Unit 2-18: Non-Interacting Particles in the Grand Canonical Ensemble

We had for the grand canonical partition function,

$$\mathcal{L} = \sum_{N=0}^{\infty} z^N Q_N(T,V) \qquad \text{where } z = \mathrm{e}^{\beta\mu} \text{ is the fugacity, and } Q_N \text{ is the canonical partition function.} \tag{2.18.1}$$

For non-interacting particles we had,

$$Q_N(T,V) = \frac{1}{N!}\Big[Q_1(T,V)\Big]^N \qquad \text{for } \textit{indistinguishable} \text{ particles, as in the ideal gas} \tag{2.18.2}$$

and

$$Q_N(T,V) = \Big[Q_1(T,V)\Big]^N \qquad \text{for } \textit{distinguishable} \text{ particles, as in paramagnetic spins} \tag{2.18.3}$$

where Q_1 is the single particle partition function.

Indistinguishable Particles

$$\mathcal{L} = \sum_{N=0}^{\infty} z^N Q_N = \sum_{N=0}^{\infty} \frac{(zQ_1)^N}{N!} = \mathrm{e}^{zQ_1} \tag{2.18.4}$$

Distinguishable Particles

$$\mathcal{L} = \sum_{N=0}^{\infty} z^N Q_N = \sum_{N=0}^{\infty} (zQ_1)^N = \frac{1}{1 - zQ_1} \qquad \text{assuming } zQ_1 < 1 \text{ for the series to converge.} \tag{2.18.5}$$

Indistinguishable Particles

For *indistinguishable* particles we thus have $\ln \mathcal{L} = z\,Q_1$ and so,

$$-pV = \Phi = -k_BT\ln\mathcal{L} = -k_BT z\,Q_1 \qquad \Rightarrow \qquad p = \frac{k_BT}{V} z\,Q_1 \tag{2.18.6}$$

Also

$$N = -\left(\frac{\partial\Phi}{\partial\mu}\right)_{T,V} = k_BT\left(\frac{\partial z}{\partial\mu}\right)_T Q_1 = k_BT\,\beta\,z\,Q_1 = z\,Q_1 \tag{2.18.7}$$

So, combining these last two results, we have,

$$p = \frac{Nk_BT}{V} \qquad \text{the ideal gas law, no matter what is } Q_1. \tag{2.18.8}$$

So, no matter what is the single particle Hamiltonian (i.e. no matter what is Q_1), indistinguishable non-interacting particles will always obey the ideal gas law.

Ideal Gas of Indistinguishable Particles

For a simple gas of point particles,

$$Q_1 = \frac{1}{h^3}\int d^3p \int d^3r\, \mathrm{e}^{-\beta p^2/2m} = (2\pi m k_BT)^{3/2}\frac{V}{h^3} = V f(T), \qquad \text{with } f(T) = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \tag{2.18.9}$$

For a more complicated gas, for example where the particles might have internal degrees of freedom, Q_1 will have this same form but with a different $f(T)$.

We have,

$$\mathcal{L} = \mathrm{e}^{zQ_1} = \mathrm{e}^{zVf(T)} \qquad \Rightarrow \qquad \ln \mathcal{L} = zVf(T) \tag{2.18.10}$$

The grand potential is then

$$\Phi = -k_B T \ln \mathcal{L} = -k_B T zVf(T) = -pV \qquad \Rightarrow \qquad p = k_B T z f(T) \qquad \text{recall, } z = \mathrm{e}^{\beta\mu} \tag{2.18.11}$$

and

$$N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = -\left(\frac{\partial \Phi}{\partial z}\right)_{T,V}\left(\frac{\partial z}{\partial \mu}\right)_T = k_B T V f(T) \beta \mathrm{e}^{\beta\mu} = zVf(T) \tag{2.18.12}$$

Combining the above two results give,

$$\frac{p}{k_B T} = zf(T) \quad \text{and} \quad \frac{N}{V} = zf(T) \qquad \Rightarrow \qquad pV = Nk_B T \tag{2.18.13}$$

So we get the ideal gas law no matter what is $f(T)$, i.e. no matter what might be the internal degrees of freedom of the particles.

Also,

$$E = -\left(\frac{\partial \ln \mathcal{L}}{\partial \beta}\right)_{V,z} = k_B T^2 \left(\frac{\partial \ln \mathcal{L}}{\partial T}\right)_{V,z} = k_B T^2 zV \frac{df}{dT} \qquad \text{using } \ln \mathcal{L} = zVf(T) \tag{2.18.14}$$

$$= k_B T^2 N \frac{1}{f}\frac{df}{dT} = k_B T^2 N \left(\frac{\partial \ln f}{\partial T}\right) \qquad \text{using } N = zVf(T) \tag{2.18.15}$$

and so,

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{V,N} = 2k_B T N \left(\frac{\partial \ln f}{\partial T}\right) + k_B T^2 N \left(\frac{\partial^2 \ln f}{\partial T^2}\right) \tag{2.18.16}$$

If the single particle Hamiltonian has only harmonic degrees of freedom (for example $\mathbf{p}$, or harmonic internal degrees of freedom such as internal vibrations of a molecule), one has $f \propto T^n$ for some power n (for a simple point particle, where $\mathbf{p}$ is the only harmonic degree of freedom, one has $n = 3/2$ as in Eq. (2.18.9)). In this case,

$$\left(\frac{\partial \ln f}{\partial T}\right) = \left(\frac{\partial [n \ln T]}{\partial T}\right) = \frac{n}{T} \qquad \Rightarrow \qquad E = k_B T^2 N \left(\frac{\partial n}{\partial T}\right) = nk_B T N \tag{2.18.17}$$

and

$$C_V = 2nk_B N + k_B T^2 N \left(\frac{-n}{T^2}\right) = nk_B N \tag{2.18.18}$$

The Helmholtz free energy is,

$$A = \Phi + \mu N = -k_B T zVf(T) \;+\; (k_B T \ln z)(zVf(T)) \qquad \text{using } \mu = k_B T \ln z \text{ and } N = zVf(T) \tag{2.18.19}$$

$$= zVf(T)\, k_B T \Big[\ln z - 1\Big] = Nk_B T \Big[\ln z - 1\Big] \tag{2.18.20}$$

and so,

$$A(T,V,N) = Nk_B T \left[\ln\left(\frac{N}{Vf(T)}\right) - 1\right] \qquad \text{where we used } N = zVf \;\Rightarrow\; z = \frac{N}{Vf} \tag{2.18.21}$$

This result agrees with a direct calculation from the canonical ensemble,

$$Q_N = \frac{[Q_1]^N}{N!} = \frac{V^N f^N}{N!} \quad \Rightarrow \quad A = -k_B T \ln Q_N = -k_B T \ln\left(\frac{V^N f^N}{N!}\right) \tag{2.18.22}$$

$$A = -k_B T N \ln V f + k_B T(N \ln N - N) = -N k_B T + N k_B T \ln\left(\frac{N}{V f}\right) = N k_B T\left[\ln\left(\frac{N}{V f(T)}\right) - 1\right] \tag{2.18.23}$$

And, lastly, the entropy is,

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} = N k_B\left[\ln\left(\frac{N}{V f(T)}\right) - 1\right] - N k_B T\,\frac{d(\ln f)}{dT} \tag{2.18.24}$$

Distinguishable Particles

This corresponds to a situation in which particles are *localized*, so that we can distinguish them by their spatial location.

Now we expect $Q_1 = \phi(T)$ – it is not proportional to the volume V since the particles are localized. Then,

$$\mathcal{L} = \frac{1}{1 - zQ_1} = \frac{1}{1 - z\phi(T)} \qquad \text{note, if we had } Q_1 \propto V\text{, then the series in Eq. (2.18.5) would not converge!} \tag{2.18.25}$$

Then

$$\Phi = -k_B T \ln \mathcal{L} \tag{2.18.26}$$

$$N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = -\left(\frac{\partial z}{\partial \mu}\right)_T\left(\frac{\partial \Phi}{\partial z}\right)_{T,V} = -\beta \mathrm{e}^{\beta\mu}(-k_B T)\frac{1}{\mathcal{L}}\frac{\partial \mathcal{L}}{\partial z} \tag{2.18.27}$$

$$= z(1 - z\phi)\frac{\phi}{(1 - z\phi)^2} = \frac{z\phi}{1 - z\phi} \tag{2.18.28}$$

$$\Rightarrow \quad (1 - z\phi)N = z\phi \quad \Rightarrow \quad z\phi = \frac{N}{1 + N} = \frac{1}{1 + 1/N} \approx 1 - \frac{1}{N} \quad \text{for } N \gg 1 \tag{2.18.29}$$

and

$$E = -\left(\frac{\partial \ln \mathcal{L}}{\partial \beta}\right)_{V,z} = k_B T^2\left(\frac{\partial \ln \mathcal{L}}{\partial T}\right)_{V,z} = k_B T^2(1 - z\phi)\frac{z(d\phi/dT)}{(1 - z\phi)^2} \tag{2.18.30}$$

$$= \frac{k_B T^2 z(d\phi/dT)}{1 - z\phi} = k_B T^2 N\frac{1}{\phi}\frac{d\phi}{dT} = k_B T^2 N\left(\frac{\partial \ln \phi}{\partial T}\right) \tag{2.18.31}$$

and

$$A = \Phi + \mu N = -k_B T \ln\left(\frac{1}{1 - z\phi}\right) + (k_B T \ln z)N = k_B T\Big[\ln(1 - z\phi) + N \ln z\Big] \tag{2.18.32}$$

Now use $1 - z\phi \approx 1/N$ and $z \approx 1/\phi$ to get,

$$A = -k_B T N \ln \phi(T) + O(\ln N) \tag{2.18.33}$$