rangle$ along $|n\rangle$

$$|\Psi\rangle = \sum_n \langle n|\Psi\rangle\, |n\rangle = \sum_n \underbrace{|n\rangle\langle n|}_{\text{projection on } |n\rangle}\Psi\rangle$$

E.g. basis $|x\rangle$; $\langle x|\psi\rangle = \psi(x)$ is the wave function.

Observables, fluctuations & averages

classical observables are functions $O(x,p)$; e.g. x, p, H

* quantum ——— operators $\hat{O}$; e.g. $\hat{x}, \hat{p}, \hat{H}$

E.g. $\hat{p}$ is an operator such that $\langle x|\hat{p} = -i\hbar\vec{\nabla}\langle x|$

Take $|\psi_{\vec{p}}\rangle$ such that $\langle x|\psi_{\vec{p}}\rangle = e^{i\frac{\vec{p}\cdot\vec{x}}{\hbar}}$

then $\langle x|\vec{p}|\psi\rangle = -i\hbar\vec{\nabla}e^{i\frac{\vec{p}\cdot\vec{x}}{\hbar}} = \vec{p}\,e^{i\frac{\vec{p}\cdot\vec{x}}{\hbar}} = \vec{p}\langle x|\psi\rangle$

$\Rightarrow |\psi_{\vec{p}}\rangle$ is an eigenvector of $\hat{p}$ with eigenvalue $\vec{p}$.

* Consider a system in a state $|\psi\rangle$. The average of an observable over quantum fluctuations is given by

$$\langle\hat{O}\rangle_{QM} = \langle\psi|\hat{O}|\psi\rangle$$

* Typically, we do not know in which state is a system.
  - → If the system has a probability p_α to be in $|\psi_\alpha\rangle$, then the average of $\hat{O}$ over quantum fluctuations would lead to $\langle\psi_\alpha|\hat{O}|\psi_\alpha\rangle$.
  - → Two sources of uncertainty ① statistical → p_α & ② quantum

All in all,

$$\langle\hat{O}\rangle_{stat} = \sum_\alpha p_\alpha\langle\psi_\alpha|\hat{O}|\psi_\alpha\rangle$$

Classical: $\langle O\rangle = \int dx\, p(x)\, O(x)$; Here $O(x)$ is itself an average over quantum fluctuations.

6

Density matrix

$$\boxed{\hat{\rho} = \sum_\alpha p_\alpha |\psi_\alpha\rangle\langle\psi_\alpha|}$$

Take any basis $|n\rangle$

$$\langle\hat{O}\rangle_{stat} = \sum_\alpha \sum_n \sum_k p_\alpha \langle\psi_\alpha|n\rangle\langle n|\hat{O}|k\rangle\langle k|\psi_\alpha\rangle$$

$$= \sum_{n,k} p_\alpha \langle n|\hat{O}|k\rangle \quad \langle k|\Big(\sum_\alpha |\psi_\alpha\rangle\langle\psi_\alpha|\Big)|n\rangle$$

$$= \sum_{n,k} \langle n|\hat{O}|k\rangle\langle k|\hat{\rho}|n\rangle$$

$$\boxed{\langle\hat{O}\rangle_{stat} = \sum_n \langle n|\hat{O}\hat{\rho}|n\rangle = \sum_n \langle n|\hat{\rho}\hat{O}|n\rangle = \mathrm{Tr}(\hat{\rho}\hat{O})}$$

Properties:

positivity: $\langle\phi|\hat{\rho}|\phi\rangle = \sum_\alpha p_\alpha \underbrace{\langle\phi|\psi_\alpha\rangle\langle\psi_\alpha|\phi\rangle}_{|\langle\phi|\psi_\alpha\rangle|^2} \geq 0$

hermiticity: $\hat{\rho} = \hat{\rho}^+$

proof: $\langle n|\hat{\rho}^+|m\rangle = \langle m|\hat{\rho}|n\rangle^* = \sum_\alpha \langle m|\psi_\alpha\rangle^* \langle\psi_\alpha|n\rangle^*$

$$= \sum_\alpha \langle\psi_\alpha|m\rangle\langle n|\psi_\alpha\rangle = \langle n|\hat{\rho}|m\rangle$$

Normalization: $\mathrm{Tr}(\hat{\rho}) = \langle 1\rangle = 1$

$$\mathrm{Tr}(\hat{\rho}) = \sum_n \langle n|\hat{\rho}|n\rangle = \sum_n \sum_\alpha p_\alpha \langle n|\psi_\alpha\rangle\langle\psi_\alpha|n\rangle = \sum_\alpha p_\alpha \langle\psi_\alpha|\sum_n |n\rangle\langle n|\psi_\alpha\rangle$$

$$= \sum_\alpha p_\alpha \langle\psi_\alpha|\psi_\alpha\rangle = \sum_\alpha p_\alpha = 1$$

Evolution: $i\hbar \frac{\partial\hat{\rho}}{\partial t} = \sum_\alpha p_\alpha\, i\hbar\, \partial_t |\psi_\alpha\rangle\langle\psi_\alpha|$; $\quad i\hbar\,\partial_t|\psi_\alpha\rangle = \hat{H}|\psi_\alpha\rangle$

$$-i\hbar\,\partial_t\langle\psi_\alpha| = \langle\psi_\alpha|\hat{H}^+$$

$$= \langle\psi_\alpha|\hat{H}$$

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = \sum_\alpha p_\alpha \left(\hat{H} |\psi_\alpha\rangle\langle\psi_\alpha| - |\psi_\alpha\rangle\langle\psi_\alpha| \hat{H} \right) = [\hat{H}, \hat{\rho}]$$ 7

Similarly, $i\hbar\, \partial_t \langle \hat{O} \rangle = [\hat{H}, \hat{O}]$

Quantum version of $i\hbar\, \partial_t \hat{\rho} = \{\hat{H}, \hat{\rho}\}$

Steady state: $\partial_t \hat{\rho} = 0 \iff [\hat{H}, \hat{\rho}] = 0$

As in classical mechanics $f(\hat{H})$ will do the job!

$\Rightarrow \rho_{eq}(H)$ replaced by $\hat{\rho}_{QM}(\hat{H})$

$|n\rangle$ the eigenbasis of $\hat{H}$

$$\hat{\rho} = \sum_n \hat{\rho}\, |n\rangle\langle n| = \sum_n f(\hat{H})\, |n\rangle\langle n| = \sum_n f(E_n)\, |n\rangle\langle n|$$

$\Rightarrow p_n = f(E_n)$ as in classical stat mech!

Microcanonical

$$p_n = \begin{cases} 1/\Omega(E) & \text{if } E_n = E \\ 0 & \text{otherwise} \end{cases} \quad ; \quad \Omega(E) = \sum_n \delta_{E_n, E}$$

Entropy $S = k_B \ln \Omega(E)$

Canonical

$$p_n = \frac{1}{Z} e^{-\beta E_n} \iff \hat{\rho} = \frac{1}{Z} e^{-\beta \hat{H}}$$

$\mathrm{Tr}(\hat{\rho}) = 1 \Rightarrow Z = \mathrm{Tr}(e^{-\beta \hat{H}}) = \sum_n e^{-\beta E_n} \Rightarrow$ validates the approach of chapter 5!

Grand canonical

$$\hat{\rho} = \frac{1}{Q} e^{-\beta \hat{H} + \beta \mu \hat{N}} \quad ; \quad Q(\beta, \mu) = \mathrm{Tr}\left(e^{-\beta \hat{H} + \beta \mu \hat{N}}\right)$$

comment: steady state requires $[\hat{\rho}, \hat{H}] = 0$

Grand canonical $\Rightarrow$ $[\hat{N}, \hat{H}] = 0$ or $\mu = 0$

(Heisenberg: $i\hbar \partial_t \hat{N} = [\hat{N}, \hat{H}]$, non-conservation of particle number requires $\mu = 0$. E.g. stimulated emission & absorption for photons)

Thermodynamic properties:

$$\langle \hat{H} \rangle = \mathrm{Tr}(\hat{\rho}\hat{H}) = \mathrm{Tr}\left(\frac{e^{-\beta\hat{H}}}{Z}\hat{H}\right) = -\frac{1}{Z}\partial_\beta \mathrm{Tr}(e^{-\beta\hat{H}}) = -\frac{1}{Z}\partial_\beta Z$$

$$\langle \hat{H} \rangle = -\partial_\beta \ln Z$$ as in classical stat mech!

Maximum entropy & quantum ensembles

Also works here with $S = -k_B \mathrm{Tr}(\hat{\rho} \ln \hat{\rho})$

* In a given basis $|n\rangle$, the diagonal elements of $\hat{\rho}$ give the proba that the system is measured in $|n\rangle$: $\langle n|\hat{\rho}|n\rangle = \sum_\alpha p_\alpha \underbrace{\langle n|\Psi_\alpha\rangle\langle\Psi_\alpha|n\rangle}_{p(E_n|\text{system } \Psi_\alpha)} = p(E_n)$

* If $|\Psi_\alpha\rangle \in \{|n\rangle\}$; $|\Psi_\alpha\rangle = |n_0\rangle$; then $\langle n|\hat{\rho}|k\rangle = 0$

$\Rightarrow$ no intrication between $|n\rangle$ & $|k\rangle$ in $\hat{\rho}$.

Conversely, if $\langle n|\hat{\rho}|k\rangle \neq 0 \Rightarrow$ some level of intrication in this basis in the statistical mixture.

Ex: $|\Psi_+\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle)$; $|\Psi_-\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle - |\downarrow\rangle)$; $p_+ = \frac{1}{4}$, $p_- = \frac{3}{4}$

$$\rho = \frac{1}{4}|\Psi^+\rangle\langle\Psi^+| + \frac{3}{4}|\Psi^-\rangle\langle\Psi^-| = \frac{1}{8}\left(|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow| + |\uparrow\rangle\langle\downarrow| + |\downarrow\rangle\langle\uparrow|\right)$$
$$+ \frac{3}{8}\left(|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow| - |\uparrow\rangle\langle\downarrow| - |\downarrow\rangle\langle\uparrow|\right)$$