use $Z_1\left(\frac{T}{n}\right) = V\left(\frac{2\pi m k_B T}{h^2 n}\right)^{3/2} = n^{-3/2}\frac{V}{\lambda_T^3} = n^{-3/2} Z_1(T)$

$$Z_3^{(\pm)}(T) = \underbrace{\frac{1}{3!}\left(\frac{V}{\lambda_T^3}\right)^3}_{\text{classical partition function}}\left[1 \pm \frac{3}{2^{3/2}}\left(\frac{\lambda_T^3}{V}\right) + \frac{2}{3^{3/2}}\left(\frac{\lambda_T^3}{V}\right)^2\right]$$

quantum corrections become larger as density increases and temperature becomes smaller

quantum correction different for bosons and fermions

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = k_B T\left(\frac{\partial \ln Z}{\partial V}\right)_{T,N}$$

$$= k_B T\left(\frac{\partial}{\partial V}\; 3\ln V + \ln\left[1 \pm \frac{3}{2^{3/2}}\left(\frac{\lambda_T^3}{V}\right) + \frac{2}{3^{3/2}}\left(\frac{\lambda_T^3}{V}\right)^2\right]\right)_{T,N}$$

$$= 3k_B T\frac{1}{V} + \frac{\mp\frac{3\lambda_T^3}{2^{3/2}V^2} - \frac{4}{3^{3/2}}\frac{(\lambda_T^3)^2}{V^3}}{1 \pm \frac{3}{2^{3/2}}\left(\frac{\lambda_T^3}{V}\right) + \frac{2}{3^{3/2}}\left(\frac{\lambda_T^3}{V}\right)^2}$$

$$\Rightarrow PV = 3k_B T \mp \frac{3}{2^{3/2}}\left(\frac{\lambda_T^3}{V}\right) + O\left(\left(\frac{\lambda_T^3}{V}\right)^2\right) \quad \text{"virial expansion"}$$

fermions : increased pressure
bosons : decreased pressure

VI.4 The ideal Bose-Einstein gas

$$\hat{H} = \sum_{i=1}^{N} \frac{\hat{\vec{p}}_i^{\,2}}{2m}$$

box of volume $L^3 = V$

periodic boundary conditions

$\rightarrow \vec{p} = \hbar \vec{k}$ with

$$\vec{k} = \frac{2\pi l_x}{L_x}\hat{x} + \frac{2\pi l_y}{L_y}\hat{y} + \frac{2\pi l_z}{L_z}\hat{z}$$

$l_x, l_y, l_z = \dots, -1, 0, 1, \dots$ integers

single particle energies

$$\varepsilon_{\vec{k}} = \frac{\hbar^2 \vec{k}^2}{2m}$$

note: ground state energy $\varepsilon_0 = 0$

do not fix particle number

$\rightarrow$ basis of Hilbert space

$$|\underbrace{n_0}_{\text{number of particles in ground state}} \; \underbrace{n_{\vec{k}_1}\; n_{\vec{k}_2}\; n_{\vec{k}_3}\; n_{\vec{k}_4}\; \dots}_{\text{number of particles in state } \vec{k}_i} \rangle$$

partition function

$$Z(\mu', T) = \mathrm{Tr}\, e^{-\beta \hat{H} + \beta\mu' \hat{N}}$$

$$= \sum_{\{n_{\vec{k}}\}} \prod_{\vec{k}} e^{-\beta \varepsilon_{\vec{k}} n_{\vec{k}} + \beta\mu' n_{\vec{k}}}$$

$$= \prod_{\vec{k}} \sum_{n=0}^{\infty} e^{-\beta(\varepsilon_{\vec{k}} - \mu') n_{\vec{k}}} = \prod_{\vec{k}} \frac{1}{1 - e^{-\beta(\varepsilon_{\vec{k}} - \mu')}}$$

$$\Omega = -k_B T \ln \mathcal{Z}(\mu', T) = k_B T \sum_{\vec{k}} \ln\left(1 - e^{-\beta(\varepsilon_{\vec{k}} - \mu')}\right)$$

$$\langle N \rangle = -\left(\frac{\partial \Omega}{\partial \mu'}\right)_{T,V} = \sum_{\vec{k}} \frac{e^{-\beta(\varepsilon_{\vec{k}} - \mu')}}{1 - e^{-\beta(\varepsilon_{\vec{k}} - \mu')}} = \sum_{\vec{k}} \frac{e^{\beta\mu'}}{e^{\beta\varepsilon_{\vec{k}}} - e^{\beta\mu'}}$$

$$= \sum_{\vec{k}} \frac{z}{e^{\beta\varepsilon_{\vec{k}}} - z} \qquad z = e^{\beta\mu'} \text{ fugacity}$$

average number of particles in level $\varepsilon_{\vec{k}}$:

$$\langle n_{\vec{k}} \rangle = k_B T \left(\frac{\partial \ln \mathcal{Z}}{\partial \varepsilon_{\vec{k}}}\right)_{\mu', T, V} = \frac{e^{-\beta(\varepsilon_{\vec{k}} - \mu')}}{1 - e^{-\beta(\varepsilon_{\vec{k}} - \mu')}} = \frac{z}{e^{\beta\varepsilon_{\vec{k}}} - z}$$

$$\langle n_{\vec{k}} \rangle \geq 0 \Rightarrow 0 \leq z \leq e^{\beta\varepsilon_{\vec{k}}} \text{ for all } \vec{k}$$

$$e^{\beta\varepsilon_{\vec{k}}} \geq 1 \text{ for all } \vec{k} \text{ with equality for } \vec{k} = 0$$

$$\Rightarrow 0 \leq z \leq 1 \Rightarrow \boxed{\mu' \leq 0}$$

adding particles to a Bose-Einstein gas is easy!

ground state occupancy:

$$\langle n_0 \rangle = \frac{z}{1-z} \longrightarrow \infty \quad \text{as } z \to 1$$

can become macroscopic!

$\vec{k} \neq 0$

$$\langle n_{\vec{k}} \rangle = \frac{z}{e^{\beta\varepsilon_{\vec{k}}} - z} \leq \frac{1}{e^{\beta\varepsilon_{\vec{k}}} - 1}$$

microscopic for a given $\vec{k}$

$\Rightarrow$ ground state ($\vec{k}=0$) can behave differently from all other states

$$\Omega = k_B T \sum_{\vec{k}} \ln(1 - e^{-\beta\varepsilon_{\vec{k}}} z)$$

$$= k_B T \ln(1-z) + k_B T \sum_{\vec{k}\neq 0} \ln(1 - e^{-\beta\varepsilon_{\vec{k}}} z)$$

$$= k_B T \ln(1-z) + k_B T \sum_{\substack{(l_x,l_y,l_z)\neq(0,0,0)\\ \text{integers}}} \ln(1 - e^{-\beta\frac{4\pi^2\hbar^2}{2mL^2}(l_x^2+l_y^2+l_z^2)} z)$$

$$\approx k_B T \ln(1-z) + k_B T \int_{l\neq 0} d^3l \, \ln(1 - e^{-\beta\frac{h^2}{2mL^2}\vec{l}^2} z)$$

$$= k_B T \ln(1-z) + k_B T \, 4\pi \int_1^\infty dl \, l^2 \ln(1 - e^{-\beta\frac{h^2}{2mL^2} l^2} z)$$

$$= k_B T \ln(1-z) + k_B T \, 4\pi \left(\frac{2mL^2}{\beta h^2}\right)^{3/2} \int_{\left(\frac{h^2}{2mk_BTL^2}\right)^{1/2}}^\infty dx \, x^2 \ln(1 - e^{-x^2} z)$$

$$x^2 = \beta \frac{h^2}{2mL^2} l^2$$

use $\lambda_T = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2}$

$$= k_B T \ln(1-z) + \frac{4 k_B T V}{\sqrt{\pi}\,\lambda_T^3} \int_{\lambda_T \frac{\sqrt{\pi}}{L}}^\infty dx \, x^2 \ln(1 - e^{-x^2} z)$$

2/24