Effect of changing External parameters

- Let the external parameters be denoted by $x_1, x_2, \ldots x_n$ and let the state of the system be denoted by r
- The energy of the state r depends on the external parameters

$$E_r = E_r(x_1, x_2, \ldots x_n).$$

Partition function

⊛ The partition function is given by

$$Z = \sum_{r} e^{-\beta E_r(x_1, \dots x_n)}$$

and therefore

$$Z = Z(\beta, x_1, x_2 \dots x_n).$$

a function of fundamental temperature β and external parameters $x_1, x_2, \dots x_n$.

Average Energy

⊙ Suppose the states are distributed according to thermal equilibrium at temp. τ then

$$\bar{E} = \sum_{r} P_r(x_1, x_2 .. x_n, \tau)\, E_r(x_1, -- x_n)$$

$$= \sum_{r} \frac{e^{-\beta E_r}}{Z} E_r$$

$$\Rightarrow \quad \bar{E} = -\frac{\partial \ln Z}{\partial \beta}$$

and $\bar{E} = \bar{E}(\beta, x_1, x_2 .. x_n)$.

Entropy of a System

⊛ The entropy of a System in thermal equilibrium with fundamental temperature τ is determined entirely by τ and external parameters $x_1, x_2 \ldots x_n$.

→ Note that we have defined entropy as

$\Omega(E, x_1, x_2, \ldots x_n)$ = # of accessible states of the System
when Energy is between E and $E + \delta E$
when external parameters are $x_1, \ldots x_n$

Entropy of a System.

→ when the temperature τ is provided then the most probable energy of the system is given by

$$\frac{\partial \ln \Omega(E)}{\partial E}\bigg|_{E=\tilde{E}} = \beta = 1/\tau$$

$$\left(\text{i.e. } \frac{\partial \sigma(E)}{\partial E}\bigg|_{E=\tilde{E}} = 1/\tau \right).$$

⊙ We have also shown that $P(|E-\tilde{E}| > \Delta^* E) \simeq 0$ with $\Delta^* E \approx \bar{E}/\sqrt{f}$; f being # of states.

Entropy of a System

- Thus, the entropy of a system in thermal equilibrium at temperature τ is determined by

$$\sigma(\bar{E}) = \ln \Omega(\bar{E})$$

where $\bar{E}$ is determined by the canonical distribution

- Thus, $\sigma = \sigma(\tau, x_1, x_2 \ldots x_n)$.

Entropy in terms of partition function

⊙ Note that

$$Z = \sum_{r} e^{-\beta E_r}$$

$$= \sum_{E} \Omega(E)\, e^{-\beta E}$$

$$\simeq \left(\Omega(\bar{E})\, e^{-\beta \bar{E}}\right) \frac{\Delta^{*}E}{\delta E}$$

$\Omega(E)$ is the # of accessible states between E and $E+\delta E$

$\therefore \frac{\Omega(E)}{\delta E}$ is the density of states

$$\therefore \ln Z = \ln \Omega(\bar{E})\, e^{-\beta \bar{E}} + \ln \frac{\Delta^{*}E}{\delta E}$$

$$= \ln \Omega(\bar{E}) - \beta \bar{E} + O(\ln f) \simeq \ln \Omega(\bar{E}) - \beta \bar{E}$$

Entropy in terms of partition function

$$\Rightarrow \quad \ln Z = \ln \Omega(\bar{E}) - \beta \bar{E}$$

$$\Rightarrow \quad \boxed{\sigma = \ln \Omega(\bar{E}) = \ln Z + \beta \bar{E}}$$

and $\quad \sigma = \sigma(\tau, x_1, x_2, \cdots x_n)$.

Entropy Expression

Thus $\sigma = \ln Z + \beta \bar{E}$

$$= \ln Z + \beta \sum_r P_r E_r$$

$$= \ln Z + \beta \sum P_r \left(-\frac{1}{\beta}\right) \ln(ZP_r)$$

$$P_r = \frac{e^{-\beta E_r}}{Z}$$

$$\Rightarrow Z P_r = e^{-\beta E_r}$$

$$\Rightarrow \ln(Z P_r) = -\beta E_r$$

$$\Rightarrow -\frac{1}{\beta} \ln(Z P_r) = E_r$$

$$= \ln Z - \sum P_r \ln(Z P_r)$$

$$= \ln Z - \sum_r P_r \ln Z - \sum_r P_r \ln P_r$$

$$= \ln Z - (\ln Z) \sum_r P_r - \sum_r P_r \ln P_r$$

$$= -\sum_r P_r \ln P_r$$

$$\therefore \quad \boxed{\sigma = -\sum_r P_r \ln P_r}$$

Work done in state r

⊛ Evidently if the external variable x_α is changed from $x_\alpha \longmapsto x_\alpha + dx_\alpha$ then

$$dE_r = \sum_\alpha \frac{\partial E_r}{\partial x_\alpha} dx_\alpha$$

and the work done by the system (if it were in state r and parameter $x_\alpha \longmapsto x_\alpha + dx_\alpha$) is

$$\text{đ}W_r = -dE_r = \sum_\alpha \overbrace{\left(-\frac{\partial E_r}{\partial x_\alpha}\right)}^{X_{\alpha,r}} dx_\alpha = \sum_\alpha X_{\alpha,r} dx_\alpha$$

Average Work done

⊛ If the probability distribution of states $P_r(x_1, \dots x_n)$ is known

then the average work done when parameter $x_\alpha \mapsto x_\alpha + dx_\alpha$ is

$$\text{đ}W = \sum_r P_r \, \text{đ}W_r$$

$$= \sum_r P_r(x_1, x_2, \dots x_n)\left(-\sum_\alpha \frac{\partial E_r}{\partial x_\alpha} dx_\alpha\right)$$

$$= -\sum_\alpha \sum_r P_r(x_1, \dots x_n) \, \partial E_r / \partial x_\alpha \, dx_\alpha$$

Average Work done

$$\bar{d}W = -\sum_{\alpha} \sum_{r} P_r(x_1, \dots x_n) \frac{\partial E_r}{\partial x_\alpha} \, dx_\alpha$$

We define

$$\bar{X}_\alpha \overset{\circ}{\underset{\circ}{=}} \sum_{r} \left(P_r(x_1, x_2, \dots x_n) \frac{\partial E_r}{\partial x_\alpha} \right)$$

assuming that P_r is governed by thermal equilibrium.

Average Work done

- Note that

  $P_r(x_1, x_2, \ldots x_n, \tau)$ is completely determined by thermal equilibrium statistics

  $$\left[\; P_r = \frac{e^{-E_r(x_1, \ldots x_n)/\tau}}{Z} \;;\; \tau \text{ is the fundamental temp.} \right]$$

- Also $\dfrac{\partial E_r}{\partial x_\alpha}$ is completely determined by $x_1, x_2 \ldots x_n$ and therefore

Generalized force

① $$\bar{X}_\alpha = -\sum_r P_r(x_1, \dots x_n, \tau)\frac{\partial E_r}{\partial x_\alpha}$$ is

completely determined by $(x_1, \dots x_n, \tau)$

② Therefore

$$đW = \sum_{\alpha=1}^{n} \bar{X}_\alpha \, dx_\alpha$$ (in a quasistatic process)

where $\bar{X}_\alpha$ is determined by external parameter $(x_1, x_2, \dots x_n)$ and temperature τ

Generalized force

⊛ Thus, the generalized force $\bar{X}_\alpha$ determined by the external parameters and temperature τ.

⊛ Indeed if $Z = \sum_r e^{-\beta E_r}$

Then, $\text{đ}W = \sum_\alpha \sum_r \frac{e^{-\beta E_r}}{Z}\left(-\frac{\partial E_r}{\partial x_\alpha}\right) dx_\alpha$

$$\therefore \quad \bar{X}_\alpha = \frac{1}{\beta}\,\frac{\partial \ln Z}{\partial x_\alpha} = \tau\,\frac{\partial \ln Z}{\partial x_\alpha}.$$

Generalized force

Thus,

$$\bar{X}_\alpha = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x_\alpha}$$

is the generalized force and

$$\bar{X}_\alpha = \bar{X}_\alpha(\beta, x_1, x_2 \cdots x_n).$$

is a function of $\beta (= 1/\tau)$ and external parameters.

Heat

Note that for a quasistatic process.

$$\bar{E} = \sum_r P_r(x_1, x_2 .. x_n, \tau)\, E_r(x_1, .. x_n)$$

$$\Rightarrow d\bar{E} = \sum_r \left(P_r\, dE_r + E_r\, dP_r \right)$$

$$= -\sum_r P_r\, \text{đ}W_r + \sum_r E_r\, dP_r$$

$$= -\text{đ}W + \sum_r E_r\, dP_r.$$

But $\text{đ}Q = d\bar{E} + \text{đ}W = \sum_r E_r\, dP_r.$

$$\therefore \quad \boxed{\text{đ}Q = \sum_r E_r\, dP_r}$$

Summary

Thus for a quasistatic process

ⓐ Entropy is fixed if (τ, x_α) are fixed

ⓑ Generalized forces are fixed if (τ, x_α) are fixed

ⓒ Mean Energy is fixed if (τ, x_α) are fixed.

$$d\sigma = \frac{đQ}{T}$$

⊛ Now,

$$Z = Z(\beta, x_\alpha)$$

[Z is the canonical partition function]

$$\Rightarrow \quad \ln Z = \ln Z(\beta, x_\alpha)$$

$$\Rightarrow \quad d\ln Z = \frac{\partial}{\partial \beta} \ln Z(\beta, x_\alpha)\, d\beta + \frac{\partial}{\partial x_\alpha} \ln (Z, x_\alpha)\, dx_\alpha$$

$$= -\bar{E}\, d\beta + \beta\, đW$$

$$= -d(\bar{E}\beta) + \beta\, d\bar{E} + \beta\, đW$$

$$\Rightarrow \quad d\ln Z = -d(\bar{E}\beta) + \beta(d\bar{E} + đW)$$

$$d\sigma = \bar{d}Q/\tau$$

$$\Rightarrow \quad d(\ln Z - \beta\bar{E}) = \beta(\bar{d}W + d\bar{E})$$

$$\Rightarrow \quad d\sigma = \beta\, \bar{d}Q$$

$$\Rightarrow \quad \boxed{d\sigma = \frac{\bar{d}Q}{\tau}}$$

Thus, for a quasistatic process

$$\boxed{d\sigma = \frac{\bar{d}Q}{\tau}} \quad \text{or} \quad \tau\, d\sigma = \bar{d}Q = d\bar{E} + \bar{d}W.$$

$$= d\bar{E} + \bar{X}_\alpha\, dx_\alpha .$$

Generalized Forces

Thus,

$$d\sigma = \frac{1}{\tau} d\bar{E} + \frac{1}{\tau} \bar{X}_\alpha \, dx_\alpha$$

$$\therefore \quad \sigma = \sigma(\bar{E}, x_\alpha)$$

with

$$\boxed{\begin{aligned} \left(\frac{\partial \sigma}{\partial \bar{E}}\right)_{x_\alpha} &= 1/\tau \\ \left(\frac{\partial \sigma}{\partial x_\alpha}\right)_{\bar{E}} &= \frac{1}{\tau} \bar{X}_\alpha \end{aligned}}$$

Free Energies

- We have seen that the probability distribution of any state r of a system S in thermal contact with a heat Reservoir R is determined by <u>maximizing</u> the entropy of the closed system $A^{(0)} = R \cup S$.
- However, we would like to determine a function dependent only on system S that achieves an extremum at the equilibrium condition

Free Energy (Helmholtz)

- This function should not depend on the Reservoir properties

(α) Consider the function Free-Energy

$$F \doteq \overset{\text{(average energy of } S)}{E} - \tau \overset{\text{(Entropy of } S)}{\sigma}$$

[E is the average Energy]

- Suppose all external parameters are kept constant
- Suppose temperature is kept constant

Free Energy

→ Here σ, E and τ are all properties of the system &

Now

$$dF = dE - \tau\, d\sigma$$

$$= dE - \left[dE + \bar{X}_\alpha\, dx_\alpha \right]$$

and as all external parameters are kept constant

$$dF = dE - dE = 0.$$

Thus, F is an extremum w.r.t. all variations at constant τ and x_α.

Free Energy

Also

$\sigma^{(0)}$ the entropy of the isolated system satisfies

$$\sigma^{(0)} = \sigma + \sigma_R$$

and thus

$$\sigma^{(0)}(E) = \sigma(E) + \sigma_R(E^{(0)} - E)$$

$$\simeq \sigma_R(E^{(0)}) - \frac{\partial \sigma_R(E')}{\partial E'}\Big|_{E'=E^{(0)}} E$$

$$+ \sigma(E)$$

$$\Rightarrow \quad \sigma^{(0)}(E) \approx \sigma_R(E^{(0)}) - \beta E + \sigma(E).$$

Free Energy

⊛ Thus

$$\sigma^{(0)} \simeq \tau\sigma_R(E^{(0)}) - E + \tau\sigma(E)$$

$$\simeq \tau\sigma_R(E^{(0)}) - [E - \tau\sigma(E)].$$

$$\simeq \tau\sigma_R(E^{(0)}) - F(E)$$

Thus, $\sigma^{(0)}(E)$ is maximized at thermal eqlbm; and any change in E from $\tilde{E}$ will decrease σ^0. Thus, F must be a minimum with respect to E at constant temp. and volume.

Free Energy (Helmholtz).

(*) The free Energy is entirely determinable from the properties of the system & itself and does not require the characteristics of the reservoir.

Thus, at Constant external parameters and constant temperature free energy of the system can be determined and its variation dF set to zero to determine Equilibrium conditions.

Helmholtz free Energy

ⓕ Note that if $A^{(0)}$ is the isolated System then

$$\Delta S^{(0)} \geq 0$$

ⓕ Suppose $A^{(0)} = S \cup R$ with S being the System and R is the reservoir at temperature T_0.

ⓕ $\Delta S^{(0)} = \Delta S + \Delta S'$ [ΔS is the change in entropy of S and $\Delta S'$ that of R]

Helmholtz free Energy

→ Suppose the heat absorbed during the process is by $\mathcal{S}$ is Q. Then the heat absorbed by the Reservoir is $+Q' = -Q$

and

$$\Delta S' = \frac{-Q'}{T_0}$$

[note that the reservoir temperature does not change]

→ and

$$Q = \Delta \bar{E} + W$$

where $\Delta \bar{E}$ is the change in mean energy of $\mathcal{S}$.

Helmholtz free Energy

Thus we have

$$\Delta S^{(0)} = \Delta S + \Delta S'$$

$$= \Delta S - \frac{Q}{T_0}$$

$$= \Delta S - \frac{(\Delta \bar{E} + W)}{T_0}$$

$$= \frac{T_0 \Delta S - \Delta \bar{E} - W}{T_0}$$

$$= \frac{\Delta(T_0 S - \bar{E}) - W}{T_0} = \frac{-\Delta F_0 - W}{T_0}$$

where $F_0 = \bar{E} - T_0 S$ is the Helmholtz free energy at temp T_0.

energy at temp T_0.

Helmholtz free Energy

as $\Delta S^{(0)} \geq 0$ it follows that

$$-\Delta F^{0} - W \geq 0$$

$$\Rightarrow \quad -\Delta F^{0} \geq +W$$

and thus, the maximum work that can be done by a system in contact with a heat reservoir is $-\Delta F_0$.

⊛ Also, if the external parameter is kept constant then $W=0$ and $\Delta F^{0} \leq 0$

Helmholtz free Energy

Thus,

If a system whose external parameters are fixed is in thermal contact with a heat reservoir; the stable equilibrium situation is characterized by the condition that

F_0 is a minimum

Helmholtz Free Energy

→ Suppose the external parameters of A are fixed; $\Rightarrow W = 0$

→ Suppose A is described by a parameter y.

→ Suppose the parameter changes from y_1 to y with $\Delta S = S(y) - S(y_1)$; $\Delta \bar{E} = \bar{E}(y) - \bar{E}(y_1) = Q$

→ Then we have

$$\Delta S^{(0)} = -\frac{\Delta F_0}{T_0} = -\frac{(F(y) - F(y_1))}{T_0}$$

Helmholtz free Energy

Now, the probability of finding S ~~to~~ with parameter y is $P(y)$ is proportional to the # of accessible states of the system $A^{(0)}$ with S described by parameter y.

Thus

$$P(y) \propto \Omega^{(0)}(y) = e^{S^{(0)}(y)/k_B}$$

Helmholtz free Energy

Thus

$$P(y) \propto e^{S^{(0)}(y)/k}$$

$$S^{(0)}(y) = S^{(0)}(y_1) + \Delta S^{(0)}(y)$$

$$= S^{(0)}(y_1) - \frac{\Delta F_0(y)}{T_0}$$

$$\therefore \quad P(y) \propto e^{S^{(0)}(y_1)} \, e^{-\frac{\Delta F_0(y)}{kT_0}}$$

$$\Rightarrow \quad \boxed{P(y) = C \, e^{-\Delta F_0(y)/kT_0}} .$$

Gibbs Free Energy

① Suppose τ and generalized force X_α are kept constant. Consider

$$G := E - \tau\sigma + X_\alpha x_\alpha$$

Then

$$\begin{aligned} dG &= dE - \tau d\sigma + X_\alpha dx_\alpha \\ &= dE - [dE + X_\alpha dx_\alpha] + X_\alpha dx_\alpha \\ &= 0 \end{aligned}$$

Thus G is an extremum when X_α and temperature are kept constant.

Gibbs free Energy

[Use Gibbs free Energy when τ and $\bar{X}_\alpha$ are constant]

⊗ We have thus shown that

Gibbs free Energy is an extremum under thermal Equilibrium and constant generalized force and constant temperature

⊛ HW: prove that G achieves a minimum under conditions above.

Energy [Independent variables S and V]

We know that (assuming $\bar{X}_\alpha = p$ and $x_\alpha = V$)

$$TdS = dE + pdV$$

$$\Rightarrow \quad dE = TdS - pdV.$$

$$E = E(S,V)$$

then

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV$$

$dE = 0$ under constant entropy and external variables.
(constant entropy of systems)

Maxwell's Relations

$$\Rightarrow \left(\frac{\partial E}{\partial S}\right)_V = T$$

$$(\partial E/\partial V)_S = -p$$

$$\left(\frac{\partial}{\partial V}\right)_S \left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial}{\partial S}\right)_V \left(\frac{\partial E}{\partial V}\right)_S \rightarrow$$ because dE is an exact differential.

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V.$$

When we view $E = E(S,V)$

$$\left(\frac{\partial E}{\partial S}\right)_V = T; \left(\frac{\partial E}{\partial V}\right)_S = -p; \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V.$$

Enthalpy [Independent variable S and P]

$$Tds = dE + pdV.$$

$$\Rightarrow \quad dE = Tds - pdV.$$

$$d(pV) = pdV + Vdp \Rightarrow pdV = d(pV) - Vdp.$$

$$dE = Tds - d(pV) + Vdp$$

$$\Rightarrow \quad dE + d(pV) = Tds + Vdp$$

$$\Rightarrow \quad d(\underbrace{E + pV}) = Tds + Vdp.$$

$$H \overset{\Delta}{=} \text{Enthalpy} \equiv E + pV.$$

$$\Rightarrow \quad dH = Tds + Vdp.$$

$dH = 0$ under constant entropy and generalized force

Maxwells Relations

$$\Rightarrow \left(\frac{\partial H}{\partial S}\right)_p = T \; ; \; \left(\frac{\partial H}{\partial p}\right)_S = V.$$

$$\frac{\partial^2 H}{\partial p \partial S} = \frac{\partial^2 H}{\partial S \partial p}$$ (as dH is an exact differential)

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\Rightarrow \left(\frac{\partial H}{\partial S}\right)_p = T \; ; \; \left(\frac{\partial H}{\partial p}\right)_S = V \; ; \; \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p .$$

Helmholtz Free Energy [independent Variables T and V]

$$dE = Tds - pdV.$$

$$d(Ts) = SdT + Tds$$

$$dE = d(TS) - SdT - pdv$$

$$\Rightarrow dE - d(TS) = -SdT - pdv.$$

$$\Rightarrow d(E-TS) = -SdT - pdv$$

$$\Rightarrow dF = -SdT - pdv$$

$F \hat{=} E - TS.$ is called the Helmholtz free energy

$dF = 0$ under constant temperature and external variables.

Maxwells Relations

$$\Rightarrow \left(\frac{\partial F}{\partial T}\right)_V = -S \; ; \quad \left(\frac{\partial F}{\partial V}\right)_T = -p.$$

$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

Gibbs free Energy [Independent Variables T and p]

$$dE = TdS - pdV \quad - \quad ①$$

$$TdS = d(TS) - SdT \quad -- \quad ②$$

$$pdV = d(pV) - Vdp. \quad - \quad ③$$

$$dE = d(TS) - SdT - d(pV) + Vdp$$

$$\Rightarrow d(E - TS + pV) = -SdT + Vdp$$

$G = E - TS + pV$ is called the Gibbs free energy

$= F + PV.$

$dG = 0$ under constant temperature and generalized forces

MAXWELL'S RELATIONS

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad ; \quad \left(\frac{\partial G}{\partial p}\right)_T = V,$$

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p .$$

Summary

$E = E(S,V)$,

$H = E + pV$; $H = H(S,p)$

$F = E - TS$; $F = F(T,V)$

$G = E - TS + pV$; $G = G(T,p)$

Summary

$$dE = Tds - pdv$$
$$dH = Tds + vdp$$

$$dF = -sdT - pdv$$
$$dG = -sdT + vdp.$$

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial S}\right)_v$$
$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$
$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p.$$

Maxwells relations.

Gibbs Factor and the Grand Canonical Ensemble.

(i) Consider a very large body $A^{(0)}$ with constant energy $E^{(0)}$ and constant number of particles $N^{(0)}$

(ii) $A^{(0)}$ is composed of two parts
(a) a large reservoir R
(b) The System S.

R and S can exchange particles as well as energy

Probabilities

Question: What is the probability of finding the system A with N particles and to be in a state s with energy ε_s?

Answer: All accessible states of $A^{(0)}$ are equally likely.

① The number of ways in which $A^{(0)}$ can be in a state where A has N particles, in a state s with energy ε_s is proportional to

$$\Omega^{(0)}(\varepsilon_s, N) = \Omega_R(E^{(0)} - \varepsilon_s, N^{(0)} - N)$$

Probability

Thus

$$P(N, \varepsilon_s) \propto \Omega_R(E^{(0)} - \varepsilon_s, N^{(0)} - N)$$

and let $\sigma_R := \ln \Omega_R$

$$\ln P(N, \varepsilon_s) \propto \ln \Omega_R(\varepsilon^{(0)} - \varepsilon_s, N^{(0)} - N)$$

$$= \Omega_R(\varepsilon^{(0)}, N^{(0)}) - \varepsilon_s \overbrace{\left(\frac{\partial \sigma_R}{\partial \varepsilon}\Big|_{\varepsilon = \varepsilon^{(0)}}\right)_{N_0}}^{``\frac{1}{\tau}" = \beta}$$

$$- \left(N \frac{\partial \sigma_R}{\partial N}\Big|_{N = N^{(0)}}\right)_E + \cdots$$

$$= \Omega_R(\varepsilon^{(0)}, N^{(0)}) - \varepsilon_s \beta + \mu \beta N$$

where $\mu := -1/\beta \left(\frac{\partial \sigma}{\partial N}\right)_E \Big|_{N' = N^{(0)}}$.

Probability

Thus

$$\ln P(N, \varepsilon_s) = \ln C\, e^{-\beta \varepsilon_s + \mu \beta N}.$$

$$\Rightarrow \quad P(N, \varepsilon_s) = C\, e^{+\beta[\mu N - \varepsilon_s]}$$

and $\quad C = \mathcal{Z}^{-1}$

$$\mathcal{Z} = \sum_{N} \sum_{s(N)} e^{-\beta[\varepsilon_s - \mu N]}$$

$\uparrow$ Note that the possible states depend on the Number of particles N

Grand Canonical Ensemble.

$$\mathcal{Z} = \sum_{N_1} \sum_{N_2} \cdots \sum_{N_M} \sum_{s_M(N_M)} \cdots \sum_{s_1(N_1)} e^{-\beta\left[\mathcal{E}_i(s_i) - \mu_i N_i\right]}$$

is called the grand canonical ensemble.