Chapter 4.3: The Ideal Gas in the Grand Canonical Ensemble

Can we recover known ideal gas law in grand canonical ensemble?

Previous results: $Z_1 \approx \frac{V}{\lambda_T^3}$ and $Z_N = \frac{Z_1^N}{N!}$ $\qquad \lambda_T = \hbar\sqrt{\frac{2\pi}{mk_BT}}$

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{-\alpha N} \sum_{|\cancel{r(N)}\rangle} e^{-\beta \cancel{\varepsilon_r(N)}} = \sum_{N=0}^{\infty} z^N Z_N = \sum_{N=0}^{\infty} \frac{z^N Z_1^N}{N!} = e^{zZ_1}$$

$\{r\}$ $\qquad E(\{r\})$

$$\ln \mathcal{Z} = z Z_1$$

$$\phi = -k_BT \ln \mathcal{Z} = -k_BT\, z Z_1$$

* more general

$$Z_1 = \frac{V}{\lambda_T^3} \cdot Z_{rot} \cdot Z_{vib} \cdot Z_{spin} \cdots$$

* For more particle types $A, B, \ldots$

$$\mathcal{Z} = \mathcal{Z}_A \mathcal{Z}_B \cdots$$

$$\ln \mathcal{Z} = \ln \mathcal{Z}_A + \ln \mathcal{Z}_B + \ldots$$

$z = e^{-\alpha}$ $\quad \frac{\partial z}{\partial \alpha} = -z$

1.) Find relation between N and $\mu = -k_B T \alpha$ $\longrightarrow$ get rid of fugacity z

$$N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_T = -\left(\frac{\partial \ln \mathcal{Z}}{\partial \alpha}\right)_\beta = -\left(\frac{\partial z Z_1}{\partial \alpha}\right)_\beta = z Z_1$$

$$z = \frac{N}{Z_1} = \frac{N\lambda_T^3}{V}$$

$\ln N! \approx N \ln N - N$

$$F = -k_B T \ln Z_N$$

$$= -k_B T N \ln \frac{Z_1}{N} - N k_B T$$

$$= \phi + \mu N$$

$$\phi = -k_B T \ln \mathcal{Z} = -k_B T V$$

reminds $\frac{N\lambda_T^3}{V} \gg 1$ quantum behavior

$\frac{N\lambda_T^3}{V} \ll 1$ classical behavior

$$\frac{N\lambda_T^3}{V} \approx z + \text{higher order}$$

$$N = z Z_1 = \ln \mathcal{Z}$$

$$Z_1 = \frac{V}{\lambda_T^3} \propto T^{-3/2}$$

2.) Determine rest

$$E = -\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_{\alpha,V} = -z \frac{\partial Z_1}{\partial \beta} = + z \frac{1}{\beta} \frac{3}{2} Z_1 = \frac{3}{2} N k_B T$$

in general $+ E_{rot} + E_{vib} + E_{spin}$

+ other particles

$$p = -\left(\frac{\partial \Phi}{\partial V}\right)_{\alpha,T} = k_B T \left(\frac{\partial (z Z_1)}{\partial V}\right)_{\alpha,T} = \frac{k_B T z Z_1}{V} = \frac{k_B T N}{V}$$

$$\frac{\partial Z_1}{\partial V} = \frac{Z_1}{V}$$

"did nothing wrong"