Ideal Quantum Gases

- collection of indistinguishable particles
- low temperature

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thermal wavelength $\lambda_T = \left(\frac{2\pi\hbar^2}{m k_B T}\right)^{1/2} \to \infty$ as $T \to 0$

- when $\lambda_T \sim r$ on the order of interatomic distance expect that quantum effects make a difference
- bosons and fermions behave <u>very</u> <u>differently</u>

Partition function:

$$Z_\mu(T,V) = \mathrm{Tr}\left[e^{-\beta(\hat{H}-\mu\hat{N})}\right]$$

$\hat{H} = \sum_{\vec{l}} \epsilon_{\vec{l}}\, \hat{n}_{\vec{l}}$ → Hamiltonian

$\epsilon_{\vec{l}}$ - single particle eigenstates

→ $\hat{n}_l$ - occupation of state with index $\vec{l}$

$\hat{N} = \sum_l \hat{n}_l$

- assume: particles are non-interacting and in a box with side length L ($V = L^3$) ⇒ periodic boundary conditions

$$\epsilon_{\vec{l}} = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 [l_x^2 + l_y^2 + l_z^2] \quad l_x, l_y, l_z \text{ - integer}$$

- to evaluate trace: introduce ~~...~~ wavefns. in number representation

$$|\{n_{\vec{l}}\}\rangle = |n_{-\infty,-\infty,-\infty} \dots n_{0,0,0}, n_{0,0,1} \dots n_{\infty\infty\infty}\rangle$$

$$\hat{n}_{\vec{l}} \, |\{n_{\vec{l}}\}\rangle = n_{\vec{l}} \, |\{n_{\vec{l}}\}\rangle$$

number operator for state $\vec{l}$

occupation of state $\vec{l}$ (eigenvalue of number operator)

- evaluate trace:

$$Z_\mu(T,V) = \underbrace{\sum_{n_{-\infty-\infty-\infty}} \dots \sum_{n_{\infty\infty\infty}}}_{} \langle\{n_{\vec{l}}\}| e^{-\beta(\hat{H}-\mu\hat{N})} |\{n_{\vec{l}}\}\rangle$$

$$= \{\sum_{\{n_{\vec{l}}\}}\} \prod_{\vec{l}} e^{-\beta(\epsilon_{\vec{l}}-\mu)n_{\vec{l}}}$$

$$= \prod_{\vec{l}} \left[\sum_{n_{\vec{l}}} e^{-\beta(\epsilon-\mu)n_{\vec{l}}}\right]$$

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for fermions: Pauli principle states that $n_{\vec{l}} \in 0, 1$ (only one particle can occupy a state)

$$Z_{FD}(T,V) = \prod_{\vec{l}} \left[1 + e^{-\beta(\epsilon_{\vec{l}}-\mu)}\right]$$

for bosons: $n_{\vec{l}} = 0, \dots, \infty$

$$Z_{BE}(T,V) = \prod_{\vec{l}} \left[\frac{1}{1 - e^{-\beta(\epsilon_{\vec{l}} - \mu)}} \right]$$

Ideal Bose - Einstein Gas

given the partition function

$$Z_{BE}(T,V) = \prod_{\vec{l}} \frac{1}{1 - e^{-\beta(\epsilon_{\vec{l}} - \mu)}}$$

we can write thermodynamic properties

- grand potential:

$$\Omega_{BE} = -k_B T \ln Z_{BE}(T,V)$$
$$= + k_B T \sum_{\vec{l}} \ln(1 - e^{-\beta(\epsilon_{\vec{l}} - \mu)})$$

- average number of particles

$$\langle N \rangle = -\frac{\partial \Omega_{BE}}{\partial \mu} = -k_B T \sum_{\vec{l}} \frac{1}{1 - e^{-\beta(\epsilon_{\vec{l}} - \mu)}} \{ e^{-\beta(\epsilon_{\vec{l}} - \mu)} \} \beta$$

$$= \sum_{\vec{l}} \frac{e^{\beta\mu}}{e^{\beta\epsilon_{\vec{l}}} - e^{\beta\mu}} = \sum_{\vec{l}} \frac{z}{e^{\beta\epsilon_{\vec{l}}} - z}$$

since $\langle N \rangle = \sum_{\vec{l}} \langle n_{\vec{l}} \rangle$

we can associate $\langle n_{\vec{l}} \rangle = \dfrac{z}{e^{\beta\epsilon_{\vec{l}}} - z}$

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nature of phase transition: (9)

- investigate occupation numbers
- since minimum $\epsilon_{\vec{i}} = \epsilon_{000} = 0$

$$1 \leq e^{\beta \epsilon_{\vec{i}}} \leq \infty$$

$\Downarrow$

for $\langle n_{\vec{i}} \rangle = \frac{z}{e^{\beta \epsilon_{\vec{i}}} - z}$ to be positive (and physically meaningful) $z < 1 \Rightarrow \mu < 0$

- as $\mu \to 0_-$ $\qquad \langle n_{000} \rangle = \frac{z}{1-z} \to \infty$

$\Downarrow \qquad \Downarrow$

lowest momentum state becomes <u>thermodynamically occupied</u> $\Rightarrow$ there will be a peak in the zero momentum occupation $\Rightarrow$ Bose-Einstein condensation

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to evaluate thermodynamic properties: change sum to integral

$$\sum_{\vec{i}} \to \frac{V}{(2\pi)^3} \int d\vec{k} = \frac{V}{(2\pi\hbar)^3} \int d\vec{p}$$

but since $\epsilon \to \epsilon(p)$

$$\sum_{\vec{i}} \to \frac{V 4\pi}{(2\pi\hbar)^3} \int p^2 dp = \frac{V}{2\pi^2 \hbar^3} \int p^2 dp$$

but, one must also consider singularity

$\sum_{\vec{e}} \rightarrow \underbrace{\cancel{\sum} + \sum}_{}$ 000 term $+ \sum_{\vec{i} \neq 0}$

000 $\quad \vec{e} \neq 0$

$$-\Omega_{BE}(T,V,\mu) = k_B T \ln(1-z) + k_B T \sum_{\vec{e}\neq\vec{0}} \ln\left(1-e^{-\beta(\varepsilon_{\vec{e}}-\mu)}\right)$$

$$= \frac{V k_B T}{2\pi^2\hbar^3} \int_0^\infty p^2 dp \ln\left[1-e^{-\frac{\beta p^2}{2m}} z\right] + k_B T \ln(1-z)$$

$$\langle N\rangle = -\frac{\partial \Omega_{BE}}{\partial\mu} = +\frac{V k_B T}{2\pi^2\hbar^3}\int_0^\infty p^2 dp \frac{e^{-\frac{\beta p^2}{2m}} e^{\beta\mu}}{1-e^{-\frac{\beta p^2}{2m}} z}\beta$$

$$\cancel{-}\; k_B T \frac{(-z)}{1-z}\beta$$

$$\langle n\rangle = \frac{\langle N\rangle}{V} = +\frac{1}{2\pi^2\hbar^3}\int_0^\infty p^2 dp \frac{z}{e^{\frac{\beta p^2}{2m}}-z} + \frac{1}{V}\frac{z}{1-z}$$

since

$$-\Omega_{BE} = -PV$$

$$\Downarrow$$

$$P = -\frac{k_B T}{V}\ln(1-z) - \frac{k_B T}{2\pi^2\hbar^3}\int_0^\infty p^2 dp \ln\left[1-e^{-\frac{\beta p^2}{2m}} z\right]$$

can be expressed in an easier form using

$$g_{5/2}(z) = \sum_{\alpha=1}^\infty \frac{z^\alpha}{\alpha^{5/2}} = -\frac{4}{\sqrt{\pi}}\int_0^\infty x^2 dx \ln\left(1-z e^{-x^2}\right)$$

apply variable transformation $\frac{\beta}{2m} p^2 = x^2$

$$\Rightarrow P = -\frac{k_B T \ln(1-z)}{V} - \frac{k_B T}{2\pi^2\hbar^3}\left(\frac{2m}{\beta}\right)^{3/2}\int_0^\infty x^2 dx \ln\left[1-e^{-x^2} z\right]$$

$$\Rightarrow \quad P = -\frac{k_B T \ln(1-z)}{V} + \frac{k_B T}{\lambda_T^3} g_{5/2}(z)$$

$$\langle n \rangle = \frac{1}{V}\frac{z}{1-z} + \frac{g_{3/2}(z)}{\lambda_T^3}$$

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g functions:

$$g_{5/2}(z) = -\frac{4}{\sqrt{\pi}} \int_0^\infty x^2 dx \ln(1-ze^{-x^2}) = \sum_{\alpha=1}^{\infty} \frac{z^\alpha}{\alpha^{5/2}}$$

prove by Taylor expanding $\ln(1-ze^{-x^2})$ in z

$$\ln(1-ze^{-x^2}) = f(z)$$

$$f(0) = 0$$

$$f'(0) = \frac{1}{1-ze^{-x^2}}(-e^{-x^2})\Big|_{z=0} = -e^{-x^2}$$

$$f''(0) = -\frac{1}{(1-ze^{-x^2})^2}(-e^{-x^2})(-e^{-x^2})\Big|_{z=0} = -e^{-2x^2}$$

$$f^{(n)}(0) = (n-1)!\, e^{-nx^2}$$

$$\Downarrow$$

$$\ln(1-ze^{-x^2}) = \sum_{n=1}^{\infty} z^n \frac{e^{-nx^2}}{n}$$

$$g_{5/2}(z) = -\frac{4}{\sqrt{\pi}} \int_0^\infty x^2 dx \left[\sum_{n=1}^{\infty} \frac{e^{-nx^2}}{n} z^n\right]$$

$$= \sum_{n=1}^{\infty} z^n \left(-\frac{4}{\sqrt{\pi}}\right)\frac{1}{n} \underbrace{\int_0^\infty x^2 e^{-nx^2} dx}_{\frac{\sqrt{\pi}}{4n^{3/2}}} = \sum_{n=1}^{\infty} \frac{z^n}{n^{5/2}}$$

$$g_{3/2}(z) = z\frac{d}{dz} g_{5/2}(z) = z\frac{d}{dz} \sum_{n=1}^{\infty} \frac{z^n}{n^{5/2}} = z \sum_{n=1}^{\infty} \frac{n z^{n-1}}{n^{5/2}} \checkmark$$

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we have:
$$P = -\frac{k_B T \ln(1-z)}{V} + \frac{k_B T}{\lambda_T^3} g_{5/2}(z)$$

$$\langle n \rangle = \frac{1}{V}\frac{z}{1-z} + \frac{g_{3/2}(z)}{\lambda_T^3}$$

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investigate $\vec{l}=0$ term

write: $z = 1 - \frac{1}{n_0 V}$ in the neighborhood of $z=1$

$$z(V) = 1 - \frac{1}{n_0 V}$$

$$\lim_{V\to\infty} \frac{\ln(1-z)}{V} = -\frac{\ln(n_0 V)}{V} \to 0$$

$$\lim_{V\to\infty} \frac{1}{\cancel{V}} \frac{\left(1-\frac{1}{n_0 V}\right)}{1/n_0 \cancel{V}} \to n_0$$

$\Downarrow$

so $\vec{l}=0$ term does not contribute to P

but contributes to $\langle n \rangle$

$$P = \frac{k_B T}{\lambda_T^3} g_{5/2}(z)$$

$$\langle n \rangle = n_0 + \frac{g_{3/2}(z)}{\lambda_T^3}$$

as $z \to 1$ $\quad g_{5/2}(1)$ and $g_{3/2}(1)$ are $\quad$ 8

just numbers (no divergence)

$$g_{5/2}(1) = 1.342 \qquad g_{3/2}(1) = 2.612$$

$$\Downarrow$$

$$P = \begin{cases} \dfrac{k_B T}{\lambda_T^3}\, g_{5/2}(z) & z < 1 \\[2ex] \dfrac{k_B T}{\lambda_T^3}\, g_{5/2}(1) & z = 1 \end{cases}$$

$$\langle n \rangle = \begin{cases} \dfrac{g_{3/2}(z)}{\lambda_T^3} & z < 1 \\[2ex] \dfrac{g_{3/2}(1)}{\lambda_T^3} & z = 1 \end{cases}$$

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plots: