# Thermodynamic functions and statistics

We defined <u>entropy</u> as $S = \frac{E}{T} + \ln Z$

$F = E - TS = -T \ln Z$, which makes it very easy to find through statistical properties

$$\boxed{F = -T \ln Z}$$

<u>Pressure</u>

$$-P\,\delta V = \sum (w_i\, \delta \varepsilon_i) w_i$$

$w_i = \frac{1}{Z} e^{-\frac{\varepsilon_i}{T}}$, according to the Gibbs distribution

Then $P = -\frac{1}{Z} \sum_i \frac{\partial \varepsilon_i}{\partial V} e^{-\frac{\varepsilon_i}{T}}$

Let's try to express it through $Z$

$$\frac{\partial Z}{\partial V} = \frac{\partial}{\partial V} \sum_i e^{-\frac{\varepsilon_i}{T}} = -\frac{1}{T} \sum_i \frac{\partial \varepsilon_i}{\partial V} e^{-\frac{\varepsilon_i}{T}}$$

Thus, $P = T \cdot \frac{1}{Z} \frac{\partial Z}{\partial V} = T \frac{\partial \ln Z}{\partial V} = -\left(\frac{\partial F}{\partial V}\right)_T$

(But we knew it before from the definition of entropy and 1st law of thermodynamics)

The formula $P = -\left(\frac{\partial F}{\partial V}\right)_T$ gives the way to find the equation of state from the partition function $Z$.

<u>Thermodynamic potential</u>

$(T, P)$

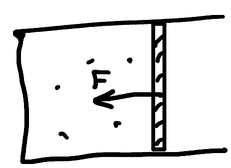
# Thermodynamic potential

Let's write $Z = Z(T, P)$

Note: when we do that, P is now an independent parameter, and volume is a variable which is a function of P.

I.e. when we considered a gas in a cylinder, the number of degrees of freedom was 3N. When we now consider it under constant pressure,

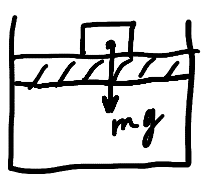
then $f = 3N + 1$ ← Piston's coordinate




$$\varepsilon_i(P) = \varepsilon_i + (\varepsilon_{kin} + U)$$

$\varepsilon_{kin}$: Kin energy of the wall

$U$: Pot. energy = work against force F




Having this mass m is equivalent to having some external pressure

Consider a quasistatic process : $\varepsilon_{kin} \to 0$

Then $$\tilde{Z}(P,T) = \sum_i e^{-\frac{\varepsilon_i + PV}{T}}$$

$$\varphi = T \ln \tilde{Z}(P,T) = E - TS + PV$$

(Compare with $F = T \ln Z(V,T)$ )

$$\frac{\partial \ln \tilde{Z}(P,T)}{\quad} = -\frac{V}{T} \frac{\sum_i e^{-\frac{\varepsilon_i + PV}{T}}}{\quad} = -\frac{V}{T}$$

$$\frac{\partial \ln \tilde{Z}(P,T)}{\partial V} = -\frac{V}{T} \frac{\sum_i e^{-\frac{\quad}{T}}}{\tilde{Z}} = -\frac{V}{T}$$

$$\boxed{V = \left(\frac{\partial \varphi}{\partial P}\right)_T}$$

The above equations demonstrate how to get thermodynamic functions by knowing the microscopic states and their probabilities