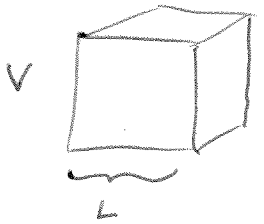
Tutorial 23/10/2014

(Statistical Physics)

Topic of today: IDEAL QUANTUM GAS



$\mathcal{H} = \frac{\vec{p}^{\,2}}{2m}$ in volume V

- free, non-interacting particles
- INDISTINGUISHABLE

QM: Solution to Schrödinger equation

$$\psi_{\vec{k}}(\vec{r}) = \langle \vec{r} | \psi_{\vec{k}} \rangle = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \quad \text{with } \epsilon_{\vec{k}} = \frac{|\vec{k}|^2 \hbar^2}{2m} = \frac{p^2}{2m}$$

→ Single-particle wavefunction. For multi-particle solution, we have two options (INDIST. PTCLS)

- symmetric under ptcl exchange: $\psi(r_1, r_2) = \psi(r_2, r_1)$
- antisymmetric " " " : $\psi(r_1, r_2) = -\psi(r_2, r_1)$

$$\Rightarrow \psi_{\{k_i\}}(r_1, r_2 \ldots r_N) = \frac{1}{\sqrt{N!}} \sum_P \delta_P \, P\left[\psi_{\vec{k}_1}(r_1) \ldots \psi_{\vec{k}_N}(\vec{r}_N)\right]$$

$\sum_P$: Permutations over $\{\vec{k}_1, \ldots \vec{k}_N\}$

δ_P: $\begin{cases} +1 & \text{if } P \text{ is even} \\ -1 & \text{if } P \text{ is odd} \end{cases}$ (FERMIONS); $\{+1$ (BOSONS)

→ $\psi_{\{k_i\}}$ vanishes for fermions if $\vec{k}_i = \vec{k}_j$ for some $i \neq j$

⇒ For fermions & bosons,

$$\boxed{\{n_{\vec{k}}\} \text{ uniquely specifies } \psi(r_1, r_2, \ldots r_N)!}$$

So, in the following, it will be enough just to work with those to calculate partition function & statistical properties.

"2" options:

a) grand-canonical ensemble (lectures): convenient as sum in $\mathcal{Z}$ simplifies

b) microcanonical ensemble (will give here in tutorial)

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By the way: if we want to calculate a classical version, we would have a pre-factor of $\prod_{\vec{k}} \frac{1}{n_{\vec{k}}!}$ here

(the Gibbs "correct counting" is implicit here)

a) Grand-canonical ensemble (see lectures)

$$\mathcal{Z} = \sum_{\{n_{\vec{k}}\}} e^{-\beta(E-\mu N)_{\{n_{\vec{k}}\}}} \quad \text{with} \quad E = \sum_{\vec{k}} \epsilon_{\vec{k}} n_{\vec{k}}$$

$$N = \sum_{\vec{k}} n_{\vec{k}}$$

$\boxed{\text{FERMIONS}}$ $\quad n_{\vec{k}} = 0, 1$

$\boxed{\text{BOSONS}}$ $\quad n_{\vec{k}} = 0, 1, 2, \ldots$

$$\Rightarrow \mathcal{Z} = \sum_{n_{\vec{k}_1}, n_{\vec{k}_2}, \ldots} \left[\left\{ z e^{-\beta \epsilon_{\vec{k}_1}} \right\}^{n_{\vec{k}_1}} \left\{ z e^{-\beta \epsilon_{\vec{k}_2}} \right\}^{n_{\vec{k}_2}} \cdots \right] \qquad (z = e^{\beta\mu})$$

this is where grand-canonical ensemble comes in handy

$$= \prod_{\vec{k}} \sum_{n_{\vec{k}}} \left(z e^{-\beta\epsilon_{\vec{k}}} \right)^{n_{\vec{k}}} = \begin{cases} \prod_{\vec{k}} \left(1 + z e^{-\beta\epsilon_{\vec{k}}}\right) & \text{FERMIONS} \\ \prod_{\vec{k}} \frac{1}{1 - z e^{-\beta\epsilon_{\vec{k}}}} & \text{BOSONS} \end{cases}$$

Thermodynamics

$$\Rightarrow \langle n_{\vec{k}} \rangle = \begin{cases} \frac{1}{z^{-1} e^{\beta\epsilon_{\vec{k}}} + 1} & \text{fermions} \\ \frac{1}{z^{-1} e^{\beta\epsilon_{\vec{k}}} - 1} & \text{bosons} \end{cases}$$

&

$$-\beta\Omega(T,V,\mu) = \pm \sum_{\vec{k}} \ln\left(1 \pm z e^{-\beta\epsilon_{\vec{k}}}\right) \qquad \begin{pmatrix} + \text{ fermions} \\ - \text{ bosons} \end{pmatrix}$$

in thermodynamic limit, k-space is packed!

of $\vec{k}$ between k and $k+dk$ in 3D

$$= \pm \int g(k)\,dk \ln\left(1 \pm z e^{-\beta\epsilon_k}\right) \quad \text{with} \quad g(k)\,dk = \frac{4\pi k^2}{(\frac{2\pi}{L})^3}\,dk$$

$$= \pm \int g(\epsilon)\,d\epsilon \ln\left(1 + z e^{-\beta\epsilon}\right) \quad \text{with} \quad g(\epsilon)\,d\epsilon = g(k)\,dk \;\&\; d\epsilon = \frac{\hbar^2 k}{m}$$

$$= \pm \int d\epsilon \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2} \ln\left(1 \pm z e^{-\beta\epsilon}\right)$$

$$\Rightarrow g(\epsilon) = \frac{4\pi k^2}{(\frac{2\pi}{L})^3} \cdot \frac{m}{\hbar^2 k} = \frac{4\pi L^3 m}{(2\pi)^3 \hbar^2} \sqrt{\frac{2m\epsilon}{\hbar^2}} = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2}$$

integration by parts!

$$= \pm\left(\underbrace{\left[\frac{2}{3} \epsilon^{3/2} \ln\left(1 \pm z e^{-\beta\epsilon}\right) \cdot \text{const.} \right]_0^\infty}_{=0} \pm \frac{2\beta}{3} \text{const} \int_0^\infty \frac{\epsilon^{3/2}}{z^{-1} e^{\beta\epsilon} \pm 1}\,d\epsilon \right)$$

$$= \frac{2\beta}{3} \int_0^\infty g(\epsilon)\, \epsilon \,/\, (z^{-1} e^{\beta\epsilon} \pm 1)$$

Similarly,

from $\langle n_{\vec{k}} \rangle$ $\qquad$ $\Omega = -pV$

$$U = \sum_{\vec{k}} \langle n_{\vec{k}} \rangle \epsilon_{\vec{k}} \approx \int_0^\infty d\epsilon\, g(\epsilon)\epsilon / (z^{-1} e^{\beta\epsilon} \pm 1) = -\frac{3}{2}\Omega = \frac{3}{2} pV$$

$\rightarrow$ looks like equipartition!

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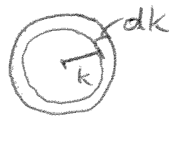
Let us check this! What would happen in 2D, or 1D?

$\boxed{2D}$ What changes is $g(\epsilon)$!



Now $\quad g(k)\,dk = 2\pi k\,dk/\left(\frac{2\pi}{L}\right)^2$

and so $\quad g(\epsilon) = \dfrac{2\pi m}{\left(\frac{2\pi}{L}\right)^2 \hbar^2}$ (constant!)

$$\Rightarrow \Omega = \mp k_B T \int_0^\infty d\epsilon\, g(\epsilon) \ln\left(1 \pm z e^{-\beta\epsilon}\right)$$

$$= \mp k_B T \left(\underbrace{\left[\frac{2\pi m}{\hbar^2 \left(\frac{2\pi}{L}\right)^2} \epsilon \ln\left(1 \pm z e^{-\beta\epsilon}\right) \right]_0^\infty}_{0} \pm \int_0^\infty \beta g(\epsilon) \; \epsilon / \left(z^{-1} e^{\beta\epsilon} \pm 1\right) \right)$$

$$= -\int_0^\infty g(\epsilon) \frac{\epsilon}{z^{-1} e^{\beta\epsilon} \pm 1}\, d\epsilon$$

$$\Rightarrow U = \int_0^\infty g(\epsilon) \frac{\epsilon}{z^{-1} e^{\beta\epsilon} \pm 1}\, d\epsilon = -\Omega = pV \qquad \checkmark$$

$\boxed{1D}$ All we really have to check is whether

$$\left[G(\epsilon) \ln\left(1 \pm z e^{-\beta\epsilon}\right) \right]_0^\infty \text{ vanishes (see above).}$$

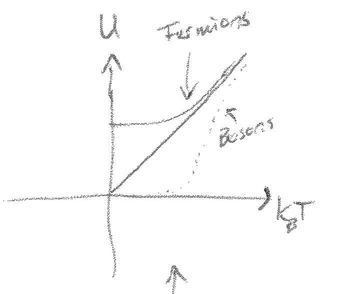
($g(\epsilon)$ integrated)

Now $\quad g(k)\,dk = \dfrac{dk}{(2\pi/L)}$ in 1D and so $g(\epsilon) = \epsilon^{-1/2} \cdot \text{const.}$

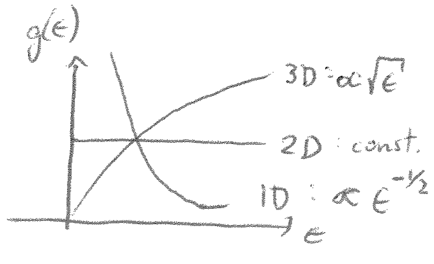
$$\Rightarrow G(\epsilon) \propto 2\epsilon^{1/2}$$

$\Rightarrow [\ldots]_0^\infty$ vanishes as required

$$\Rightarrow \Omega = -\int_0^\infty 2\epsilon \cdot g(\epsilon) / \left(z^{-1} e^{\beta\epsilon} \pm 1\right) = -2U \quad \Rightarrow \boxed{U = \tfrac{1}{2} pV} \qquad \checkmark$$



We shall see later that this is what happens: For large T, $pV \approx k_B T$ and classical equipartition is recovered!



Behaviour of $g(\epsilon)$ in 1D, 2D, 3D

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(Statistical Physics)

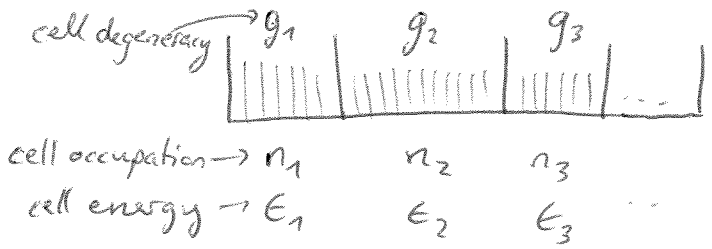
b) Microcanonical ensemble:

(following Kerson Huang: "Introduction to statistical physics")

Fixed total Energy $\boxed{E = \sum_\ell \epsilon_\ell n_\ell}$

" " Particle Number $\boxed{N = \sum_\ell n_\ell}$

Simplified Picture:



(to capture the situation of k-space and associated energies)

Now, for a given set of occupations $\{n_i\}$, the number of configurations is given by

$$\Omega\{n_i\} = \prod_j \omega_j(n_j),$$

where $\omega_j(n_j)$ is the number of ways in which n_j particles can be put into g_j compartments.

|FERMIONS| Each compartment can be either occupied or not. Hence

$$\omega_j(n_j) = \frac{g_j}{n_j!(g_j - n_j)!}$$

Assume $g_j, n_j \gg 1$.

Then

$$\ln \Omega\{n_i\} = \sum_j \left[\ln g_j! - \ln n_j! - \ln(g_j - n_j)!\right]$$

$$\approx \sum_j \left[g_j \ln g_j - n_j \ln n_j - (g_j - n_j)\ln(g_j - n_j)\right]$$

To get the microcanonical ensemble, we can now maximize this quantity over variations on $\{n_i\}$ subject to the constraints of fixed N & E!

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→ Use Lagrange multipliers!

$$\delta\Big[\ln \Omega\{n_i\} + \alpha \sum_j n_j - \beta \sum_j \epsilon_j n_j\Big] = 0$$

for independent variation of n_j.

$$\Rightarrow \sum_j \delta n_j \Big[-\ln n_j + \ln(g_j - n_j) + \alpha - \beta\epsilon_j\Big] = 0$$

Now δn_j are independent & arbitrary, so each term independently must vanish!

$$\Rightarrow -\ln n_j + \ln(g_j - n_j) + \alpha - \epsilon_j\beta = 0$$

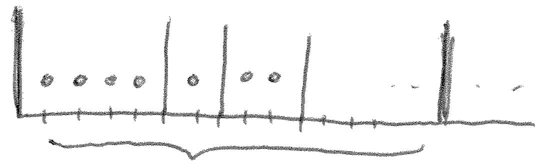
$$\Rightarrow n_j\left(e^{-\alpha+\beta\epsilon_j} + 1\right) = g_j$$

$$\Rightarrow \boxed{n_j = \frac{g_j}{e^{-\alpha+\beta\epsilon_j} + 1}}$$ Fermi distribution

BOSONS

arbitrary amount of ptcl/compartment

⟺



$n_j + (g_j - 1)$ slots for particles & partitions

⇒ number of ways of distributing n_j ptcles:

$$\omega_j(n_j) = \frac{(n_j + g_j - 1)!}{n_j!\,(g_j - 1)!}$$

$g_j - 1 \approx g_j$; Stirling

$$\Rightarrow \ln \Omega\{n_i\} = \prod_j \frac{(n_j + g_j - 1)!}{n_j!\,(g_j - 1)!} \approx \sum_j \Big((n_j + g_j)\ln(n_j + g_j) - n_j \ln n_j - g_j \ln g_j\Big)$$

Most probable distribution:

$$\sum_j \delta n_j \Big[\ln(n_j + g_j - 1) - \ln n_j + \alpha - \beta\epsilon_j\Big] = 0$$ (Lagrange multipliers, similar to above)

$$\Rightarrow \frac{n_j + g_j - 1}{n_j} = e^{\beta\epsilon_j - \alpha}$$

$$\Rightarrow \boxed{n_j = \frac{g_j - 1}{e^{-\alpha+\beta\epsilon_j} - 1} \approx \frac{g_j}{e^{\beta\epsilon_j - \alpha} - 1}}$$ Bose distribution

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Comparison with grandcan. solution

In the microcan. ensemble, we found

$$n_j = \frac{g_j}{e^{-\alpha+\beta\epsilon_j} \pm 1} \qquad \begin{matrix} + \text{fermion} \\ - \text{bosons} \end{matrix}$$

Because the g_j was really a tool to capture degeneracy within ϵ and $\epsilon + \Delta\epsilon$, we can now realize

$$\sum_j g_j \rightarrow \sum_{\vec{k}}$$

$$\Rightarrow N = \sum_j \frac{g_j}{e^{-\alpha+\beta\epsilon_j} \pm 1} \rightarrow \sum_{\vec{k}} \frac{1}{e^{-\alpha+\beta\epsilon_j} \pm 1}.$$

In the thermodynamic limit, we thus get

$$n = \frac{N}{V} = \int \frac{d^3k}{(2\pi)^3} \frac{1}{e^{-\alpha+\beta\epsilon_{\vec{k}}} \pm 1} = \frac{8}{\pi^2} \int_0^\infty dk \frac{k^2}{e^{-\alpha+\beta\epsilon_k} \pm 1}.$$

Now for $T \rightarrow \infty$, this should be equal to Maxwell-Boltzmann distribution, and so we can find (for integral to be finite for $\beta \to 0$, we need $e^{-\alpha} \xrightarrow[\beta\to 0]{} \infty$. Hence $n_{\vec{k}} \xrightarrow[\beta=0]{} e^{\alpha-\beta\epsilon_{\vec{k}}}$)

$$\beta = \frac{1}{k_B T}.$$

Also, we can define

$$\mu = \frac{\alpha}{\beta} \quad ; \quad z = e^{\beta\mu}$$

Now we see that

$$\boxed{n_{\vec{k}} = \frac{1}{z^{-1} e^{\beta\epsilon_{\vec{k}}} \pm 1}}$$

which corresponds to $\langle n_{\vec{k}} \rangle$ from the grand-canonical ensemble!

Final Remark: classical particles! (see box on page 1)

For $e^{-\beta(\epsilon_k - \mu)} \ll 1$ (high temperature / low density)

$$\Omega = -\beta^{-1} \ln \underbrace{\mathcal{Z}}_{\text{grand-can. part. funct.}} \approx -\beta^{-1} \sum_{\vec{k}} e^{-\beta(\epsilon_{\vec{k}} - \mu)} \approx -\frac{z}{\beta} \frac{V}{(2\pi)^3} \int d^3k \, e^{-\beta\hbar^2 k^2/2m} = \frac{-zV}{\beta\lambda^3},$$

with $\lambda = \frac{h}{\sqrt{2\pi m k T}}$ (thermal wavelength).

Now classically, we calculate

$$\mathcal{Z} = \left(\sum_{N=0}^\infty e^{\beta\mu N} \overset{\text{(canonical)}}{Z_N} \right) = \sum_{N=0}^\infty \frac{1}{N!} e^{\beta\mu N} \left(\frac{V}{\lambda^3} \right)^N = e^{zV/\lambda^3}$$

OR equivalently:

$$\mathcal{Z} = \sum_{n_{\vec{p}_1}, n_{\vec{p}_2}, \dots} \left[\frac{1}{n_{\vec{p}_1}!} \left\{ z e^{-\beta\epsilon_{\vec{p}_1}} \right\}^{n_{\vec{p}_1}} \frac{1}{n_{\vec{p}_2}!} \left\{ \cdot \right\}^{n_{\vec{p}_2}} \dots \right] = \sum^\infty z^N \frac{1}{N!} \left\{ \sum_{\vec{p}} e^{-\beta\epsilon_{\vec{p}}} \right\}^N$$

(SEE BOX ON PAGE 1!) "correct counting"

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