Phys. 528 Lecture 14

Quantum Ideal Gas

1) Density matrix and partition function of a system of identical particles

$$\langle \vec{r}_1, \dots, \vec{r}_N | \hat{\rho} | \vec{r}_1{}', \dots, \vec{r}_N{}' \rangle$$

$$= \frac{1}{Z_N(\beta)} \langle \vec{r}_1, \dots, \vec{r}_N | e^{-\beta \hat{H}} | \vec{r}_1{}', \dots, \vec{r}_N{}' \rangle$$

$$Z_N(\beta) = \int d^3r_1 \cdots d^3r_N \, \langle \vec{r}_1, \dots, \vec{r}_N | e^{-\beta \hat{H}} | \vec{r}_1, \dots, \vec{r}_N \rangle$$

$$\langle \vec{r}_1, \dots, \vec{r}_N | e^{-\beta \hat{H}} | \vec{r}_1{}', \dots, \vec{r}_N{}' \rangle = \sum_E e^{-\beta E} \psi_E(\vec{r}_1, \dots, \vec{r}_N) \times \psi_E^*(\vec{r}_1{}', \dots, \vec{r}_N{}')$$

Noninteracting particles

$$E = \sum_{i=1}^{N} \varepsilon_{n_i} \qquad \hat{H}_1 \psi_n(\vec{r}) = \varepsilon_n \psi_n(\vec{r})$$

$$\psi_{\{n_i\}}(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \sum_{P \in S_N} (\pm 1)^P \prod_{i=1}^{N} \psi_{n_i}(\vec{r}_{P_i})$$

$$\langle \vec{r}_1, \dots, \vec{r}_N | e^{-\beta \hat{H}} | \vec{r}_1{}', \dots, \vec{r}_N{}' \rangle$$

$$= \sum_{\{n_i\}} e^{-\beta(\varepsilon_{n_1} + \dots + \varepsilon_{n_N})} \frac{1}{N!} \sum_{P \in S_N} \sum_{P' \in S_N} (\pm 1)^P (\pm 1)^{P'}$$

$$\prod_{i=1}^{N} \psi_{n_i}(\vec{r}_{P_i}) \, \psi^*_{n_i}(\vec{r}\,'_{P'_i})$$

Even for independent particles, it is not so straightforward to carry out the sum, because not all sets of quantum #s are allowed.

Free particles in a (large) box, $V = L^3$

$$\varepsilon_{\vec{n}} = \frac{\hbar^2 \vec{k}_{\vec{n}}^{\,2}}{2m} \qquad \vec{k}_{\vec{n}} = \frac{2\pi \vec{n}}{L}$$

$$\sum_{\{\vec{n}_i\}} \longrightarrow \frac{V^N}{(2\pi)^{3N}} \int \frac{d^3k_1 \cdots d^3k_N}{N!}$$

In the double sum above, all that matters is $P - P'$, so we can choose $P' = \mathbb{1}$ $(\times N!)$.

$$\langle \vec{r}_1, \ldots, \vec{r}_N | e^{-\beta \hat{H}} | \vec{r}_1', \ldots, \vec{r}_N' \rangle$$

$$= \frac{V^N}{(2\pi)^{3N}} \frac{1}{N!} \sum_{P \in S_N} (\pm 1)^P \prod_{i=1}^{N} \int d^3k \, \frac{e^{-\beta \frac{\hbar^2 k^2}{2m} + i\vec{k}\cdot(\vec{r}_{P_i} - \vec{r}_i')}}{V}$$

$$= \frac{1}{N!} \sum_{P \in S_N} (\pm 1)^P \prod_{i=1}^{N} \underbrace{\int \frac{d^3k}{(2\pi)^3} e^{-\beta \frac{\hbar^2 k^2}{2m} + i\vec{k}\cdot(\vec{r}_{P_i} - \vec{r}_i')}}_{\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} e^{-\frac{m}{2\beta\hbar^2}|\vec{r}_{P_i} - \vec{r}_i'|^2}}$$

Introducing the <u>Thermal deBroglie wavelength</u>

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}} = \hbar \sqrt{\frac{2\pi\beta}{m}},$$ we have

$$\boxed{\langle \vec{r}_1, \ldots, \vec{r}_N | e^{-\beta \hat{H}} | \vec{r}_1', \ldots, \vec{r}_N' \rangle = \frac{1}{N!} \lambda^{-3N} \sum_{P \in S_N} (\pm 1)^P \prod_{i=1}^{N} e^{-\pi \frac{|\vec{r}_{P_i} - \vec{r}_i'|^2}{\lambda^2}}}$$

Let $f_{ij} \equiv e^{-\pi \frac{|\vec{r}_i - \vec{r}_j|^2}{\lambda^2}}$

$$\sum_{P \in S_N} (\pm 1)^P \prod_{i=1}^{N} f_{P_i j}$$

$$= 1 \pm \sum_{i<j} f_{ij} f_{ji} + \sum_{i<j<k} f_{ij} f_{jk} f_{ki} \pm \cdots$$

$$\boxed{\begin{aligned} Z_N(\beta) &= \int d^3r_1 \cdots d^3r_N \, \langle \vec{r}_1, \ldots, \vec{r}_N | e^{-\beta \hat{H}} | \vec{r}_1, \ldots, \vec{r}_N \rangle \\ &\approx \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N , \end{aligned}}$$

dropping terms involving $P \neq 1$, which are smaller by factors of $\frac{\lambda^3}{V}$.

Notice, this expression agrees with the classical result

$$Z_N(\beta) = \frac{1}{N!} \frac{1}{h^{3N}} \int d^3q_1 \cdots d^3q_N \int d^3p_1 \cdots d^3p_N \; e^{-\beta\left(\frac{p_1^2}{2m} + \cdots + \frac{p_N^2}{2m}\right)}$$

$$= \frac{1}{N!} \left(\frac{V}{h^3} \right)^N \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}}$$

This confirms the Gibbs correction factor and the volume of the unit cell in phase space introduced earlier.

Special case: $N = 2$

$$\langle \vec{r}_1 \vec{r}_2 | e^{-\beta \hat{H}} | \vec{r}_1 \vec{r}_2 \rangle = \frac{1}{2\lambda^6} \left(1 \pm e^{-2\pi r_{12}^2/\lambda^2} \right)$$

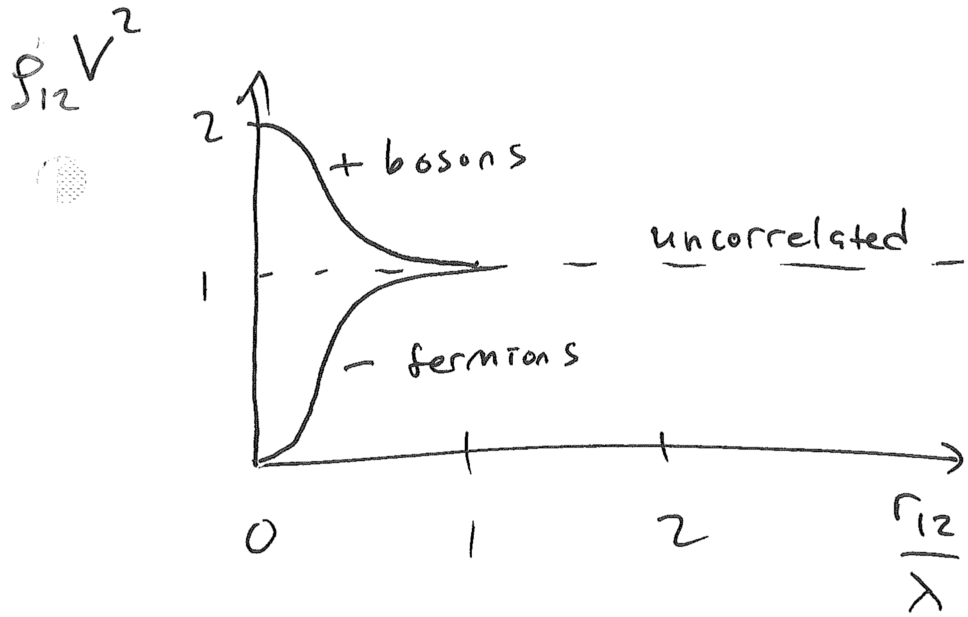
$$Z_2 = \frac{1}{2\lambda^6} \int d^3 r_1 \int d^3 r_2 \left(1 \pm e^{-2\pi r_{12}^2/\lambda^2} \right)$$

$$= \frac{1}{2} \left(\frac{V}{\lambda^3} \right)^2 \left(1 \pm \frac{1}{V} \int_0^\infty e^{-2\pi r^2/\lambda^2} \, 4\pi r^2 dr \right)$$

$$Z_2 = \frac{1}{2} \left(\frac{V}{\lambda^3} \right)^2 \left(1 \pm \frac{1}{2^{3/2}} \left(\frac{\lambda^3}{V} \right) \right) \approx \frac{1}{2} \left(\frac{V}{\lambda^3} \right)^2$$

$$\langle \vec{r}_1 \vec{r}_2 | \hat{\rho} | \vec{r}_1 \vec{r}_2 \rangle = \frac{1}{V^2} \frac{1 \pm e^{-2\pi r_{12}^2/\lambda^2}}{1 \pm \frac{1}{2^{3/2}} \left(\frac{\lambda^3}{V} \right)}$$

$$\simeq \frac{1}{V^2} \left(1 \pm e^{-2\pi r_{12}^2/\lambda^2} \right)$$



2) Grand partition function

Back to the problem of independent particles with single-particle energy levels ε_i.

$$\mathcal{F} = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{\{n_i\}}{}' e^{-\beta \sum_{i=1}^{N} n_i \varepsilon_i} \qquad \left(\sum_i n_i = N\right)$$

$$= \sum_{N=0}^{\infty} \sum_{\{n_i\}}{}' \prod_i \left(e^{-\beta(\varepsilon_i - \mu)}\right)^{n_i}$$

$$= \sum_{n_0, n_1, n_2, \ldots} \left(e^{-\beta(\varepsilon_0 - \mu)}\right)^{n_0} \left(e^{-\beta(\varepsilon_1 - \mu)}\right)^{n_1} \cdots$$

$$= \sum_{n_0} \left(e^{-\beta(\varepsilon_0 - \mu)}\right)^{n_0} \sum_{n_1} \left(e^{-\beta(\varepsilon_1 - \mu)}\right)^{n_1} \cdots$$

$$\mathcal{Z} = \begin{cases} \prod_i \left(1 + e^{-\beta(\varepsilon_i - \mu)}\right), & \text{fermions} \\ \prod_i \dfrac{1}{1 - e^{-\beta(\varepsilon_i - \mu)}}, & \text{bosons} \end{cases}$$

Grand canonical potential

$$\Omega = -k_B T \ln \mathcal{Z}$$

$$= \mp k_B T \sum_i \ln\left(1 \pm e^{-\beta(\varepsilon_i - \mu)}\right)$$

$$= \mp k_B T \int d\varepsilon \, g(\varepsilon) \ln\left(1 \pm e^{-\beta(\varepsilon - \mu)}\right)$$

$$= E - TS - \mu N$$

But $G = E - TS + pV = \mu N$

so $\Omega = -pV$

Digression on thermodynamics

$$\Omega = E - TS - \mu N$$

In problem 1.9, you showed that

$$N\mu = E + pV - TS$$

Thus

$$\Omega = E - TS - \mu N = -pV.$$

Let's show this another way.

$$dE = T\,dS - p\,dV + \mu\,dN$$

$$\Rightarrow \quad d\Omega = -p\,dV - S\,dT - N\,d\mu$$

$$\Omega = \Omega(V, T, \mu)$$

Extensivity:

$$\Omega = V\,\omega(T, \mu)$$

But $p = -\left.\dfrac{\partial \Omega}{\partial V}\right|_{T,\mu} = -\omega(T, \mu)$

$$\therefore \quad \Omega(V,T,\mu) = -p(T,\mu)V$$

Maxwell relations

$$\left.\frac{\partial p}{\partial T}\right|_{V,\mu} = \left.\frac{\partial S}{\partial V}\right|_{T,\mu}$$

$$\left.\frac{\partial P}{\partial \mu}\right|_{V,T} = \left.\frac{\partial N}{\partial V}\right|_{T,\mu}$$

$$\left.\frac{\partial S}{\partial \mu}\right|_{V,T} = \left.\frac{\partial N}{\partial T}\right|_{V,\mu}$$

But $\quad S = -V \left.\frac{\partial \omega}{\partial T}\right|_{\mu} \qquad N = -V \left.\frac{\partial \omega}{\partial \mu}\right|_{T}$

so $\quad \left.\frac{\partial S}{\partial V}\right|_{T,\mu} = -\left.\frac{\partial \omega}{\partial T}\right|_{\mu} = \left.\frac{\partial P}{\partial T}\right|_{V,\mu}$

and $\quad \left.\frac{\partial N}{\partial V}\right|_{T,\mu} = -\left.\frac{\partial \omega}{\partial \mu}\right|_{T} = \left.\frac{\partial P}{\partial \mu}\right|_{V,T}$

This confirms the relation

$$\omega(T,\mu) = -P(T,\mu).$$

$$\langle N \rangle = -\frac{\partial \Omega}{\partial \mu}\Big|_{T,V} = \int d\varepsilon \, g(\varepsilon) \frac{e^{-\beta(\varepsilon-\mu)}}{1 \pm e^{-\beta(\varepsilon-\mu)}}$$

$$= \int d\varepsilon \, g(\varepsilon) f_{\pm}(\varepsilon) = \sum_i f_{\pm}(\varepsilon_i)$$

$$f_{\pm}(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} \pm 1}$$

$$\langle E \rangle = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} = \sum_i \varepsilon_i f_{\pm}(\varepsilon_i)$$

<u>Classical limit $e^{-\beta(\varepsilon-\mu)} \ll 1$</u>

$$\langle N \rangle \approx \int d\varepsilon \, g(\varepsilon) \, e^{-\beta(\varepsilon-\mu)}$$

$$\Omega = -pV \approx -k_B T \int d\varepsilon \, g(\varepsilon) \, e^{-\beta(\varepsilon-\mu)}$$

$$pV \approx N k_B T$$

$$\Omega = \mp k_B T \int_{-\infty}^{\infty} d\varepsilon \; g(\varepsilon) \ln\left(1 \pm e^{-\beta(\varepsilon-\mu)}\right)$$

Integrating by parts:

$$\Omega = -\int_{-\infty}^{\infty} d\varepsilon \; \frac{\sigma(\varepsilon)}{e^{\beta(\varepsilon-\mu)} \pm 1},$$

where $\sigma(\varepsilon) = \int_{-\infty}^{\varepsilon} g(\varepsilon')\, d\varepsilon'$.

$$E = \int_{-\infty}^{\infty} d\varepsilon \; \frac{g(\varepsilon)\,\varepsilon}{e^{\beta(\varepsilon-\mu)} \pm 1}$$

Suppose $g(\varepsilon) = a \cdot \varepsilon^{\nu}$. Then

$$\sigma(\varepsilon) = a\int_0^{\varepsilon} \omega^{\nu} d\omega = \frac{a\,\varepsilon^{\nu+1}}{\nu+1} = \frac{\varepsilon\, g(\varepsilon)}{\nu+1}$$

$$\Rightarrow \Omega = -\frac{E}{\nu+1}$$

In 3D, we have $g(\varepsilon) = a\varepsilon^{1/2}$

so $\Omega = -\frac{2}{3}E$

$$-pV = -\frac{2}{3}E$$

$$\boxed{pV = \frac{2}{3}E}$$

$$pV = -\Omega = \int_0^\infty d\varepsilon \frac{b\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)} \pm 1}$$

$$\simeq b\int_0^\infty d\varepsilon\, \varepsilon^{3/2} e^{-\beta(\varepsilon-\mu)} \left(1 \mp e^{-\beta(\varepsilon-\mu)} + \cdots\right)$$

$$= -\Omega_{\text{Boltzmann}} \mp \frac{Vm^{3/2}T^{5/2}}{16\pi^{3/2}\hbar^3} e^{2\beta\mu}$$

$$pV \cong Nk_BT\left[1 \pm \frac{\pi^{3/2}}{2}\frac{N\hbar^3}{V(mk_BT)^{3/2}}\right]$$

Fermions have pressure greater than that of a classical ideal gas; bosons have pressure less than a classical ideal gas.