# (6) Quantum SM

dilute gas molecules, each molecule w/ n atoms:

$$Z = \frac{Z_1^N}{N!} = \frac{1}{N!}\left\{\int \prod_{i=1}^{n} \frac{d^3p_i\, d^3q_i}{h^3} \exp\left[-\beta \sum_{i=1}^{n} \frac{\vec{p}_i^{\,2}}{2m} - \beta \mathcal{V}(q_1, \dots, q_n)\right]\right\}^N$$

assume not interaction between the N molecules.

assume equilibrium at $(\vec{q}_1^{\,*}, \dots, \vec{q}_n^{\,*})$ thus.

$$\mathcal{V} = \mathcal{V}^* + \frac{1}{2}\sum_{i,j=1}^{n}\sum_{\alpha,\beta=1}^{3} \underbrace{\frac{\partial^2 \mathcal{V}}{\partial q_{i\alpha}\partial q_{j\beta}}}_{\text{positive definite}} u_{i\alpha} u_{j\beta} + O(u^3) \quad ; \quad \frac{\partial^2 \mathcal{V}}{\partial q_{i\alpha}\partial q_{j\beta}} \xrightarrow{\text{diag}} \underset{\text{stiff. matrix}}{K_s} \quad \text{w/ } u_i \to \tilde{u}_s \text{ unitary.}$$

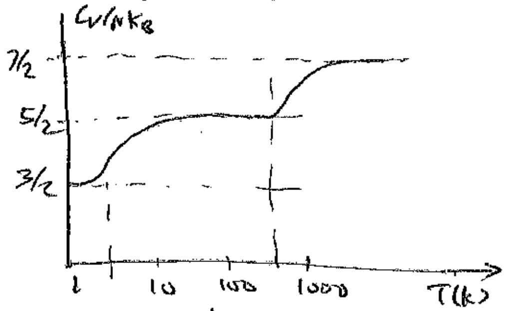
now $$H_1 = \mathcal{V}^* + \sum_{s=1}^{3n}\left[\frac{1}{2m}\hat{p}_s^2 + \frac{K_s}{2}\hat{u}_s^2\right]$$ and meas. $\prod_{i\alpha} du_{i\alpha} dp_{i\alpha} = \prod_s d\hat{u}_s d\hat{p}_s$ preserved.

thus $$\langle H_1 \rangle = \mathcal{V}^* + \frac{\underset{\text{KE}}{(3n)} + \underset{\mathcal{V}\text{ stiff matrix w/ non-zero eig. val}}{(m)}}{2} k_B T$$

where $m = 3n - \underset{\text{trans. sym}}{(3)} - \underset{\text{rot. sym.}}{(r)}$

$$\boxed{\langle H_1 \rangle = \frac{6n-3-r}{2} k_B T} \quad \boxed{C_v = \frac{6n-3-r}{2} k_B} \quad \& \quad \boxed{C_p = C_v + k_B = \frac{6n-1-r}{2} k_B}$$

Consider diatomic molecule.




Experimentally
- $C_v = \frac{7}{2} k_B$ at $T > 1000$ K
- $C_v = \frac{5}{2} k_B$ at $T_{rm}$

energy quantized and no energy stored in rot. and vib. modes.

Consider Vibrational modes

Classic $$Z_{vib}^c = \int \frac{dp\, dq}{h} \exp\left[-\beta\left(\frac{p^2}{2m} + \frac{m\omega^2 q^2}{2}\right)\right] = \frac{k_B T}{\hbar\omega}$$ here $h = h^c$ corr. term in Classic.

energy stored in this mode

$$\langle H_{vib} \rangle^c = -\frac{\partial \ln Z}{\partial \beta} = k_B T \qquad C_{vib}^c = k_B$$

Quantum. SHO in QM

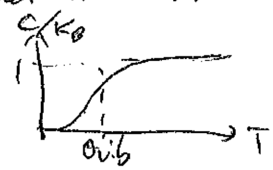
$$H = \hbar\omega(n + \tfrac{1}{2})$$

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

high temp, $\beta \to 0$ $\quad Z_{vib}^q = \frac{k_B T}{\hbar\omega}$ $\quad$ Remark agree w/ classical and $h^c = 2\pi\hbar$

$$E_{vib}^q = -\frac{\partial \ln Z}{\partial \beta} = \underbrace{\frac{\hbar\omega}{2}}_{\text{due to quant. fluc.}} + \underbrace{\hbar\omega \frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}}_{\text{therm. fluc.}} \quad ; \quad C_{vib}^q = k_B\left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{\beta\hbar\omega}}{(1 - e^{\beta\hbar\omega})^2}$$

char. temp $\Theta_{vib} = \frac{\hbar\omega}{k_B}$




$T \gg \Theta_{vib}$ $\quad C \to k_B$ class.

Rot. modes  o—o

class.

$$L = \frac{I}{2}\left(\dot\theta^2 + \sin^2\theta\,\dot\phi^2\right) \qquad H = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) = \frac{L^2}{2I}$$

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

$$\langle E_{rot}\rangle^c = -\frac{\partial \ln Z}{\partial\beta} = k_BT$$

QM

$$L^2 = \hbar^2 l(l+1) \qquad H = \frac{L^2}{2I}\underbrace{(2l+1)}_{\#\text{ of deg. states due to } z \text{ comp.}}$$

thus

$$Z_{rot}^q = \sum_{l=0}^{\infty} e^{-\beta\frac{\hbar^2 l(l+1)}{2I}}(2l+1)$$

def char. temp $\Theta_{rot} = \frac{\hbar^2}{2Ik_B}$ which assoc w/ quanta of rot. energy.

Remarks

- $T \gg \Theta_{rot}$ arg in exp small thus $\Sigma \to \int$

$$Z_{rot}^q = \int_0^\infty dx\,(2x+1)\,e^{-\frac{\Theta_{rot}(x^2+x)}{T}} = \int_0^\infty dy\, e^{-\frac{\Theta_{rot}\,y}{T}} = \frac{T}{\Theta_{rot}} \quad \simeq \text{classical}$$

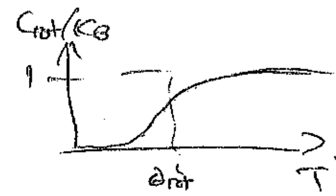
- $T \ll \Theta_{rot}$, first few terms dominate,

$$Z_{rot}^q \approx 1 + 3e^{-2\Theta_{rot}/T} \qquad \left(\text{note } 3e^{-\frac{2\Theta_{rot}}{T}} = 3e^{-\frac{2\hbar^2}{2I}\beta} \quad \frac{\partial}{\partial\beta} \to -\frac{6\hbar^2}{2Ik_B}k_B e^{-\frac{2\Theta_{rot}}{T}}\right)$$

$$E_{rot}^q = -\frac{\partial \ln Z}{\partial\beta} \approx 6k_B\Theta_{rot}e^{-2\Theta_{rot}/T}$$

typically $\Theta_{rot} \sim 1$ to $10\,K$

Thus at low temp the only contributions are from KE of COM. Molecule as monatomic particle.

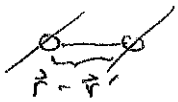


## (6) Vibrations of Solid

locations of atoms in simple crystal/lattice can be given in terms of 3 basis $\hat{a}, \hat{b}, \hat{c}$ w/ integer triplet $\{l, m, n\}$. $\vec{r} = \{l, m, n\}$ or $l\hat{a} + m\hat{b} + n\hat{c}$ (equilibrium p-t)
struct. subject to small deform. at finite temp.

$$\vec{q}_{\vec{r}} = \vec{r} + \vec{u}(\vec{r})$$

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



<u>Ansatz</u> $\quad \frac{\partial^2 V}{\partial q_{\vec{r}\alpha} \partial q_{\vec{r}'\beta}} = K_{\alpha\beta}(\vec{r} - \vec{r}')$

using <u>Fourier Basis</u> $\quad u_\alpha(\vec{r}) = \sum_{\vec{k}'} \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{N}} \tilde{u}_\alpha(\vec{k}) \quad$ w/ $\vec{k}$ inside Brillouin zone

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

<u>Change of coord</u> $\quad \vec{\rho} = \vec{r} - \vec{r}' \quad \vec{R} = \frac{\vec{r} + \vec{r}'}{2} \quad \vec{r} = \vec{R} + \frac{\vec{\rho}}{2} \quad \vec{r}' = \vec{R} - \frac{\vec{\rho}}{2}$

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

<u>Note</u> $\boxed{\sum_{\vec{R}} e^{i(\vec{k} + \vec{k}')\cdot\vec{R}} = N\delta_{\vec{k}+\vec{k}', 0}}$ Also Fourier Basis $\boxed{\tilde{K}_{\alpha\beta}(\vec{k}) = \sum_{\vec{\rho}} K_{\alpha\beta}(\vec{\rho}) e^{i\vec{k}\cdot\vec{\rho}}}$

Assuming $\tilde{K}_{\alpha\beta}(\vec{k}) = \delta_{\alpha\beta} \tilde{K}(\vec{k})$ diag.

<u>Recalled</u> $\vec{q}_{\vec{r}} = \vec{r} + \vec{u}(\vec{r})$ so KE $\quad \sum_{i=1}^{N} \frac{m}{2} \dot{q}_i^2 = \sum_{\vec{k}, \alpha} \frac{m}{2} \dot{\tilde{u}}_\alpha(\vec{k}) \dot{\tilde{u}}_\beta(\vec{k})^* = \sum_{\vec{k}, \alpha} \frac{1}{2m} \tilde{p}_\alpha(\vec{k}) \tilde{p}_\alpha(\vec{k})^*$

the deform Ham can now.

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

This corresponds. $\langle H \rangle = 3Nk_BT \quad C_V = 3Nk_B \quad C_V \to 0$ as $T \to 0$

<u>Now</u>. <u>QM</u>

Quantizing each harmonic mode

$$H^q = \mathcal{V}^* + \sum_{\vec{k}, \alpha} \hbar\omega_\alpha(\vec{k}) \left( n_{\vec{k}\alpha} + \frac{1}{2} \right) \quad (\text{for conv. } \mathcal{V}^* = 0)$$

$$Z^q = \sum_{\{n_{\vec{k}\alpha}\}} e^{-\beta H^q} = e^{-\beta \varepsilon_0} \prod_{\vec{k}, \alpha} \left[ \frac{1}{1 - e^{-\beta\hbar\omega_\alpha(\vec{k})}} \right]$$

$$E(T) = -\frac{\partial \ln Z^q}{\partial \beta} = \varepsilon_0 + \sum_{\vec{k}, \alpha} \hbar\omega_\alpha(\vec{k}) \langle n_\alpha(\vec{k}) \rangle \quad ; \quad \langle n_\alpha(\vec{k}) \rangle = \frac{e^{-\beta\hbar\omega_\alpha(\vec{k})}}{1 - e^{-\beta\hbar\omega_\alpha(\vec{k})}}$$

<u>Remark</u>
We need further simplification.

## Einstein Model

Assume all oscillators have same freq. $\omega_E$

thus
$$E = E_0 + 3N \frac{\hbar\omega_E e^{-\beta\hbar\omega_E}}{1 - e^{-\beta\hbar\omega_E}}$$
here def char. temp $T_E = \frac{\hbar\omega_E}{k_B}$

now
$$C = \frac{dE}{dT} = 3Nk_B\left(\frac{T_E}{T}\right)^2 \frac{e^{-T_E/T}}{(1-e^{-T_E/T})^2}$$

Remark: Exp. shows $C \to 0$ as $T^3$

Debye Model: Discrepancy rectified by Debye model: contribution to heat cap at low temp is due to lowest freq. oscillators w/ $\lambda = \frac{2\pi}{k}$

As $k \to 0$ $\tilde{K}(\vec{k}) \to 0$ thus $\tilde{K}(\vec{k}) \approx \beta k^2 + O(k^4)$

$\omega(\vec{k}) = \sqrt{\frac{\beta k^2}{m}} = vk$ $\quad v = \sqrt{\frac{\beta}{m}}$ speed of sound. (since $\omega = \sqrt{\frac{K}{m}}$)

using $\omega = vk$,
$$\langle H^q \rangle = E_0 + \sum_{\vec{k},\alpha} \frac{\hbar v k}{e^{\beta\hbar v k} - 1}$$

for a box of $L_x \times L_y \times L_z$ $\quad \vec{k} = \left(\frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z}\right)$

$$dN = \frac{V}{(2\pi)^3} d^3k = \rho\, d^3k \quad \text{w/ } \rho \equiv \frac{V}{(2\pi)^3} \text{ dos.}$$

now
$$E = E_0 + \underbrace{3}_{\text{from 3 comp of sound vel.}} V \int_{B.Z} \frac{d^3k}{(2\pi)^3} \frac{\hbar v k}{e^{\beta\hbar v k} - 1}$$
Def char. temp (Debye) $T_D = \frac{\hbar v k_{max}}{k_B} = \frac{\hbar v}{k_B}\frac{\pi}{a}$

Thus for $T \gg T_D$ $\beta \ll 1$ then $k_B T\left(3V\int_{B.Z}\frac{d^3k}{(2\pi)^3}\right) \approx 3Nk_B T$

$E = E_0 + 3Nk_B T$ in classic. regime

$C = 3Nk_B$

As $T \ll T_D$, let $x = \beta\hbar v k$ $\quad dx = \beta\hbar v\, dk$ $\quad d^3k = 4\pi k^2 dk = \frac{4\pi x^2 dx}{(\beta\hbar v)^3}$ $\quad$ w/ $\boxed{\int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}}$

then
$$E = E_0 + \frac{\pi^2}{10} V \left(\frac{k_B T}{\hbar v}\right)^3 k_B T$$
$$C = \frac{dE}{dT} = k_B V \frac{2\pi^2}{5}\left(\frac{k_B T}{\hbar v}\right)^3 \quad \text{so} \quad C \propto T^3$$
since only some phonon modes are thermally excited.

# (6) Black-body Radiation

EM wave $\nabla\cdot\vec{G}=0 \Rightarrow$ F.T $\vec{k}\cdot\vec{G}=0$ thus normal mode zero but only transverse mode allowed.

w/ $\omega = ck$ and

$$H = \frac{1}{2}\sum_{\vec{k},\alpha}\left[|\tilde{P}_{\vec{k}\alpha}|^2 + \omega_\alpha(\vec{k})^2|\tilde{a}_\alpha(\vec{k})|^2\right]$$

Periodic in the box thus $\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$

As in phonon, quantizing Ham.

$$H^q = \sum_{\vec{k},\alpha}\hbar ck\left(n_\alpha(\vec{k})+\frac{1}{2}\right) \qquad n_\alpha(\vec{k})=0,1,2,\dots$$

$$E = \sum_{\vec{k},\alpha}\hbar ck\left(\frac{1}{2}+\frac{e^{-\beta\hbar ck}}{1-e^{-\beta\hbar ck}}\right) = V\underbrace{E_0}_{} + \underbrace{\frac{2V}{(2\pi)^3}\int d^3k\,\frac{\hbar ck}{e^{\beta\hbar ck}-1}}_{(*)}$$

- $\infty$ zero pt energy
- ignored for energy diff.

thus the excited energy

$$\frac{E}{V} = \frac{\hbar c}{\pi^2}\left(\frac{k_BT}{\hbar c}\right)^4\int_0^\infty \frac{dx\,x^3}{e^x-1} \qquad \text{w/ } x=\beta\hbar ck$$

$$\frac{E^*}{V} = \frac{\pi^2}{15}\left(\frac{k_BT}{\hbar c}\right)^3 k_BT$$

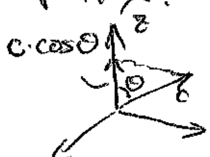
EM radiation pressure.

$$Z = \prod_{\vec{k},\alpha}\frac{e^{-\beta\hbar ck/2}}{1-e^{-\beta\hbar ck}}, \quad F = -k_BT\ln Z = 2V\int\frac{d^3k}{(2\pi)^3}\left[\frac{\hbar ck}{2}+k_BT\ln\left(1-e^{-\beta\hbar ck}\right)\right]$$

$$P = -\left.\frac{\partial F}{\partial V}\right|_T \quad \text{int. by part} \quad P = \underbrace{P_0}_{\text{zero pt "}\infty\text{"}} + \frac{\varepsilon}{3} \quad \text{w/ } \varepsilon = \frac{E}{V}$$

a hole in the wall gives escap. flux.

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




$$\langle c_\perp\rangle = \frac{2\pi}{4\pi}\int_0^{\pi/2} c\cos\theta\, d\cos\theta = \frac{c}{4}$$

thus $\phi = \frac{c}{4}\frac{E}{V} = \frac{c}{4}\frac{\pi^2}{15}\left(\frac{k_BT}{\hbar c}\right)^3 k_BT = \sigma T^4$

Let $\frac{E}{V} = \int dk\,\mathcal{E}(k,T)$ from (*), $\mathcal{E} = \frac{\hbar c}{\pi^2}\frac{k^3}{e^{\beta\hbar ck}-1}$

Emitted flux is then

$$I = \frac{c}{4}\mathcal{E}$$

## Quantum macrostates

ensemble average

Classical

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

Quantum

$$\mathcal{O} = \sum_\alpha P_\alpha \langle\psi_\alpha|O|\psi_\alpha\rangle = tr(\rho O)$$

Properties
- $\rho$ pure state iff $\rho^2=\rho$
- $tr(\rho) = 1$
- $\langle\Phi|\rho|\Phi\rangle \geq 0$ positive definite.
- Liouville's thm $\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} - \{H,\rho\} = 0$
- $i\hbar \frac{\partial}{\partial t}\rho = [H,\rho]$ equilibrium requires $\frac{\partial\rho}{\partial t}=0$

$\Big\}$ both cond satisfies if $\rho=\rho(H)$

Canonical example

$$\rho = \frac{e^{-\beta H}}{Z}$$

(obtain from Lagrange multiplier w/ constraints $tr(\rho)=1$ $E=tr(\rho H)$)

Given $H = P\Lambda P^{-1}$ $\Lambda = \begin{bmatrix} \epsilon_1 & & 0 \\ & \epsilon_2 & \\ 0 & & \ddots\ \epsilon_n \end{bmatrix}$ then

$$tr(H) = tr(\Lambda)$$

$$e^{-\beta H} \Rightarrow 1 - \beta\Lambda + \frac{\beta^2}{2!}\Lambda^2 - \frac{\beta^3}{3!}\Lambda^3 + \cdots$$

$$tr(e^{-\beta H}) = tr\left(1 - \beta\Lambda + \frac{\beta^2}{2!}\Lambda^2 - \cdots\right) = \sum_n \left(1 - \beta\epsilon_n + \frac{\beta^2}{2!}\epsilon_n^2 - \cdots\right)$$

thus $Z = tr(e^{-\beta H}) = \sum_n e^{-\beta\epsilon_n}$