$$\downarrow$$

$$S = \frac{kT^2}{T}\left(\frac{\partial \ln Q}{\partial T}\right)_V + k \ln Q$$

$$\downarrow$$

$$\boxed{S = kT\left(\frac{\partial \ln Q}{\partial T}\right)_V + k \ln Q}$$

From thermodynamics, the Helmholtz free energy

$$A = E - TS$$

$$\downarrow$$

$$A = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_V - T\left[kT\left(\frac{\partial \ln Q}{\partial T}\right)_V + k \ln Q\right]$$

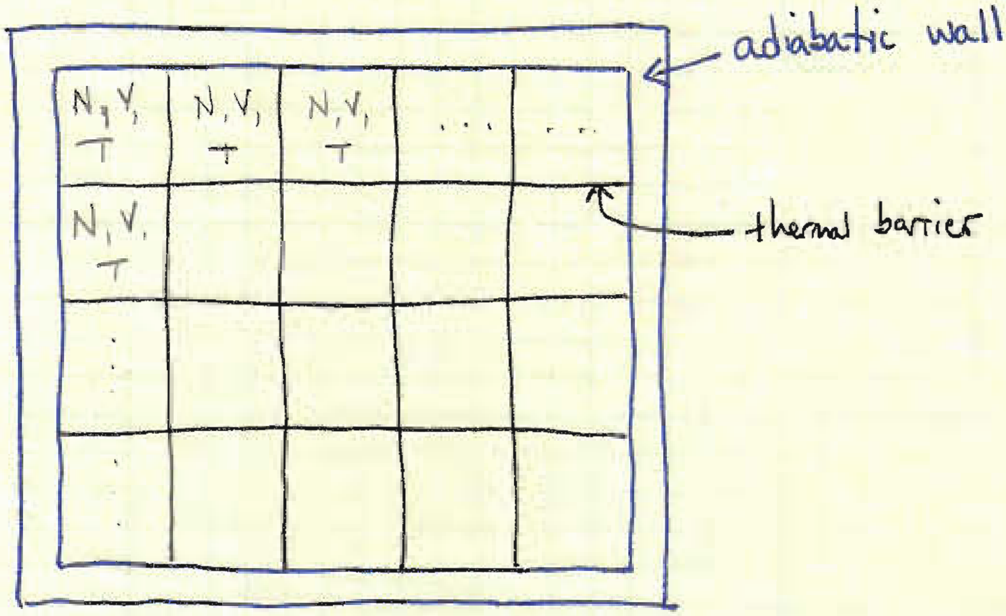
$$\downarrow$$

$$\boxed{A = -kT \ln Q}$$

Also, we know the pressure

$$\boxed{P = -\left(\frac{\partial A}{\partial V}\right)_T = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T}$$

Generalized Canonical Ensemble



- the ensemble consists of $\mathcal{N}$ replicas of a subsystem of N particles at volume V and temperature T
- the ensemble is in thermal equilibrium
- each subsystem is a q.m. system with energy levels $\varepsilon_1, \varepsilon_2, \varepsilon_3, \ldots, \varepsilon_j$
- the total energy of the ensemble is E

$$\sum_j n_j \varepsilon_j = E$$

where $n_1 \Rightarrow$ # of subsystems in the ensemble with energy $\varepsilon_1 \longrightarrow n_j =$ # subsystems with energy ε_j

$$\sum_j n_j = \mathcal{N}$$

– if each subsystem is arranged in a certain order and is separately labeled from the rest (i.e. are distinguishable) then the energy arrangement for the ensemble has a familiar multiplicity

$$W \equiv \Omega = \frac{\mathcal{N}!}{\prod_j n_j!}$$

– if we want to determine the probability dist'n then we recognize this problem as identical to our simple model of throwing a t-sided die, N times

$$P_i = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} = \frac{e^{-\beta E_i}}{Q}$$

Q is called the canonical partition function

$$Q \equiv Q(N, V, T)$$

N, V, T are the natural variables of the canonical ~~partition function~~ ensemble.

- I have introduced the symbol Ω to now represent the multiplicity (i.e. number of microstates) in energy arrangement

    - we can use Ω_j to represent the multiplicity of the energy state j
    - in quantum mechanics this multiplicity is called the degeneracy (i.e. number of states with same energy)

- the degeneracy is useful mathematically

$$Q = \sum_j e^{-\beta \varepsilon_j} \equiv \sum_E \Omega_E \, e^{-\beta E}$$

sum over all states

this sum is now over energy levels

$$Q(N,V,T) = \sum_E \Omega_E(N,V) \, e^{-\beta E}$$