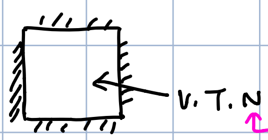
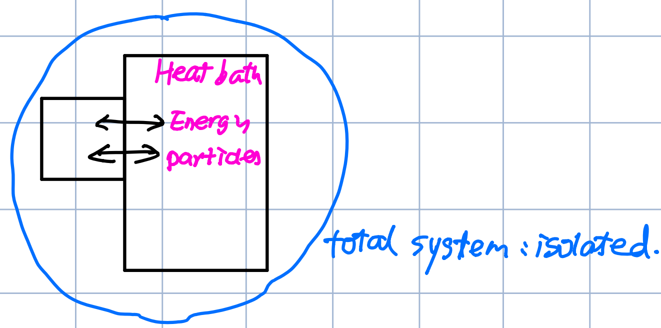
Ensembles	variables	system
Microcanonical	E.N.V	isolated system
Canonical	T.N.V	heat bath (for maintaining the temperature a constant)
Grand canonical	T.μ.V	heat bath & particle bath (maintain T & μ)

Chapter 10 Grand Canonical Ensemble

1.





Assumptions: 1° $E_{system} + E_{bath} = E_{total}$, $E_{sys} \ll E_{total} \sim E_{bath}$

2° $N_{system} + N_{bath} = N_{total}$. $N_{sys} \ll N_{total} \sim N_{bath}$

3° The total system follows microcanonical distribution.

2. Derivation

$$\underset{total}{P_{"i"}} = \begin{cases} a, & \text{if } E_{"i"tot} = E_L \\ 0, & \text{otherwise} \end{cases}$$

"i" tot $\to$ "i" bath + "i" sys

$$P_{"i"sys} = \sum_{"i"bath} P_{"i"bath} = \sum_{"i"bath} \begin{cases} a, & \text{if } E_{"i"total} = E_L = E_{"i"sys} + E_{"i"bath} \\ 0, & \text{otherwise} \end{cases}$$

$= a \cdot$ # of "i" bath having $E_{bath} = E_{Total} - E_{"sys"}$

$= a\Omega(E_{total} - E_{sys}, N_{Total} - N_{sys})$

$K_B \ln\Omega \to$ entropy

$$\ln\Omega = \ln\Omega(E_{tot} - \underline{E_{sys}}, N_{tot} - \underline{N_{sys}}) \approx \ln\Omega(E_{tot}, N_{tot}) - E_{sys}\frac{\partial \ln\Omega}{\partial E} - N_{sys}\frac{\partial \ln\Omega}{\partial N} - \cdots$$

$1^{st} + 2^{nd}$ laws of thermodynamics

$$T^{-1} = \frac{\partial S}{\partial E} \quad . \quad \frac{1}{k_B T} = \frac{1}{k_B}\frac{\partial S}{\partial E} = \frac{\partial \ln \Omega_{tot}}{\partial E}$$

$$-\mu T^{-1} = \frac{\partial S}{\partial N} \qquad \frac{-\mu}{k_B T} = \frac{\partial \ln \Omega_{tot}}{\partial N}$$

$\frac{\partial \ln \Omega}{\partial E} \equiv \beta$ $\qquad$ $\frac{\partial \ln \Omega}{\partial N} \equiv \alpha = \mu\beta$

$$\ln P_{\text{"}i\text{"}sys} = \ln a + \ln \Omega = \ln a + \ln \Omega (E_t, N_t) - E_s \frac{1}{k_B T} + N_s \frac{\mu}{k_B T} + \cdots$$

$$\Rightarrow P_{\text{"}i\text{"}sys, N_{sys}} \propto \exp(-\beta E_{\text{"}i\text{"}sys} + \mu\beta N_{\text{"}i\text{"}sys})$$

3. Normalization

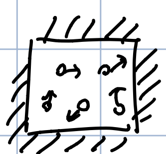
$$1 = \sum_{\text{"}i\text{"}, N} P_{\text{"}i\text{"}, N} = A \sum_{\text{"}i\text{"}, N} \exp(-\beta E_{\text{"}i\text{"}s} + \alpha N)$$

$$A = \left(\sum \exp(-\beta E_{\text{"}i\text{"}sys} + \alpha N) \right)^{-1} \qquad P_{\text{"}i\text{"}, N} = \frac{\exp(-\beta E_{\text{"}i\text{"}sys} + \alpha N)}{\sum_{\text{"}i\text{"}, N} \exp(-\beta E_{\text{"}i\text{"}sys} + \alpha N)}$$

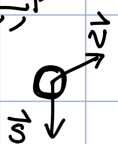
$$Z \equiv \sum_{\text{"}i\text{"}, N} \exp(-\beta E_{\text{"}i\text{"}sys} + \mu N)$$ Grand Canonical Partition Function.

Chapter 11 Quantum Ideal gas

1.



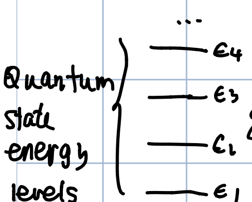
Ideal gas → No interaction between particles.
weak



particles → Quantum particles : Fermions : spin half integer $\cdot \hbar$ $\qquad e^-$
↑ $\qquad\qquad\qquad\qquad\qquad\qquad$ Bosons : spin integer $\cdot \hbar$ $\qquad \gamma$
carry spins.
intrinsic

- Pauli Exclusion Principle : No two fermions can occupy same Quantum State.
- Indistinguishability : cannot label the particles.

2. What do we determine?



$\varepsilon_{\text{"}i\text{"}}$ → energy states of a single particle
↑ $\qquad\qquad\qquad\qquad\qquad$ ↑
$i_1, i_2, i_3.$ $\qquad\qquad\qquad$ ideal gas

On average $\langle n_{"i"} \rangle \rightarrow$ average occupation number (can be non-integer)
as a function of "i"

3. Derivation

consider a distribution of occupation number

$\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4$
$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow$
$n_1 \quad n_2 \quad n_3 \quad n_4$ integers

Note: No labels for the particles

we know: $N = n_1 + n_2 + n_3 + \cdots$ # of particles in the system.

label of quantum states

system energy $E_{"i"} = n_1\epsilon_1 + n_2\epsilon_2 + \cdots$
of quantum state "i"

Gibbs Distribution of Grand Canonical Ensemble.

$$P_{"i",N} = P(n_1, n_2, n_3, \cdots)$$

$$\propto \exp(-\beta E_{"i" sys} + \alpha N) = \exp(-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots) + \alpha(n_1 + n_2 + \cdots))$$

ideal gas

Grand canonical partition function

$$Z(\alpha, \beta) = \sum_{\{n_i\}} \exp(-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots) + \alpha(n_1 + n_2 + \cdots))$$

system

$$= \prod_{"i"} \sum_{n_i=0}^{\infty} \exp(-\beta n_i \epsilon_i + \alpha n_i) = \prod_{"i"} Z_{"i"}(\alpha, \beta, \epsilon_{"i"})$$

Fermions (Fermi-Dirac Theory) $n = 0, 1$. No double/triple ... occupation.

$$Z^{FD}_{"i"} = 1 + \exp(-\beta\epsilon_i + \alpha)$$ Fermi-Dirac partial partition function.

Bosons (Bose-Einstein Theory) $n = 0, 1, 2, \cdots$

$$Z^{BE}_{"i"} = \sum_{n=0}^{\infty} \exp(-\beta n \epsilon_{"i"} + \alpha n) = \sum_{n=0}^{\infty} \exp[(-\beta\epsilon_{"i"} + \alpha) \cdot n] = \frac{1}{1 - \exp(-\beta\epsilon_{"i"} + \alpha)}$$

$\langle n_{"k"} \rangle = \sum n_k P(n_k) = \langle$ occupation number $\rangle$

$$P(n_k)=\sum_{\{n_i\}}^{n_k} P(n_1,n_2,\cdots,n_k,\cdots)$$

keep n_k unsummed

sum over all other n_i's

Probability Reduction.

$$\langle n_{"k"}\rangle=\sum_{n_k=0}^{"\infty"} n_k P(n_k)=\sum_{n_k} n_k \sum_{\{n_i\}\setminus\{n_k\}} P(n_1,n_2,\cdots,n_k,\cdots)$$

$$P(n_k)=\sum_{\{n_i\}\setminus\{n_k\}} \underbrace{\exp(-\beta(n_1\epsilon_1+n_2\epsilon_2+\cdots)+\alpha(n_1+n_2+\cdots))}_{\text{Gibbs probability}}/Z$$

partition function

$$=\frac{z_1\cdot z_2\cdot z_3\cdot z_4\cdots z_{k-1}\, z_{k+1}\cdots}{z_1\cdot z_2\cdot z_3\cdot z_4\cdots z_k\cdot z_{k+1}\cdots}\exp(-\beta n_k\epsilon_k+\alpha n_k)$$

$$=\frac{\exp(-\beta n_k\epsilon_k+\alpha n_k)}{z_k}$$

$$\langle n_{"k"}\rangle=\sum_{n_k} n_k\cdot\frac{\exp(-\beta n_k\epsilon_k+\alpha n_k)}{z_k}=\frac{1}{z_k}\sum n_k\exp(-\beta n_k\epsilon_k+\alpha n_k)$$

$$=\frac{1}{z_k}\frac{\partial}{\partial\alpha}\sum_{n_k}\exp(-\beta n_k\epsilon_k+\alpha n_k)$$

$$=\frac{1}{z_k}\frac{\partial z_k}{\partial\alpha}=\frac{\partial \ln z_k}{\partial\alpha}$$

Fermi-Dirac: $\langle n_{"k"}\rangle=\frac{\partial}{\partial\alpha}\ln(1+e^{-\beta\epsilon_k+\alpha})=\frac{e^{-\beta\epsilon_k+\alpha}}{1+e^{-\beta\epsilon_k+\alpha}}=\frac{1}{e^{\beta\epsilon_k-\alpha}+1}$

Bose-Einstein: $\langle n_{"k"}\rangle=-\frac{\partial}{\partial\alpha}\ln(1-e^{-\beta\epsilon_k+\alpha})=-\frac{-e^{-\beta\epsilon_k+\alpha}}{1-e^{-\beta\epsilon_k+\alpha}}=\frac{1}{e^{\beta\epsilon_k-\alpha}-1}$

$$\bar{n}^{FD}_{"k"}{}^{BE}=\frac{1}{e^{\beta\epsilon_k-\alpha}\pm 1}$$ Quantum ideal gas

where's the classical limit?

4. Classical Limit → Boltzmann-Einstein Distribution

$$\bar{n}^{B}_{"k"}=e^{-\beta\epsilon_{"i"}}e^{\alpha}$$

normalization constant

$\bar{n}^{FD/BE}_{"k"}$ becomes $\bar{n}^{B}_{"k"}$ when $e^{\beta\epsilon_k-\alpha}\gg 1$ (± 1 can be dropped)

when would this happen? Quantum → Classical.

5. What is α?

$$N = n_1 + n_2 + n_3 + \cdots = \sum_{\text{"k"}} n_{\text{"k"}}$$

$$\bar{N} = \sum_{\text{"k"}}{}' \bar{n}_{\text{"k"}} = \sum_{\text{"k"}} \frac{1}{e^{\beta\epsilon_k - \alpha} + 1} = \bar{N}(\alpha) \Rightarrow \alpha \text{ is a function of } \bar{N}.$$

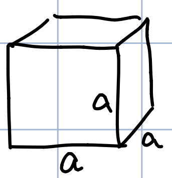
6. Classical Limit Revisited

$$e^{\beta\epsilon_k - \alpha} \gg 1 \Rightarrow \bar{n}_k^{FD/BE} \simeq \frac{1}{e^{\beta\epsilon_k - \alpha}} = e^{\alpha} e^{-\beta\epsilon_k} = \bar{n}_k^{B}$$

Meaning of $e^{\beta\epsilon_k - \alpha} \gg 1$ for all "k", it must be true for $k=0$, the ground state.

$$e^{-\alpha} \gg e^{-\beta\epsilon_0} \simeq e^{-\beta\hbar} \simeq 1 \Rightarrow e^{-\alpha} \gg 1 \quad \text{Classical limit}$$

$$\bar{N} = \sum_{\text{"k"}} \bar{n}_k \overset{\text{classical}}{\simeq} \sum_{\text{"k"}} e^{\alpha} e^{-\beta\epsilon_k} = e^{\alpha} \underbrace{\sum_k e^{-\beta\epsilon_k}}_{\text{one particle partition function}}$$



$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) = \epsilon\psi$$

$$\psi(x=0) = \psi(x=L) = 0$$

$$\psi = \left(\frac{2}{a}\right)^{3/2} \sin\frac{n_1\pi x}{a} \sin\frac{n_2\pi y}{a} \sin\frac{n_3\pi z}{a}$$

$$\epsilon_{\text{"k"}} = \frac{\hbar^2\pi^2}{2ma^2}(n_1^2 + n_2^2 + n_3^2) \qquad \text{"k"} \Leftrightarrow (n_1, n_2, n_3)$$

$$\bar{N} = e^{\alpha} z_1, \quad z_1 \overset{\text{Q.M.}}{=} \sum_{n_1,n_2,n_3=1}^{\infty} \exp\left(-\beta\frac{\hbar^2\pi^2}{2ma^2}(n_1^2+n_2^2+n_3^2)\right)$$

$$\simeq \int_0^{\infty} dn_1 \int_0^{\infty} dn_2 \int_0^{\infty} dn_3 \exp\left(-\beta\frac{\hbar^2\pi^2}{2ma^2}(n_1^2+n_2^2+n_3^2)\right)$$

$$= a^3\left(\frac{2\pi m k_B T}{h}\right)^{3/2} = V\left(\frac{2\pi m k_B T}{h}\right)^{3/2}$$

Recall: $z_1 = \frac{1}{h^3}\int d\vec{r}\, d\vec{P} \exp(-\beta P^2/2m)$ phase space, classical Hamiltonian,

$$= V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$ Gaussian Integration.

Another result: $e^{\alpha} = \bar{N}/z_1 \qquad \alpha = \mu\beta$

Go back to thermodynamics: $dF = -SdT - pdV + \mu dN$

$\mu = \frac{dF}{dN}$ $\quad \alpha = \beta \frac{dF}{dN}$. $F = -k_B T \ln Z_N$

$$= -\frac{\partial \ln Z_N}{\partial N}$$

$$= -\frac{\ln Z_{N+\Delta N} - \ln Z_N}{\Delta N}$$

$$= -\frac{\ln Z_{N+1} - \ln Z_N}{1}$$

$$= \ln \frac{Z_N}{Z_{N+1}}$$

α is partition function difference!

$$\frac{Z_{N+1}}{Z_N} = e^{-\alpha} = \frac{Z_1}{N} \qquad Z_{N+1} = \frac{Z_1 Z_N}{N} = \frac{Z_1}{N}\frac{Z_1}{N-1} Z_{N-1} = \frac{Z_1}{N}\frac{Z_1}{N-1}\frac{Z_1}{N-2} Z_{N-2} = \cdots$$

$$= \frac{Z_1^N}{N!} = Z_N$$

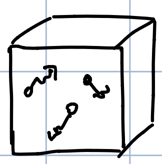
partition function of N particles

$Z_N = \frac{Z_1^N}{N!}$ ← single particle partition function.

Identical or Not, label or not.

After labelling, the need of $N!$ (Gibbs Correction)

Chapter 12 Photon Gas



EM waves

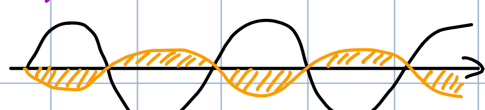
Freq. ω (each of the photons) $\qquad$ Energy $\hbar\omega = \epsilon$

Speed. c $\qquad$ $\epsilon = cp$ (not $\epsilon = p^2/2m$)

$m=0$ $\qquad$ Spin: $s = 1\hbar$ (Boson)

Degeneracy: $W = 2S+1 = 3$ (Q.M. but not correct)

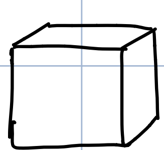
$W=2$ $\qquad$ physical interpretation:



transverse motion. 2

no longitudinal wave.

eg.



classical gas $\quad E = \sum_{\ell=1}^{N} c p_\ell$

$$Z = \frac{1}{N!}\int d\vec{r}^N d\vec{p}^N \exp\left(-\sum_{\ell=1}^{N} \beta c p_\ell\right)$$

$$= \frac{1}{N!} V^N \cdot \left[\int d\vec{p}\, e^{-\beta c p}\right]^N$$

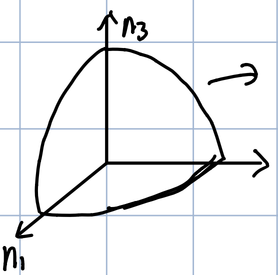
$$= \frac{1}{N!} V^N \left[4\pi \int p^2 e^{-\beta c p} dp\right]^N$$

$= \cdots$

2. Relativistic Schrödinger equation

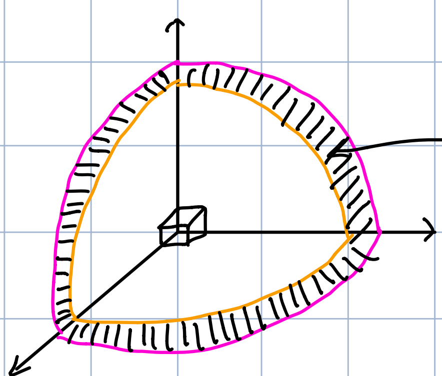
Relativistic Q.M.	Q.M.
(em wave eq.) $\nabla^2\psi = -\frac{\omega^2}{c^2}\psi$	$\nabla^2\psi = -\frac{2m\epsilon}{\hbar^2}\psi$
$\psi(x=0)=\psi(x=a)=\psi(y=0)=\psi(y=a)=\psi(z=0)=\psi(z=a)=0$	
$\psi = A\sin k_1x \sin k_2y \sin k_3z$	
$k_1=\frac{\pi n_1}{a},\ k_2=\frac{\pi n_2}{a},\ k_3=\frac{\pi n_3}{a}$	
$\epsilon = \hbar\frac{c\pi}{a}\sqrt{(n_1^2+n_2^2+n_3^2)}$ (No mass)	$\epsilon = \frac{\hbar^2}{2m}(n_1^2+n_2^2+n_3^2)\frac{\pi^2}{a^2}$

Comments: 1° $\vec{n}$-space



→ spherical surface ⇒ same $n_1^2+n_2^2+n_3^2$
⇒ same ϵ.

2° # of states in a shell $n \to n+\Delta n$



spherical shell.

"Volume" in $\vec{n}$-space $= \frac{1}{8}\cdot 4\pi n^2\Delta n$

"# of states" = "Volume" / ▢ $= \frac{1}{8}\cdot 4\pi n^2\Delta n$.

$\omega = \frac{c\pi n}{a} \Rightarrow$ "# of states" $= \frac{1}{8}4\pi\left(\frac{a}{c\pi}\right)^3\omega^2\Delta\omega = \frac{V}{2}\frac{1}{\pi^2c^3}\omega^2\Delta\omega$

3. Radiation Energy

The energy ΔE of the radiation in the frequency range $\omega \to \omega+\Delta\omega$

$= \hbar\omega\cdot\Delta N_{\omega\to\omega+\Delta\omega} = \hbar\omega\cdot$(average occupation #)$\cdot$ # of states

one photon   # of photons falling into $\omega\to\omega+\Delta\omega$ range

$$= \hbar\omega \frac{W=2}{e^{\hbar\omega/k_BT}-1} \frac{V}{2}\frac{1}{\pi^2 c^3}\omega^2\Delta\omega$$

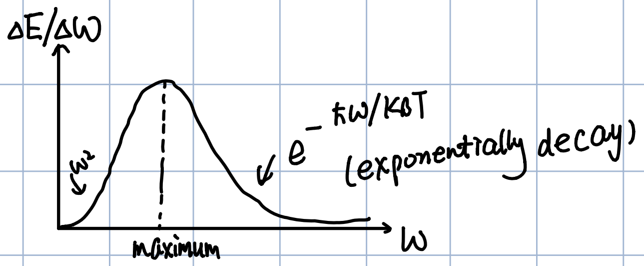
Bose-Einstein Distribution

$$\frac{1}{V}\Delta E/\Delta\omega = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\hbar\omega/k_BT}-1}$$ Planck's radiation Law

Commonly accepted assumption:

$\alpha = \frac{\mu}{k_BT} = 0$ for photons

Comments: 1°



2° Energy of the radiation at T with $[\omega_1, \omega_2]$

$$\frac{E}{V} = \int_{\omega_1}^{\omega_2} d\omega \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\hbar\omega/k_BT}-1}$$

3° Total energy density

$$E/V = \int_0^\infty d\omega \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\hbar\omega/k_BT}-1} = \frac{(k_BT)^4}{\hbar^3\pi^2 c^3}\underbrace{\int_0^\infty \frac{x^3}{e^x-1}dx}_{\text{just a number}}$$

$\Rightarrow E \propto T^4$ Stefen-Boltzmann Law.

4° ω_{max}.

$$\frac{d}{d\omega}\frac{\omega^3}{e^{\hbar\omega/k_BT}-1} = 0 \Rightarrow \frac{d}{dx}\frac{x^3}{e^x-1} = 0 \Rightarrow x_{max} = 2.7\cdots$$

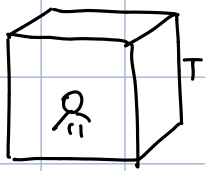
$$\Rightarrow \omega_{max} = (2.7\cdots)\frac{k_BT}{\hbar}$$ linear dependance.

Wien's law

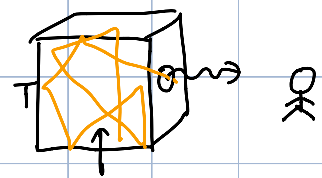
$$\left.\frac{dE}{d\omega}\right|_{\omega_{max}} \propto \omega^3$$

heat transfer $\begin{cases} \text{conduction} \\ \text{convection} \\ \text{radiation} \end{cases}$

4. Black Body Radiation



$\frac{\Delta E}{\Delta \omega}$

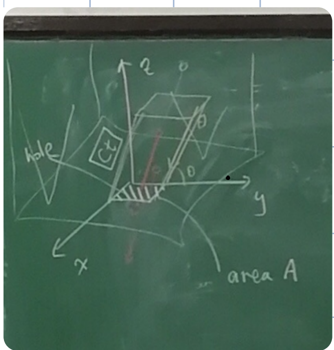


Black Body: Not affected by the radiation

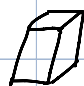
small hole $\Rightarrow$ observing inside

(everything from the outside is absorbed)

effusion: Molecules effuse ...



only the molecules inside the box can go through the hole.

The fraction of photons inside  $= V_{box}/V_{system}$

$$= \frac{\text{Area} \cdot ct\cos\theta}{V}$$

The fraction of photons inside , moving at an angle (θ, φ)

$$= \frac{\text{Area} \cdot ct\cos\theta}{V} \cdot \frac{\sin\theta\, d\theta\, d\varphi}{4\pi}$$

The energy you receive

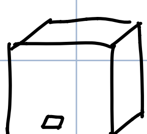
$$\frac{A \cdot ct \cdot \cos\theta}{V} \; \frac{\sin\theta\, d\theta\, d\varphi}{4\pi} \; \frac{\hbar\omega^3 d\omega}{\pi^2 c^3 (e^{\hbar\omega/k_BT} - 1)}$$

On average, per area $\frac{1}{A}$, per unit time $\frac{1}{t}$

$$\Rightarrow \frac{c}{V} \cdot \frac{1}{4\pi} \int_0^{\pi/2} d\theta \int_0^{2\pi} d\varphi \, \sin\theta\cos\theta \int_0^{\infty} \frac{\hbar\omega^2\, d\omega}{\pi^2 c^3 (e^{\hbar\omega/k_BT} - 1)}$$

Black Radiation law = Planck Radiation law.

eg. Classical gas



$$f(\vec{v}) = e^{-\frac{1}{k_BT}\frac{1}{2}mv^2} \rightarrow \bar{v}, \bar{v^2}, \text{etc.}$$

$\bar{v}_{effusion}$, $\bar{n}_{effusion}$ $\left(\frac{\text{unit time}}{\text{unit area}}\right)$

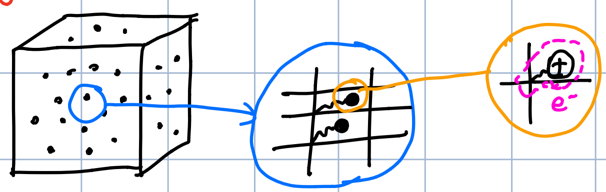
$n_{eff} = v\cos\theta\sin\theta\, d\theta\, d\varphi\, e^{-\frac{1}{k_BT}\frac{1}{2}mv^2}$ ...

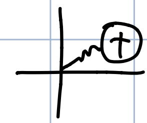
$\bar{v}_{eff} = \int d\vec{v} \cdot v\, n_{eff} \,/\, \text{Normalisation} = \dfrac{4\pi \int_0^{\infty} v^3 dv \cdot v \int_0^{\pi/2} d\theta \int_0^{2\pi} d\varphi \cos\theta\sin\theta\, e}{}$

$$4\pi\int_0^\infty v^2 dv \cdot v\int_0^{\pi/2} d\theta \int_0^{2\pi} d\varphi \cos\theta\sin\theta\, e^{\cdots}$$

Chapter 13 Fermi-Dirac statistics and electron gas

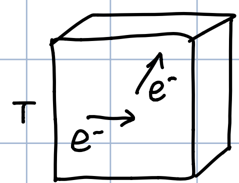
1. Physical Picture



→ vibration of ions 

→ electrons flying around

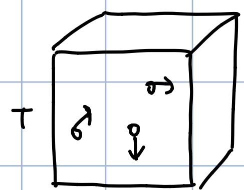
free electrons



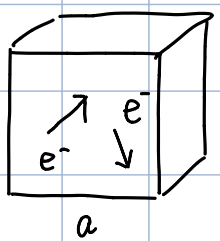
conductor → e^- gas $\quad m_e^*$ effective mass

why m star? electrons are really not free (appears more massive) $m_e^* > m_e$

N.V. spin. FD



molecular classical ideal box $\quad$ m. N. V. Boltzmann



→ Schrödinger Eq: $\epsilon_{``i"} = \epsilon(n_1, n_2, n_3) = \frac{\hbar^2}{2m_e^*}\left(\frac{\pi}{a}\right)^2(n_1^2+n_2^2+n_3^2)$

FD: $\langle n_{``i"}\rangle = \dfrac{1}{\exp(\beta\epsilon_{``i"} - \alpha)+1}$ $\quad$ spin-$\frac{1}{2}$ $\Rightarrow W = 2S+1 = 2$

2. Why use Fermi-Dirac? [room T]

$e^{-\alpha} \gg 1 \to$ classical

$$\bar{N} = \sum_{``i"}\langle n_{``i"}\rangle = \cdots = e^{\alpha} V\left(\frac{2m}{\beta}\pi\frac{1}{h^2}\right)^{3/2}$$

$$e^{\alpha} = \frac{N}{V}\left(\frac{2m}{\beta}\pi\frac{1}{h^2}\right)^{-3/2}$$ ($\ll 1$ in order to have a classical limit)

$$= \frac{N}{V}\left(\frac{\frac{h^2}{2m\pi k_B}}{T}\right)^{3/2} = \left(\frac{\left(\frac{N}{V}\right)^{\frac{2}{3}}\left(\frac{h^2}{2m\pi k_B}\right)}{T}\right)^{\frac{3}{2}} = \left(\frac{T_0}{T}\right)^{\frac{3}{2}}$$

$T_0 = \left(\frac{N}{V}\right)^{\frac{2}{3}}\frac{h^2}{2m\pi k_B} \sim 70000\,K$ $\quad$ ($m \to m_e^*$)

$e^{\alpha} = (T_0/T)^{3/2} \gg 1$ $\quad$ Electron gas is not a classical gas!

Room temperature is a very low temperature. (comparing with T_F)

$\Rightarrow$ Q.M.

3. e^- gas at $T=0K$ $\left(\frac{T_0}{T} \gg 1\right)$

$$\langle N_{"i"}^{FD} \rangle = \frac{1}{\exp(\beta\epsilon_{"i"} - \alpha) + 1} \qquad \alpha \equiv \beta\mu$$

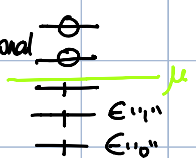
μ: [energy], chemical potential

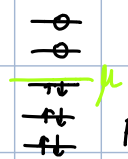
$$= \frac{1}{\exp[\beta(\epsilon_{"i"} - \mu)] + 1}$$

$$\overset{T \to 0}{=} \begin{cases} 0, & \epsilon_{"i"} \geq \mu \\ 1, & \epsilon_{"i"} < \mu \end{cases}$$

Remarks: 1° "i" space 2° spin (DOF) $W=2$ ↑↓

"i" is translational



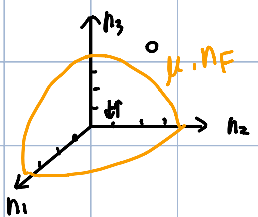


Pauli Exclusion Principle.

$\mu \to \epsilon_F$ Fermi level/energy/CP

3° $\epsilon_{"i"} = \frac{\hbar^2\pi^2}{2m_e^* a^2}(n_1^2 + n_2^2 + n_3^2)$

"n" space



$$\# \text{ of occupied states} = \underbrace{\frac{1}{8}\cdot\frac{4}{3}\pi n_F^3}_{\frac{1}{4}\pi n_F^2\ (2D)} = \frac{\pi}{6}n_F^3 = \frac{\pi}{6}\left(\frac{\epsilon_F \cdot 2m_e^* a^2}{\hbar^2\pi^2}\right)^{3/2}$$

4. ϵ_F?

$$N = W \cdot \# \text{ of occupyied States} = W\left(\frac{\epsilon_F \cdot 2m_e^* a^2}{\hbar^2\pi^2}\right)^{3/2} \cdot \frac{\pi}{6}$$

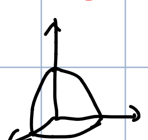
N: total #

$$= W \cdot a^3 \cdot \frac{\pi}{6} \cdot \epsilon_F^{3/2}\left(\frac{2m_e^*}{\hbar^2\pi^2}\right)^{3/2}$$

$$\frac{N}{V} = W \cdot \frac{\pi}{6} \cdot \epsilon_F^{3/2}\left(\frac{2m_e^*}{\hbar^2\pi^2}\right)^{3/2} \Rightarrow \epsilon_F = \left(\frac{6}{W}\right)^{2/3}\frac{\hbar^2\pi^{4/3}}{2m}\left(\frac{N}{V}\right)^{2/3}$$

$\Theta_F \equiv \epsilon_F / k_B$ Fermi Temperature $\Theta_F \propto T_0$ $\Theta_F \sim 10^4 K$

5. Average Energy



$$E = \sum_{"i"} \epsilon_{"i"} \langle N_{"i"} \rangle W = \sum \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 (n_1^2 + n_2^2 + n_3^2) \cdot W \cdot \begin{cases} 1 & \epsilon < \epsilon_F \\ 0 & \epsilon > \epsilon_F \end{cases}$$

$$= \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 w \sum^{n_F}(n_1^2+n_2^2+n_3^2)$$
$$= \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 w\cdot \int_0^{n_F} dn\cdot n^2\cdot 4\pi\cdot n^2$$
$$= \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 w\cdot 4\pi\cdot \frac{1}{5}n_F^5$$
$$= \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\cdot w\cdot \frac{4\pi}{5}\left(\frac{6N}{w\pi}\right)^{5/3} \qquad \frac{4}{3}\pi n_F^3\cdot\frac{1}{8}=N\ ,\ \epsilon_F=\frac{\hbar^2\pi^2}{2ma^2}n_F^2$$
$$= \frac{3}{5}N\epsilon_F$$

6. Distribution of ϵ

$$\langle n_{"i"}\rangle = \begin{cases} 1, & \epsilon_{"i"}<\mu \\ 0, & \epsilon_{"i"}>\mu \end{cases}$$

# of states between n & $n+dn$ $= 4\pi n^2 dn\cdot w$

# of states between ϵ & $\epsilon+d\epsilon$ $= 4\pi\frac{\epsilon}{A}\cdot\frac{w}{2\sqrt{A\epsilon}}d\epsilon = \frac{2\pi}{A}\sqrt{\frac{\epsilon}{A}}d\epsilon\cdot w = 2\pi\cdot\frac{W}{A^{3/2}}\sqrt{\epsilon}\,d\epsilon$

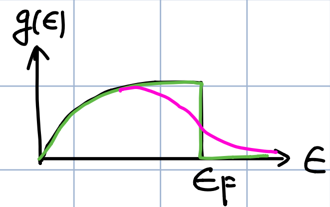
$\epsilon = An^2$

$n=\sqrt{\epsilon/A}$

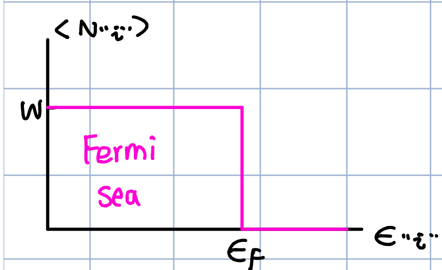
$dn=\frac{1}{2\sqrt{A\epsilon}}d\epsilon$

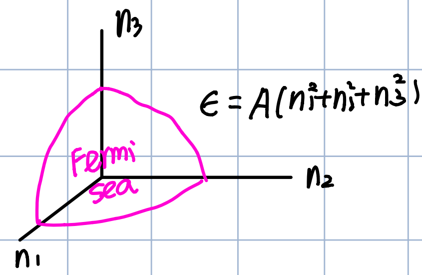
distribution of energy

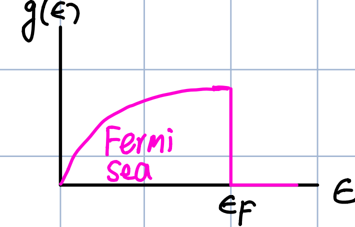
$$\Rightarrow g(\epsilon)=\begin{cases}\frac{2W\pi}{A^{3/2}}\sqrt{\epsilon}, & \epsilon<\epsilon_F \\ 0, & \epsilon>\epsilon_F\end{cases}$$



$$\bar{\epsilon}=\int_0^\infty g(\epsilon)\epsilon\, d\epsilon \Big/ \int_0^\infty g(\epsilon)d\epsilon$$
$$=\int_0^{\epsilon_F}\epsilon\sqrt{\epsilon}\,d\epsilon \Big/ \int_0^{\epsilon_F}\sqrt{\epsilon}\,d\epsilon$$
$$=\frac{3}{5}\epsilon_F$$
$$\Rightarrow \bar{E}=\frac{3}{5}N\epsilon_F$$





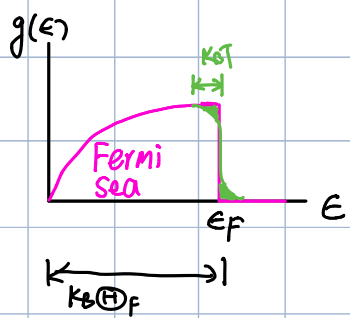


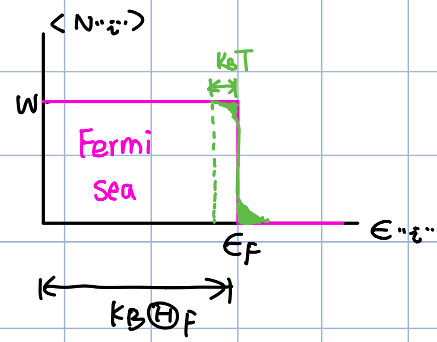
7. low temperature correction (in order to understand heat capacity)

T/Θ_F

$\Theta_F \sim T_0 \simeq 10^4 K$

"Guess" (a) Physical Picture





The top $\square\, k_BT/\epsilon_F$ fraction of e^-'s will be affected.

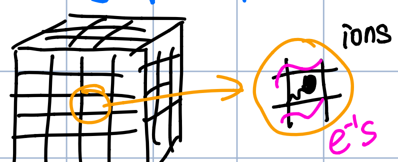
$\Delta\epsilon_{\text{"moved"}} \simeq k_BT$

Correction to the total energy

$$\Delta E = \underbrace{\frac{k_BT}{\epsilon_F}N}_{\text{total \# of affected } e^{-1}\text{'s}} \cdot \underbrace{\Delta\epsilon}_{\text{each electron}} = \square\, \frac{k_BT}{\epsilon_F} N \cdot k_BT = \square\, \frac{(k_BT)^2}{\epsilon_F} N$$

$$E = \underbrace{\frac{3}{5}N\epsilon_F}_{\text{0K contribution}} + \square\, \frac{(k_BT)^2}{\epsilon_F} N + \cdots \qquad C_V = \frac{\partial E}{\partial T} = \square\, \frac{k_B^2 T}{\epsilon_F} N \qquad \frac{C_V}{Nk_B} = \underbrace{\square}_{\left(\frac{\pi^2}{2}\text{, from exact theory}\right)} \frac{k_BT}{\epsilon_F} + \cdots$$

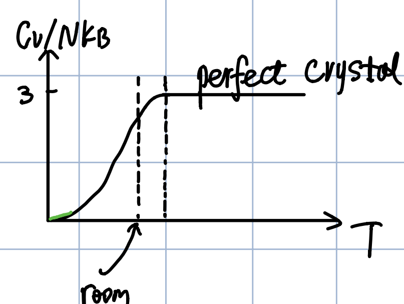
(b) Summary of C_V of a conductor



ions: $\begin{cases} \text{High T: } 3Nk_B \\ \text{low T (Debye Theory)} \sim e^{-\Theta/T} \text{ (fast} \to 0) \end{cases}$

Einstein, I think

e^-'s: $Nk_B \cdot \frac{k_BT}{\epsilon_F}$ (room temperature)



Chapter 15 Ideal Bose Gas

1. BE distribution

$$\langle N^{BE}_{"i"} \rangle = \frac{1}{e^{\beta(\epsilon_{"i"}-\mu)}-1} > 0$$

For fixed N,

$$\Rightarrow \epsilon_{"i"} \geqslant \mu \quad \text{for all "i"}$$

Use the ground state $\epsilon_0 \Rightarrow \epsilon_0 - \mu \geqslant 0$

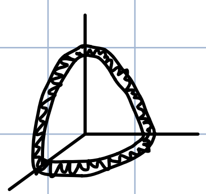
Claim $\epsilon_0 = 0$, use for discussion (if $\epsilon_0 \neq 0$, redefine $\mu' = \mu - \epsilon_0$) $\Rightarrow \mu \leq 0$

Non-relativistic bosons

From Q.M., $\epsilon_{"i"} = \epsilon_{n_1,n_2,n_3} = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 (n_1^2+n_2^2+n_3^2) = An^2$ $\quad d\epsilon_{"i"} = 2An\,dn$, $n = \sqrt{n_1^2+n_2^2+n_3^2}$ $\quad dn = \frac{1}{2\sqrt{A\epsilon}}d\epsilon$

Attempt to calculate N/V.

$$N = \sum_{"i"} \langle N_{"i"} \rangle = \sum_{n_1,n_2,n_3} \langle N_{"i"} \rangle = \int_0^\infty dn_1\, dn_2\, dn_3 \langle N_{"i"} \rangle$$



$$= 4\pi \cdot \frac{1}{8} \int_0^\infty n^2 dn \cdot \langle N_{"i"} \rangle$$

$$= 4\pi \cdot \frac{1}{8} \int_0^\infty \frac{\epsilon}{A} \cdot \frac{1}{2\sqrt{A\epsilon}} d\epsilon \langle N_{"i"} \rangle$$

$$= \frac{\pi}{4A^{3/2}} \int_0^\infty \sqrt{\epsilon} \frac{1}{e^{\beta(\epsilon-\mu)}-1} d\epsilon$$

$$= \frac{\pi a^3}{4\left(\frac{\hbar^2}{2m}\cdot\pi^2\right)^{3/2}} \int_0^\infty \frac{\sqrt{\epsilon}}{e^{\beta(\epsilon-\mu)}-1} d\epsilon$$

$$\frac{N}{V} = \frac{2\pi}{h^3}(2m)^{3/2} \int_0^\infty \frac{\sqrt{\epsilon}}{e^{\beta(\epsilon-\mu)}-1} d\epsilon$$

When the density is fixed, μ changes with the change of T.

Effects of lowering T: (we expect the integral to be the same)

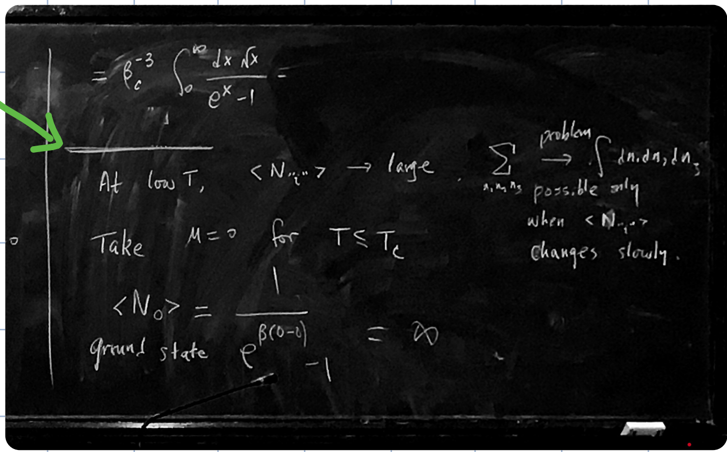
$$\int_0^\infty \frac{\sqrt{\epsilon}}{e^{\beta(\epsilon-\mu)}-1} d\epsilon \quad . \quad T\downarrow \Rightarrow \mu\uparrow$$

$$= \beta^{-3} \int_0^\infty \frac{\sqrt{x}}{e^x-1} dx \quad (T = T_c)$$

At $T = T_c$, μ increases to $\mu = 0$ (maximum μ)

What happens when $T < T_c$?

something wrong with this



Condensation in n-space

Everything is Condensed into the lowest energy level.

2. What is Tc? Critical temperature

Assume $\Sigma \to \int d\vec{n}$ still works when $T \to T_c^+$

$$\frac{N}{V} = \frac{2\pi}{h^3}(2m)^{3/2}(k_B T_c)^{3} \int_0^\infty \frac{dx\sqrt{x}}{e^x-1} = \frac{2\pi}{h^3}(2m)^{3/2}(k_B T)^3 \cdot 2.612\cdots \Rightarrow T_c$$

He^4: $T_c = 3.1\,K$

Bose-Einstein Condensation

$$T_c(n) = \frac{h^2}{2\pi m k_B}\left(\frac{n}{g\zeta_{3/2}}\right)^{2/3}.$$

Bose-Einstein Condensation (Bose systems)

1. Critical temperature Tc

$$\langle N_{"i"}^{BE}\rangle = \frac{1}{e^{\beta(\epsilon_{"i"}-\mu)}-1}$$

μ: chemical potential

$\epsilon_{"i"}$: single particle energy

$$N = \sum_{"i"} \frac{1}{e^{\beta(\epsilon_{"i"}-\mu)}-1}$$

total # of particles. $N = N(\beta, \mu, V)$

$\Rightarrow \mu = \mu(T, N, V)$ $\quad\quad$ $\mu \le 0$ in order to have $\frac{1}{e^{-\beta\mu}-1} > 0$

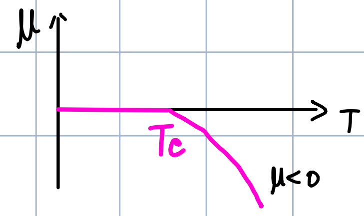
$$\epsilon_{"i"} = \epsilon_0(n_1^2+n_2^2+n_3^2)$$

Approximately, $N = \int dn_1 \int dn_2 \int dn_3 \frac{1}{e^{\beta(\epsilon_{"i"}-\mu)}-1}$

$$= \frac{4\pi}{8}\int dn \cdot \frac{n^2}{e^{\beta(\epsilon_{"i"}-\mu)}-1}$$

$$\Rightarrow \frac{N}{V} = \frac{2\pi}{h^3}(2m)^{3/2}\int_0^\infty \frac{\sqrt{\epsilon}}{e^{\beta(\epsilon-\mu)}-1}\,d\epsilon$$

$T\downarrow$, $\mu\uparrow$, in order to have N fixed.



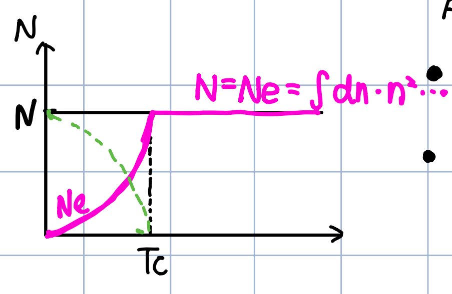
$$\frac{N}{V}=\frac{2\pi}{h^3}(2m)^{3/2}(k_B T_c)^{3/2}\int_0^\infty \frac{dx\cdot x^{\frac{1}{2}}}{e^x-1} \quad (*)$$

if $T<T_c$, we cannot keep $\underline{\frac{N}{V}=\frac{2\pi}{h^3}(2m)^{3/2}(k_B T)^{3/2}\int_0^\infty \frac{\sqrt{x}\,dx}{e^x-1}}$ constant.

What has been done wrong?

Note that $\sum \to \underbrace{\int n^2 dn}_{=N_e}$; erased contribution from $n_1=n_2=n_3\approx 0$ (ground state)

Pic:



$N_0 + N_e = N$

For $T<T_c$,

$$N=\sum\langle N\rangle = N_0+\int_0^\infty n^2 dn\cdots = N_0+N_e$$

↑ total ↑ ground state ↖ excited states

Approximations:

- $N \equiv N_e + N_0$
- $N_e=\int dn\cdot n^2\cdots$

  $=\frac{2\pi}{h^3}(2m)^{3/2}(k_B T)^{3/2}\int dx\frac{\sqrt{x}}{e^x-1}$

  valid when $T<T_c$

- esp. $T=T_c$

  $$\frac{N}{V}=\underbrace{\frac{2\pi}{h^3}(2m)^{3/2}(k_B T)^{3/2}\int dx\frac{\sqrt{x}}{e^x-1}}_{B}$$

2. Energy

$$E=\sum_{\text{"}i\text{"}}\frac{\epsilon_{\text{"}i\text{"}}}{e^{\beta(\epsilon_{\text{"}i\text{"}}-\mu)}-1}$$

when $T>T_c$, $\sum\to\int$,

$$E=\frac{2\pi V}{h^3}(2m)^{3/2}\int_0^\infty\frac{d\epsilon\cdot\sqrt{\epsilon}\cdot\epsilon}{e^{\beta(\epsilon-\mu)}-1}, \quad ①$$

constant → $$N=\frac{2\pi V}{h^3}(2m)^{3/2}\int_0^\infty\frac{d\epsilon\sqrt{\epsilon}}{e^{\beta(\epsilon-\mu)}-1} \quad ②$$

Logic: Fix N/V,

calculate $\mu=\mu(T,\frac{N}{V})$ (②),

then calculate $E=E(T,N/V)=\frac{2\pi}{h^3}(2m)^{3/2}\int_0^\infty\frac{\epsilon^{3/2}d\epsilon}{e^{\beta(\epsilon-\mu)}-1}$

$\mu=\mu(T,\frac{N}{V})$

When $T<T_c$ $\quad E = E_{ground} + E_{excited} = 0 + \frac{2\pi V}{h^3}(2m)^{3/2}\int_0^\infty \frac{d\epsilon \cdot \epsilon^{3/2}}{e^{\beta\epsilon}-1}$

$$= \underbrace{\frac{2\pi V}{h^3}(2m)^{3/2}}_{A}\cdot(k_B T_c)^{5/2}\int_0^\infty \frac{dx \cdot x^{3/2}}{e^x - 1}$$

Heat capacity: 1° $E(T=T_c) = A\cdot(k_B T_c)^{5/2}$

$T<T_c \Rightarrow E(T) = A(k_B T)^{5/2}$

$$\Rightarrow \frac{E(T)}{E(T_c)} = \left(\frac{T}{T_c}\right)^{5/2} \Rightarrow \frac{dE/dT}{E(T_c)} = \frac{5}{2}\,\frac{T^{3/2}}{T_c^{5/2}}$$

2° $T<T_c, \mu=0$, $\frac{E}{V} = \frac{2\pi}{h^3}(2m)^{3/2}\int_0^\infty \frac{d\epsilon\cdot\epsilon^{3/2}}{e^{\beta\epsilon}-1} = A\cdot(k_B T)^{5/2}$

$$\frac{N_e}{V} = \frac{2\pi}{h^3}(2m)^{3/2}\int_0^\infty \frac{d\epsilon\cdot\epsilon^{1/2}}{e^{\beta\epsilon}-1} = B\cdot(k_B T)^{3/2}$$

$$\Rightarrow \frac{E}{N_e} = \frac{\int_0^\infty \frac{d\epsilon\cdot\epsilon^{3/2}}{e^x-1}}{\int_0^\infty \frac{d\epsilon\cdot\epsilon^{1/2}}{e^x-1}} = k_B T\,\frac{\int_0^\infty \frac{x^{\frac{3}{2}}dx}{e^x-1}}{\int_0^\infty \frac{\sqrt{x}\cdot dx}{e^x-1}}$$

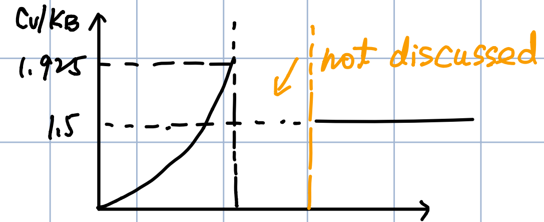
At $T=T_c$, $\frac{N}{V} = \frac{N_e}{V} = \frac{2\pi}{h^3}(2M)^{3/2}\int_0^\infty \frac{d\epsilon\cdot\sqrt{\epsilon}}{e^{\beta_c\epsilon}-1}$ $\quad \mu=0$

$$= B\cdot(k_B T_c)^{3/2} \quad ④$$

$$\Rightarrow \frac{E}{N} = \frac{③}{④} = \frac{A}{B}\,\frac{(k_B T)^{5/2}}{(k_B T_c)^{3/2}}$$

$$\Rightarrow \frac{\partial E/N}{\partial T} = \frac{5}{2}\,\frac{k_B^{5/2}T^{3/2}}{k_B^{3/2}T_c^{3/2}}\cdot\frac{A}{B} = \frac{5}{2}\cdot\frac{A}{B}\cdot k_B\cdot\left(\frac{T}{T_c}\right)^{3/2}$$

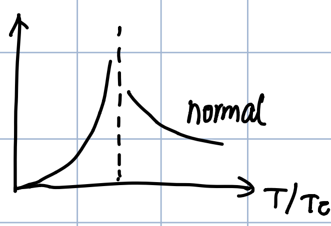
$$\Rightarrow \frac{C_v}{k_B} = \left(\frac{T}{T_c}\right)^{3/2}\cdot 1.925$$



$T\downarrow$, more particles freeze in momentum space.

↑ semiclassical

(1938) He^4 super fluidity



one point regarded as Bose-Einstein condensation
but just QM behavior

(1995) Cornell-Wieman

BEC theory (Gross-Pitaevskii)

Sodium-23 BEC

photons. Can photons have BEC? (2010)

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\uparrow}$ BEC in coupled fermions

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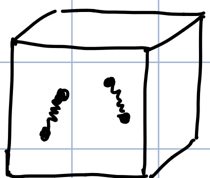
Chapter 16 Classical Diatomic Molecules.

1. The system



CO. H_2. O_2 ... C_v ?

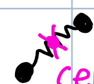
Known: N, V, T

Calculate: C_v, $\langle E(T)\rangle$

$$H = \sum_{l=1}^{N} H_i^{(l)} + V$$

$\uparrow$ single molecule

$$H_i^{(l)} = (P_x^{(l)2} + P_y^{(l)2} + P_z^{(l)2})/2m.$$



center of mass

Boltzmann-Gibbs approach: Z (partition function)

2. Equi-partition Theorem of Energy (classical)

If $H(\text{system}) = \frac{a}{2}q^2 + H'(\text{other})$, then $\langle E\rangle_{system} = \frac{1}{2}k_BT + \langle E(\text{other})\rangle$

$\uparrow$ variable, quadratic form; $\nwarrow$ other variables

eg. $H = \frac{1}{2m}(P_x^{(1)2} + \cdots)$; $H = \frac{k}{2}x^{(1)2}$

Pf: $$Z_{system} = \int \text{other} \int_{-\infty}^{+\infty} dq\, e^{-\beta\cdot\frac{a}{2}q^2 - \beta H'}$$

$$= \int_{-\infty}^{+\infty} dq \cdot e^{-\beta\cdot\frac{a}{2}q^2} \cdot \int \text{other} \cdot e^{-\beta H'}$$

$$= \int_{-\infty}^{+\infty} dq \cdot e^{-\beta\cdot\frac{a}{2}q^2} \cdot Z'$$

$$= (\beta a)^{-\frac{1}{2}} \int_{-\infty}^{+\infty} dx \cdot e^{-\frac{x^2}{2}} \cdot Z' = \beta^{-\frac{1}{2}} \cdot \underbrace{a^{-\frac{1}{2}} \cdot C}_{\text{constant}} \cdot Z'$$

$$\langle E\rangle = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\left(-\frac{1}{2}\ln\beta - \frac{1}{2}\ln a + \ln C + \ln Z'\right)$$

$$= \frac{1}{2\beta} - \frac{\partial \ln Z'}{\partial \beta} = \frac{k_BT}{2} + \langle E'\rangle_{other}$$

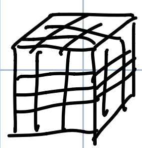
eg. Point-like ideal gas

$$H = \sum_{l=1}^{N}\frac{1}{2m}\left(p_x^{(l)2} + p_y^{(l)2} + p_z^{(l)2}\right)$$

each quadratic form contributes $\frac{1}{2}k_BT$.

$\Rightarrow \langle E\rangle = \left(\frac{1}{2}k_BT\right)\cdot 3N = \frac{3}{2}Nk_BT$ (regardless of what kind of gas)

eg. ideal crystal



N atoms

spring constant

$$H = \sum_{l=1}^{N}\frac{1}{2m}\left(p_x^{(l)2} + p_y^{(l)2} + p_z^{(l)2}\right) + \sum_{l=1}^{N}\frac{1}{2}k\left(x^{(l)2} + y^{(l)2} + z^{(l)2}\right)$$

$\Rightarrow \langle E\rangle = \left(\frac{1}{2}k_BT\right)\cdot 6N = 3Nk_BT$

3. Rigid "dumb-bell" model ($O_2, H_2, \cdots$)

$$H = \sum_{l=1}^{N}\frac{1}{2m}\left(p_x^{(l)2} + p_y^{(l)2} + p_z^{(l)2}\right) + \sum_{l=1}^{N}\left(\frac{J_x^2}{2I} + \frac{J_y^2}{2I}\right)$$

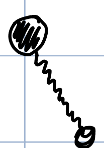
CM

moment of inertia

$\Rightarrow \langle E\rangle = \frac{1}{2}k_BT\cdot 5N = \frac{5}{2}Nk_BT \Rightarrow C_V = \frac{\partial\langle E\rangle}{\partial T} = \frac{5}{2}Nk_B$ per molar vol. $\frac{5}{2}N_Ak_B = \frac{5}{2}R$ (agree with exp.)

gas constant

4. A more realistic spring model

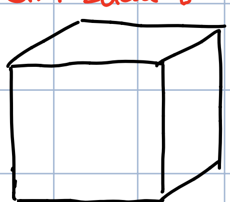


$$H = H_{Q} + \sum_{l=1}^{N}\left[\frac{k}{2}\left(r^{(l)} - r_0^{(l)}\right)^2 + \frac{1}{2\mu}\dot{r}^{(l)2}\right]$$

reduced mass $\frac{m_1m_2}{m_1+m_2}$

$\langle E\rangle = \frac{5}{2}Nk_BT + \frac{1}{2}k_BT\cdot(2N) = \frac{7}{2}Nk_BT \Rightarrow C_V = \frac{7}{2}Nk_B$. (disagree with exp.)

5. QM Ideal gas $\rightarrow Z_{rotation}$



Ideal gas

$H = H_{COM} + H_{rotation} + H_{vibration} + H_{e^-}$ always be treated Quantum Mechanically.

classically $\langle E\rangle = \frac{1}{2}k_BT(3N + 2N + 2N + \cdots)$

QM: $Z_{system} = Z_{COM}\cdot Z_{rotation}\cdot Z_{vibration}\cdot Z_{e^-}$

Z_{COM} = single atom molecule theory $\langle E_{COM}\rangle = \frac{3}{2}Nk_BT$

Z rotation

QM → angular momentum operator $\frac{\hat{J}^2}{2I}$, J_z , $\epsilon_l = \frac{l(l+1)\hbar^2}{2I}$ $\quad l = 0, 1, \cdots, \infty$

for each fixed l,
# of degeneracy is $(2l+1) = w$

$$Z_{rot} = \sum_{l_1=0}^{\infty}\sum_{l_2}\cdots\sum_{l_N}\left(w_1 e^{-\beta\epsilon_{l_1}}\right)\left(w_2 e^{-\beta\epsilon_{l_2}}\right)\cdots\left(w_N e^{-\beta\epsilon_{l_N}}\right)$$

$$= \left(\sum_{l=0}^{\infty} w e^{-\beta\epsilon_{l_1}}\right)^N = \left(Z_{rot,1}\right)^N \qquad Z_{rot,1} = \sum_{l_1=0}^{\infty}(2l_1+1)\exp\left(-\beta\cdot\frac{\hbar^2}{2I}l_1(l_1+1)\right)$$

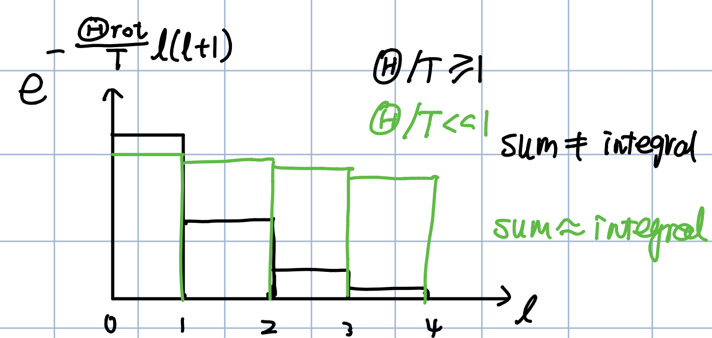
$\Theta_{rot} = \frac{\hbar^2}{2k_BI}$ $\quad Z_1 = \sum_l (2l+1)\exp\left(-\frac{\Theta_{rot}}{T}l(l+1)\right)$

	H_2	HCl	O_2	Cl_2
Θ_{rot}	85K	15K	2K	0.3K

Light molecule (H_2) ... Heavy molecule (Cl_2)

(I related to m)

$\Theta_{rot}/T \ll 1$ (for room T) spinning fast



$\therefore$ For room T , $Z_{rot} \approx \int_0^{\infty} dl\,(2l+1)\,e^{-\frac{\Theta}{T}l(l+1)}$

$$= \int_0^{\infty} d(l^2+l)\,e^{-\frac{\Theta}{T}(l^2+l)}$$

$$= \int_0^{\infty} dx\cdot e^{-\frac{\Theta}{T}x} = \frac{T}{\Theta_{rot}} = \frac{1}{k_B\Theta_{rot}}\frac{1}{\beta}$$

$$\Rightarrow \langle E_{rot}\rangle = -\frac{\partial \ln Z}{\partial\beta} = -\frac{\partial}{\partial\beta}\left(\underbrace{-N\ln(k_B\Theta)}_{\text{constant}} - N\ln\beta\right) = \frac{N}{\beta} = Nk_BT.$$

$Z \Leftarrow Z_1^N$

the same as classical theory

6. QM → Z vibration

single particle. $\epsilon_n^{(l)} = \hbar\omega(n_l+\frac{1}{2})$, $n = 0, 1, \cdots$ (l^{th} molecule)

$$Z_{vib} = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_N} e^{-\beta\hbar\omega(n_1+\frac{1}{2})}\cdots\cdots e^{-\beta\hbar\omega(n_N+\frac{1}{2})}$$

$$= (Z_{1\,vib})^N \qquad Z_{1,vib} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(\frac{1}{2}+n)} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} = \frac{e^{-\frac{\Theta}{2T}}}{1-e^{-\Theta/T}}$$

Quantum Mechanically or classically ?

$\Theta_{vib} = \frac{\hbar\omega}{k_B}$

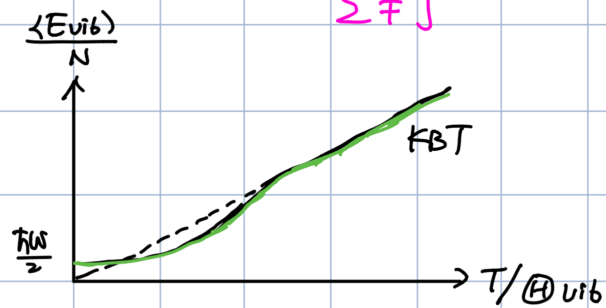
	H_2	HCl	O_2
Θ_{vib}	6210K	4140K	2230K

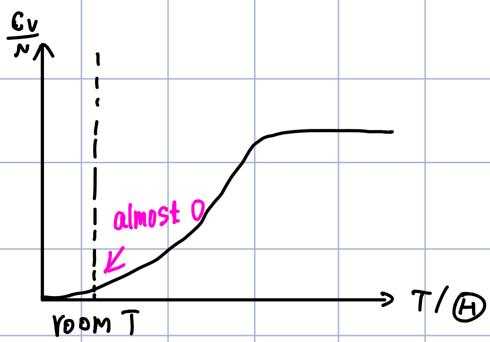
$\frac{\Theta_{vib}}{T} \gg 1$

$\therefore$ T_{room} is a low temperature

$\Sigma \neq \int$

$\langle E_{vib} \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{N\hbar\omega}{2} \coth(\Theta_{vib}/2T)$





$Z_{e^-} = e^{-\beta\epsilon_0} + e^{-\beta\epsilon_1} + \cdots$ $\quad \epsilon_0 \approx 0, \ \epsilon_1 \approx 12eV$

$\approx 1 \quad \Rightarrow$ contribution to $C_v \approx 0$

C_v of diatomic molecule $= \underset{\text{COM}}{\frac{3}{2}Nk_B} + \underset{\text{rotation}}{\frac{2}{2}Nk_BT} + \underset{\text{vib}}{0} + \underset{e^-}{0}$ (room T)