Exam statistical mechanics (19/12/2023)

① Dieterici equation of state

$$P = \frac{Nk_BT}{V-Nb} e^{-aN/k_BTV}$$

a) $\frac{N}{V} \equiv n$

$$P = \frac{nk_BT}{1-nb} e^{-an/k_BT}$$

$$\approx nk_BT\left(1-\frac{an}{k_BT}\right)(1+nb) + \mathcal{O}(n^3)$$

$$= nk_BT(1+nb) - an^2 \qquad (1)$$

In first order of n one retains

$$P = nk_BT$$

which is the ideal gas law

b) $$P_{vdW} = \frac{Nk_BT}{V-Nb} - \frac{aN^2}{V^2}$$

$$\simeq nk_BT(1+nb) - an^2$$

which matches eq. (1).

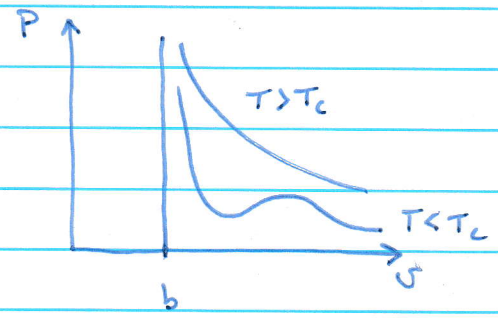
c) System becomes thermodynamically unstable when

$$\left.\frac{\partial P}{\partial V}\right|_T > 0.$$

$$\Leftrightarrow \left.\frac{\partial P}{\partial V}\right|_T = \frac{-Nk_BT}{(V-Nb)^2} \cdot \exp(\ldots) + \frac{Nk_BT}{V-Nb} \exp(\ldots) \cdot \frac{aN}{k_BTV^2} > 0$$

$$\Leftrightarrow \frac{aN(V-Nb)}{k_BV^2} > T \qquad \text{we identify } T_c = \frac{aN(V-Nb)}{k_BV^2}$$

d)



② Quantum partition function

a)

$$Z = \sum_{n=0}^{+\infty} (n+1)\, e^{-\beta(E_0 + n\gamma)}$$

$$= e^{-\beta E_0} \sum_{n=0}^{+\infty} (n+1)\, x^n \qquad x \equiv e^{-\beta\gamma}$$

$$= e^{-\beta E_0} \cdot \frac{d}{dx}\left(\sum_{n=0}^{+\infty} x^{n+1}\right)$$

$$= e^{-\beta E_0} \frac{d}{dx}\left(x \sum_{n=0}^{+\infty} x^n\right)$$

$$= e^{-\beta E_0} \frac{d}{dx}\left(\frac{x}{1-x}\right)$$

$$= e^{-\beta E_0} \left(\frac{(1-x) + x}{(1-x)^2}\right)$$

$$= \frac{e^{-\beta E_0}}{(1 - e^{-\beta\gamma})^2}$$

$$\langle E \rangle = -\frac{\partial}{\partial\beta} \log(Z) = E_0 + 2 \frac{\partial}{\partial\beta} \cdot \log\left(1 - e^{-\beta\gamma}\right)$$

$$= E_0 + \frac{2\gamma e^{-\beta\gamma}}{1 - e^{-\beta\gamma}}$$

$$= E_0 + \frac{2\gamma}{e^{\beta\gamma} - 1}$$

Low temperature : $(\beta \gg 1)$

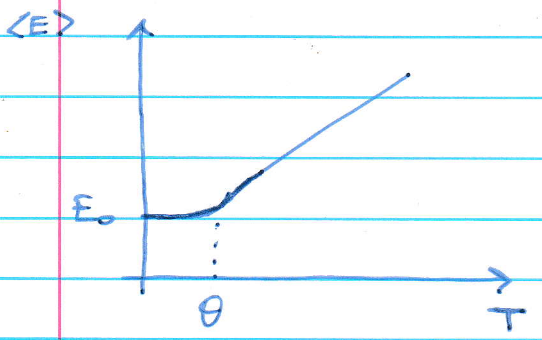
$$\langle E \rangle \simeq E_0 + 2\gamma\, e^{-\beta\gamma}$$

High temperature : $(\beta \ll 1)$

$$\langle E \rangle = E_0 + \frac{2\gamma}{\gamma} \cdot k_B T$$

$$= E_0 + 2 k_B T$$

(Insight a 2D harmonic oscillator has exactly this described energy spectrum, hence the $\underline{2}\, k_B T$.)



b) $k_B \theta = \Delta E = \gamma$

$\Rightarrow \theta = \dfrac{\gamma}{k_B}$

③ Identical particles wave function

a)

$$\Psi(\vec{q}_1, \vec{q}_2, \vec{q}_3) = \frac{1}{\sqrt{3}} \Big\{ \phi_1(\vec{q}_1)\,\phi_2(\vec{q}_2)\,\phi_2(\vec{q}_3) + \phi_1(\vec{q}_1)\,\phi_2(\vec{q}_2)\,\phi_1(\vec{q}_3)$$

$$+ \phi_2(\vec{q}_1)\,\phi_1(\vec{q}_2)\,\phi_1(\vec{q}_3) \Big\}$$

b)

$$\log \Xi_{\text{BOSONS}} = \sum_\gamma \log\Big(\sum_{n_\gamma=0}^{+\infty} e^{-\beta(\varepsilon_\gamma-\mu)n_\gamma}\Big)$$

$$= -\sum_\gamma \log\big(1 - e^{-\beta(\varepsilon_\gamma-\mu)}\big)$$

$$= -\log\big(1 - e^{+\beta\mu}\big) - \log\big(1 - e^{-\beta(\varepsilon-\mu)}\big)$$

c) $$\langle n_\gamma \rangle = -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_\gamma} \log \Xi$$

$$= -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_\gamma}\Big(-\log\big(1 - e^{-\beta(\varepsilon_\gamma-\mu)}\big)\Big)$$

$$= \frac{1}{\cancel{\beta}} \frac{\cancel{\beta} e^{-\beta(\varepsilon_\gamma-\mu)}}{1 - e^{-\beta(\varepsilon_\gamma-\mu)}} = \frac{1}{e^{\beta(\varepsilon_\gamma-\mu)} - 1}$$

$$\langle n_0 \rangle = \frac{1}{e^{-\beta\mu} - 1} \; ; \; \langle n_1 \rangle = \frac{1}{e^{\beta(\varepsilon-\mu)} - 1}$$

$$\frac{\langle n_0 \rangle}{\langle n_1 \rangle} = \frac{e^{\beta(\varepsilon-\mu)} - 1}{e^{-\beta\mu} - 1} = 2$$

$$\Rightarrow \quad e^{\beta\varepsilon} x - 1 = 2x - 2 \quad , \text{where } x \equiv e^{-\beta\mu}$$

$$\Rightarrow \quad x = \frac{1}{2 - e^{\beta\varepsilon}}$$

$$\Rightarrow \quad \mu(T) = +k_B T \log\big(2 - e^{\beta\varepsilon}\big)$$

$$2 - e^{\beta \varepsilon} > 0$$

$$\Rightarrow \frac{\varepsilon}{k_B \log(2)} < T$$

④ Blackbody spectrum

$$\langle E \rangle = \int_0^{+\infty} \frac{g(\omega)\, \hbar\omega}{e^{\beta\hbar\omega} + 1}\, d\omega$$

$$= AV\hbar \int_0^{+\infty} \frac{\omega^d \, d\omega}{e^{\beta\hbar\omega} + 1}$$

$$x = \beta\hbar\omega \rightarrow \frac{dx}{\beta\hbar} = d\omega$$

$$= \frac{AV}{\beta(\beta\hbar)^d} \int_0^{+\infty} \frac{x^d \, dx}{e^x + 1} \sim T^{d+1}$$

⑤ Fermions

$$\log \Xi_{\text{Fermions}} = \sum_\gamma \log\left(1 + e^{-\beta(\varepsilon_\gamma - \mu)}\right)$$

$$\langle n_\gamma \rangle = \frac{0 \cdot 1 + 1 \cdot e^{-\beta(\varepsilon_\gamma-\mu)}}{1 + e^{-\beta(\varepsilon_\gamma-\mu)}} = \frac{1}{e^{\beta(\varepsilon_\gamma-\mu)} + 1}$$

$$\langle n_\gamma^2 \rangle = \frac{0^2 \cdot 1 + 1^2 \cdot e^{-\beta(\varepsilon_\gamma-\mu)}}{1 + e^{-\beta(\varepsilon_\gamma-\mu)}} = \frac{1}{e^{\beta(\varepsilon_\gamma-\mu)} + 1}$$

(or use derivative trick)

$$\Delta n_\gamma^2 = \langle n_\gamma^2 \rangle - \langle n_\gamma \rangle^2$$

$$= \frac{1}{e^{\beta(\varepsilon_\gamma-\mu)}+1} - \frac{1}{\left(e^{\beta(\varepsilon_\gamma-\mu)}+1\right)^2} = \frac{1}{x+1} - \frac{1}{(x+1)^2}$$

Define $x \equiv e^{\beta(\varepsilon_\gamma-\mu)}$

$$\left.\frac{d\Delta n_\gamma^2}{dx}\right|_{x=x_{max}} = 0 = -\frac{1}{(1+x)^2} + 2\frac{1}{(x+1)^3}$$

$$= \frac{2-(1+x)}{(1+x)^3}$$

$$\Rightarrow x_{max} = 1 \Leftrightarrow e^{\beta(\varepsilon_\gamma-\mu)} = 1$$

$$\Leftrightarrow \varepsilon_\gamma = \mu$$

$$\Delta n_{\gamma\,max}^2 = \frac{1}{2} - \frac{1}{4} = \frac{1}{4}.$$