★ THERMODYNAMICS & STAT. MECH.

- All characteristic potentials can be written in terms of the relevant partition function.

REMEMBER:

$$\begin{cases} f = -k_B T \log Z \\ Z = \sum_i \exp(-\beta E_i) \end{cases}$$

GENERAL STRUCTURE FOR ANY SET OF BOUNDARY CONDITIONS:

$$P_\nu = \exp(\square_\nu)$$

$$Z_1 = \sum_\nu \exp\left(\square_\nu\right)$$

ν → sum over all states allowed by BC

Λ = char. potential $= -\dfrac{\log Z_1}{\beta} \Rightarrow -\beta\Lambda = \log Z_1$

① CANONICAL ENSEMBLE

Const. $T, V, N \Rightarrow$ fluctuating E, p, μ.

$dE = TdS - pdV + \mu dN$

$E(S, V, N)$

$\Lambda = F = E - TS$

$-\beta\Lambda = -\beta f = \dfrac{S}{k} - \beta E$ (wavy) → $\square$

$P_\nu = \exp(-\beta E_\nu)/Z \qquad Z_1 = \sum_i \exp(-\beta E_\nu)$

$-\beta f = \log Z_1$

$dF = -SdT - pdV + \mu dN$

DERIVING THE EOS

(i) $\left(\dfrac{\partial f}{\partial T}\right)_{V,N} = -S$

$$S = \left(\frac{\partial}{\partial T}\left(k_B T \log Z_1\right)\right)_{V,N} = k_B \log Z_1 + k_B T \frac{\partial \log Z_1}{\partial T} = k_B \log Z_1 + \frac{k_B T}{Z_1} \sum_\nu \frac{\partial}{\partial T}\left(\exp(-\beta E_\nu)\right)$$

$$= k_B \log Z_1 + \frac{k_B T^2}{Z} \sum_\nu (-E_\nu) \exp(-\beta E_\nu) \times \left(\frac{-1}{k_B T^2}\right) = k_B \log Z_1 + \sum_\nu \frac{E_\nu}{T}\left(\frac{\exp(-\beta E_\nu)}{Z_1}\right)$$

$$= \sum_\nu k_B P_\nu \log Z + \sum_\nu \left(-\beta E_\nu\right) \times (-k_B)\, P_\nu$$

$$S = \sum_\nu -k_B P_\nu \left[\log\left(\frac{\exp(-\beta E_\nu)}{Z_1} \right) \right] = \sum_\nu -k_B P_\nu \log P_\nu \Longrightarrow \text{GIBBS ENTROPY}$$

(iii) $$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{\partial (k_B T \log Z_1)}{\partial V} = \frac{k_B T}{Z_1} \frac{\partial Z_1}{\partial V} = \frac{k_B T}{Z_1} \sum_\nu \frac{\partial}{\partial V} \exp(-\beta E_\nu) = \frac{k_B T}{Z_1} \sum_\nu (-\beta) \frac{\partial E_\nu}{\partial V} \exp(-\beta E_\nu)$$

$$p = \sum_\nu \underbrace{-\left(\frac{\partial E_\nu}{\partial V}\right)}_{p_\nu} \frac{\exp(-\beta E_\nu)}{Z_1} = \sum_\nu p_\nu P_\nu$$

② GRAND-CANONICAL ENSEMBLE

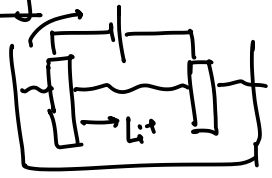
$T, V, \mu \longrightarrow$ Constant.

Note: $\mu = \mu^\circ + kT \log p$ → pressure of gas. ⇒ Control pressure → control μ.

* adsorption → system (eg) O_2 on Pt

  # of particles on the surface fluctuates but there is a thermodynamic average of N

* battery: e^-



$\mu_{Li} \sim V$ ← voltage.

$T, V, \mu \Longrightarrow$ Constant ; $E, p, N \Rightarrow$ fluctuating.

$$\Lambda = E - TS - \mu N$$

$$-\beta\Lambda = \frac{S}{k} - \beta E + \beta\mu N$$

$$P_\nu = \exp\left(-\frac{E_\nu - \mu N_\nu}{k_B T}\right) \Big/ Z_4$$

$$Z_4 = \sum_\nu \exp\left(-(E_\nu - \mu N_\nu)/k_B T\right)$$

$$-\beta\Lambda = \log Z_4 \Rightarrow \Lambda = -\frac{1}{\beta} \log Z_4$$

$$d\Lambda = -S dT - p dV - N d\mu$$

⇒ EOS

TD relations: $$\bar{p} = -\left(\frac{\partial \Lambda}{\partial V}\right)_{T,\mu} = \frac{1}{\beta}\left(\frac{\partial [\log Z_4]}{\partial V}\right)_{\beta,\mu}$$

$$\bar{N} = \frac{1}{\beta}\left(\frac{\partial \log Z_1}{\partial \mu}\right)_{T,V}$$

③ Isothermal, isobaric (const. T, p, N) $\Rightarrow$ fluctuating (E, V, μ)

$$\Delta = E - TS + pV$$

$$-\beta\Delta = \frac{S}{k_B} - \beta E - \beta pV$$

$$\square$$

$$P_\nu = \exp\left(-\frac{E_\nu + pV_\nu}{k_B T}\right) / \mathcal{Z}$$

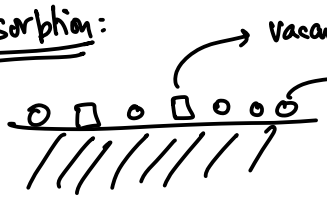
$$\mathcal{Z} = \sum_\nu \exp\left(-\frac{E_\nu + pV_\nu}{k_B T}\right)$$

$$-\beta\Delta = \log \mathcal{Z}$$

APPLICATIONS:

(I) Statistical mechanics of "configurational" degrees of freedom.

* **Adsorption:**



M - surface sites

N - adsorbed atoms

$$X = \frac{N}{M}$$

$X = 1$ when all sites on the surface have an adsorbed species on them.

(eg) - Ammonia synthesis (NH_3)

Consumes 1-2% of global energy.

$\sim$3% of CO_2 emissions.

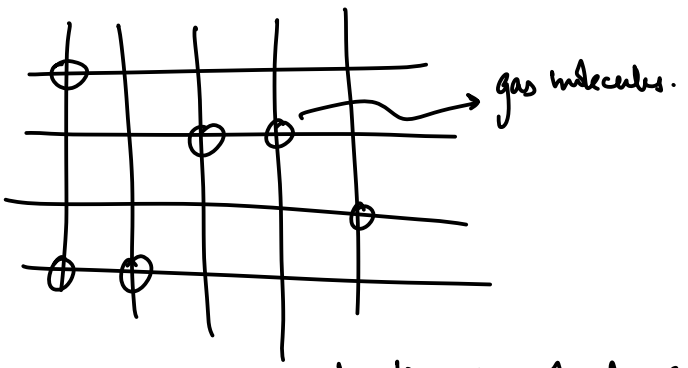
iron oxide on Alumina.

- hydrogen production from H_2O

substrate $\longrightarrow$ Ni @ K_2O

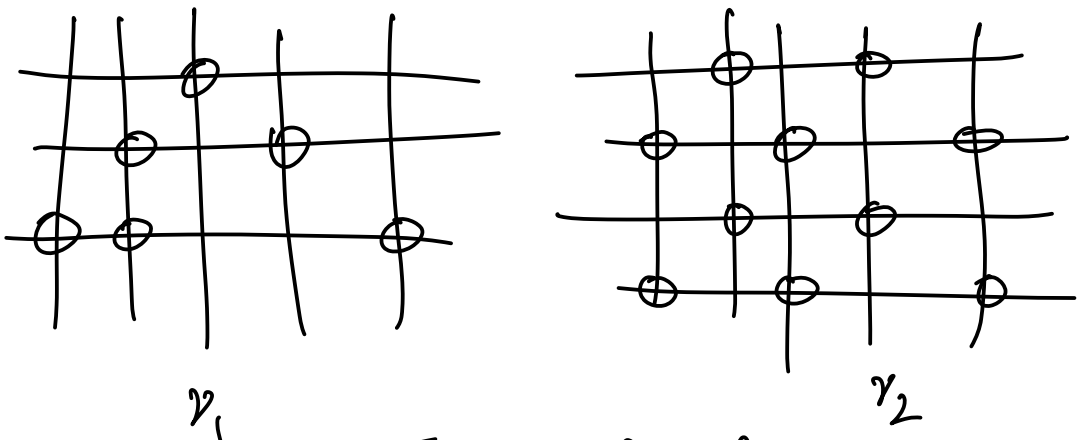
for simplicity:

Assume surface sites form a square lattice:



in general, the gas molecules can "vibrate" around the surface sites or move $\longrightarrow$ we will ignore this for the sake of simplicity

Microstates: $\longrightarrow$ different ways of arranging gas molecules on the surface



ν_1 $\qquad$ ν_2

In general $E_{\nu_1} \neq E_{\nu_2}$

We will ASSUME: energy DOES NOT depend on arrangement of atoms.

$E_\nu \longrightarrow$ only depends on the number of atoms.

$E_\nu = N_\nu \varepsilon$ $\quad \varepsilon \longrightarrow$ energy of placing a single particle on the surface.

Case I: Canonical ensemble:

Constant T, V, N.

char. potential $f = U - TS$

$$Z = \sum_\nu \exp(-E_\nu/k_BT) = \sum_E \Omega(E) \exp(-E/k_BT)$$

at constant # of particles $\Rightarrow$ only one energy, since $E_\nu = N\varepsilon$

$$\Rightarrow Z_1 = \Omega(E) \exp\left(-\frac{N\varepsilon}{k_BT}\right)$$

$\Omega(E)$: # of ways to distribute N particles over M sites

$$\Omega(E) = M \text{ choose } N = \frac{M!}{N!\,(M-N)!}$$

a) $f = -k_BT \log Z_1$

$$= -k_BT \log\left[\Omega(E) \exp(-N\varepsilon/k_BT)\right] = -k_BT\left[-\frac{N\varepsilon}{k_BT} + \log\Omega(E)\right] = N\varepsilon - k_BT \log\Omega(E)$$

b) $S = -\left(\frac{\partial f}{\partial T}\right)_N = k_B \log\Omega(E)$ $\longrightarrow$ THIS RESULT IS ONLY DUE TO THE APPROXIMATIONS WE MADE; NOT GENERAL

$$S = k_B\left[\log M! - \log N! - \log(M-N)!\right]$$

STIRLING'S APPROXIMATION:

$$\log(N!) \approx N\log N - N$$

very good approximation as $N \uparrow$

$$S = k_B\left[M\log M - M - (N\log N - N) - ((M-N)\log(M-N) - (M-N))\right]$$

$$= k_B\left[M\log M - M - N\log N + N - (M-N)\log(M-N) + M - N\right]$$

$$= k_B\left[M\log M - N\log N - (M-N)\log(M-N)\right] = k_B\left[(M-N)\log M + N\log M - N\log N - (M-N)\log(M-N)\right]$$

Add & subtract this term

$$S = -k_B M \left[(N/M) \log (N/M) + \frac{(M-N)}{M} \log \left(\frac{M-N}{M} \right) \right]$$

$$\boxed{S = -k_B M \left[x \log x + (1-x) \log (1-x) \right]}$$

CONFIGURATIONAL ENTROPY OF AN IDEAL SOLUTION

↳ A solution where there are no preferences for attraction or repulsion between particles.

$$f = N\varepsilon + k_B T M \left\{ x \log x + (1-x) \log (1-x) \right\}$$

$$\mu = \frac{\partial f}{\partial N} = \varepsilon + k_B T \log \left(\frac{x}{1-x} \right)$$