Dealing with free energy methods means probabilities!

Recall that thanks to the partition function we can get any property we like as:

$$\mathcal{P} = \langle p(x) \rangle = \frac{1}{\mathcal{Z}} \int p(x) \mathcal{F}(\mathcal{H}(x)) \, dx$$

where $$\mathcal{Z} = \int \mathcal{F}(\mathcal{H}(x)) \, dx$$

Thus, let us familiarise with the probability *P* for a generic function *f({r})* of having a value *s* within the (N,V,T) ensemble

$$P(s) = \frac{1}{Q(N,V,T)} \int \delta(f(\{\mathbf{r}\}) - s) \cdot e^{-\beta \mathcal{H}(\{\mathbf{r},\mathbf{p}\})} d\mathbf{r} d\mathbf{p}$$

$$= \underbrace{\frac{1}{Q(N,V,T)} \frac{1}{\lambda^{3N}}}_{\text{Thermal average}} \underbrace{\int \delta(f(\{\mathbf{r}\}) - s) \cdot e^{-\beta \mathcal{H}(\{\mathbf{r}\})} d\mathbf{r}}_{\text{This is a configurational canonical partition function}}$$

Thermal average

This is a ***configurational*** *canonical partition function*