§ 3. MICROCANONICAL ENSEMBLE

We consider ~~among~~ an isolated system in thermal equilibrium

If the internal energy U, which is constant, is a thermodynamic variable (out of some others e.g. V, N) then such statistical ensemble is named microcanonical ensemble

As an example we consider an ideal classical gas. We need to find a number of microstates $\Omega(U, V, N)$ for a given macrostate characterized by $U, V, N = \text{const}$.

microstate $\{\bar{x}_1, \bar{x}_2, \ldots \bar{x}_N, \bar{p}_1, \bar{p}_2, \ldots, \bar{p}_N\}$

macrostate U, V, N

\+ Total energy of the ideal gas is given by kinetic energies

$$E = \sum_{i=1}^{N} \frac{\bar{p}_i^2}{2m} \quad \text{(no interaction)}$$

In the microcanonical ensemble this energy must be equal to the internal energy, hence

$$U = \sum_{i=1}^{N} \frac{\bar{p}_i^2}{2m}.$$

There are many $\{\bar{x}_i, \bar{p}_i\}$ given the same U.

The total number of microstates therefore is

$$\boxed{\Omega(U, V, N) = \frac{1}{h^{3N} N!} \int_V d_3x_1 \dots \int d_3x_N \int_{-\infty}^{\infty} d_3p_1 \dots \int_{-\infty}^{\infty} d_3p_N \, \delta\left(U - \sum_i \frac{\bar{p}_i^2}{2m}\right)}$$

•) δ-Dirac function constrains $U = \sum_i \frac{p_i^2}{2m}$

$$\int_{-\infty}^{\infty} \delta(x - x_0) f(x) \, dx = f(x_0)$$

e.g. $$\int_{-\infty}^{\infty} \delta(x - x_0) \, dx = 1$$

••) h - Planck constant (SI units, May 2019)

$$\boxed{h = 6.62607015 \cdot 10^{-34} \quad J \cdot s}$$

h - has a dimension of angular momentum, i.e.

$$\bar{L} = \bar{r} \times \bar{p}$$

$$[\bar{L}] = [\bar{r} \times \bar{p}] = [m \cdot kg \cdot \frac{m}{s}] = [kg \frac{m^2}{s}] = [kg \frac{m^2}{s^2} \cdot s] = [J \cdot s]$$

The same dimension as an integral measure

$$[dx \, dp] = [J \cdot s]$$

The constant h in denominator cancels dimensions$^{(*)}$ and the integral measure is dimensionless $$\left[\frac{dx \, dp}{h}\right] = [1]$$

•••) $N!$ - because particles are indistinguishable. This avoids a Gibbs paradox, see later.

(*) The choice of a constant does not matter, it changes a normalization factor for probabilities

In a microcanonical ensemble the probability distribution function to find particles in a state $(\bar{x}_1 \dots \bar{x}_N, \bar{p}_1 \dots \bar{p}_N)$ at fixed internal energy U is given by (*)

$$\boxed{\begin{aligned} &P(\bar{x}_1 \dots \bar{x}_N, \bar{p}_1 \dots \bar{p}_N) = \frac{\frac{1}{h^{3N} N!}\, \delta\left(U - \sum_{i=1}^{N} \frac{\bar{p}_i^2}{2m}\right)}{\Omega(U,V,N)} \\ &\text{where} \\ &\Omega(U,V,N) = \frac{1}{h^{3N} N!} \int dx_1 \dots \int dx_N \int dp_1 \dots \int dp_N \, \delta\left(U - \sum_{i=1}^{N} \frac{\bar{p}_i^2}{2m}\right) \\ &\text{is normalization (microcanonical partition) function} \end{aligned}}$$

Example: Probability density to find a particle $(\bar{x}_1, \bar{p}_1)$

$$P(\bar{x}_1, \bar{p}_1) = \frac{1}{\Omega(U,V,N)} \int dx_2 \dots \int dx_N \int dp_2 \dots \int dp_N \, \delta\left(U - \sum_{i=1}^{N} \frac{\bar{p}_i^2}{2m}\right)$$

□

(*) This also holds for any interacting system with energy $H(\{\bar{x}_i\}, \{\bar{p}_i\})$

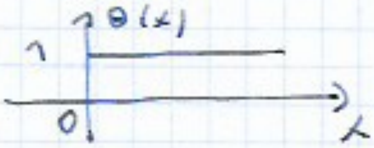
$$\boxed{\begin{aligned} &P(\{\bar{x}_i\}, \{\bar{p}_i\}) = \frac{1}{\Omega(U,V,N)} \frac{1}{h^{3N} N!} \, \delta\left(U - H(\{\bar{x}_i\}, \{\bar{p}_i\})\right) \\ &\Omega(U,V,N) = \frac{1}{h^{3N} N!} \int \prod_i^{3N} dx_i \int \prod_i^{3N} dp_i \, \delta\left(U - H(\{\bar{x}_i\}, \{\bar{p}_i\})\right) \end{aligned}}$$

$H(\{x_i\}, \{p_i\})$ - Hamiltonian (energy) function

It is easier to compute a total number of states from $U = 0$ to a given U.
It is determined by

$$\boxed{\Gamma(U,V,N) = \frac{1}{h^{3N} N!} \int d_3x_1 \ldots \int d_3x_N \int d_3p_1 \ldots \int d_3p_N \, \Theta\left(U - \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}\right)}$$

•) $\Theta(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0 \end{cases}$



step function

Note $\quad \dfrac{d\,\Theta(x)}{dx} = \delta(x)$

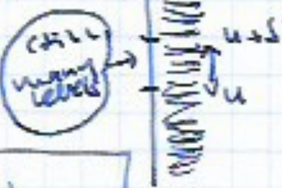
••) $\Gamma(U,V,N)$ is dimensionless

$$[\Gamma(U,V,N)] = [1]$$

•••) A number of states in the energy interval $[U, U+\delta U]$ is given by $\quad \left|\frac{\delta U}{U}\right| \ll 1$

$$\Gamma(U+\delta U,V,N) - \Gamma(U,V,N) = \left(\frac{\partial \Gamma}{\partial U}\right)_{V,N} \delta U =$$

$$= \Omega(U,V,N)\,\delta U$$



Therefore $\quad \boxed{\Omega(U,V,N) = \left(\frac{\partial \Gamma(U,V,N)}{\partial U}\right)_{V,N}}$

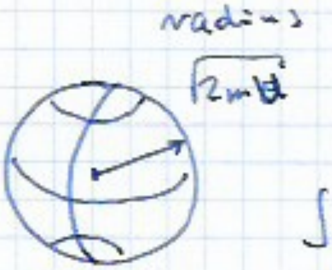
is a number of states per energy unit and has a dimensionality $[\Omega] = \left[\frac{1}{J}\right]$ (DOS)

••••) It is also known as a density of states in manybody systems (see tutorials for one particle examples).

We write this integral in spherical (3N-dimensional) coordinates in momenta and note that

$$\underbrace{\int d_3 x_1}_{V} \cdots \underbrace{\int d_3 x_N}_{V} = \underset{\uparrow \text{ volume of the system}}{V^{N \leftarrow \text{ number of particles}}}$$

$$\Gamma(U,V,N) = \frac{V^N}{h^{3N} N!} \underbrace{\int d\Omega_{3N}}_{\text{area of a } 3N\text{-dimensional ball}} \underbrace{\int_0^{\sqrt{2mU}} dp \; p^{3N-1}}_{\frac{1}{3N} p^{3N} \Big|_0^{\sqrt{2mU}}}$$



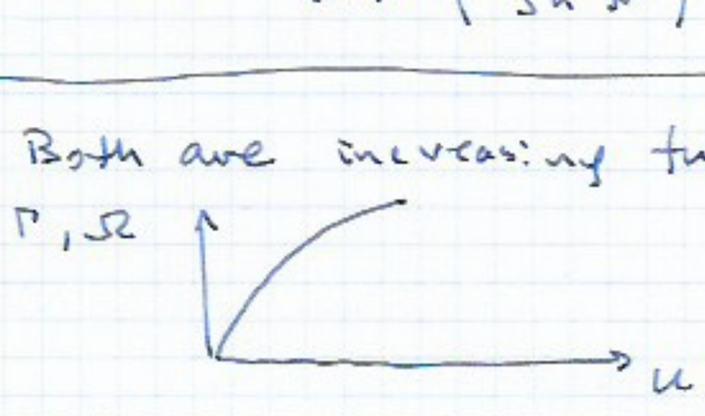
$$\int d\Omega_d = \frac{2\pi^{d/2}}{\Gamma\left(\frac{d}{2}\right)} \qquad \Gamma(n+1) = n\Gamma(n) = n!$$

$$\boxed{\begin{aligned} \Gamma(U,V,N) &= \frac{V^N}{h^{3N} N!} \frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!} (2mU)^{3N/2} \\ \Omega(U,V,N) &= \frac{\partial \Gamma}{\partial U} = \frac{V^N}{h^{3N} N!} \frac{(2\pi m)^{3N/2}}{\left(\frac{3N}{2}\right)!} \frac{3N}{2} U^{\frac{3N}{2}-1} \end{aligned}}$$

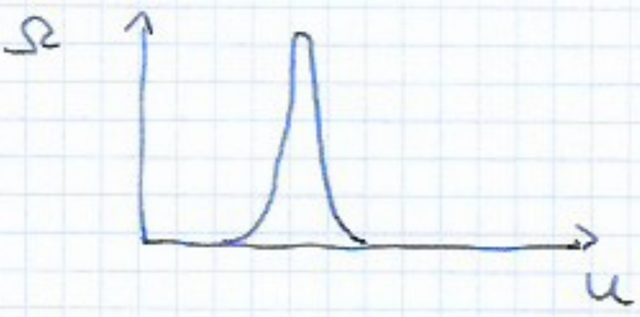
For large N $\quad N! \simeq N^N e^{-N}$ (Stirling)

$$\boxed{\begin{aligned} \Gamma(U,V,N) &\simeq \left(\frac{V}{N}\right)^N \left(\frac{4\pi m U}{3h^2 N}\right)^{\frac{3N}{2}} e^{\frac{5N}{2}} \\ \Omega(U,V,N) &\simeq \left(\frac{V}{N}\right)^N \left(\frac{4\pi m U}{3h^2 N}\right)^{\frac{3N}{2}} e^{\frac{5N}{2}} \frac{3}{2}\left(\frac{N}{U}\right) \end{aligned}}$$

Both are increasing functions of U (*)



(*) For systems with a <u>Bound spectrum</u> these functions may have very diffent behavior



this leads to certain "paradoxes" like existing a negative absolute temperature.

(see tutorials and a spin system)

Introducing densities

$$n = \frac{N}{V} \quad , \quad u = \frac{U}{N}$$

we find for logarithms

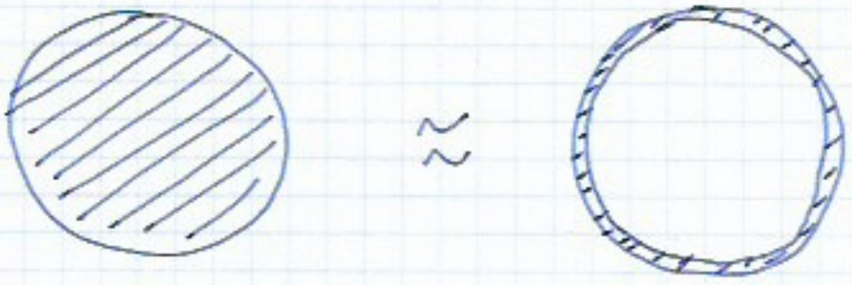
$$\ln \Gamma(U, N) \simeq -N \ln n + \frac{3}{2} N \ln\left(\frac{4\pi m u}{3h^2}\right) + \frac{5}{2} N$$

$$\ln \Omega(U, N) \simeq -N \ln n + \frac{3}{2} N \ln\left(\frac{4\pi u}{3h^2}\right) + \frac{5}{2} N - \ln\left(\frac{3}{2} u\right)$$

We thus see

$$\underbrace{\ln \Omega(U, N)}_{O(N)} \simeq \underbrace{\ln \Gamma(U, N)}_{O(N)} + O(1)$$

Almost whole volume of a ~~sphere~~ ball of radius $\sqrt{U}$ is on its sphere.



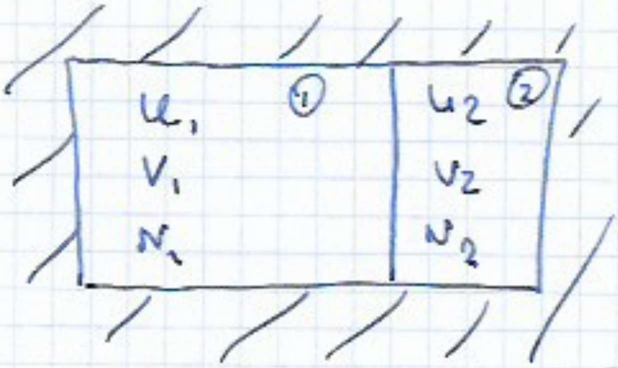
Macroscopic properties of a system are determined by a surface of constant internal energy U. This principle also holds for interacting systems.

holographic principle

§4. SUBSYSTEMS IN THERMAL EQUILIBRIUM

We consider an isolated system, i.e. microcanonical ensemble with fixed U, V, and N.

There is a partition which splits the system into two parts

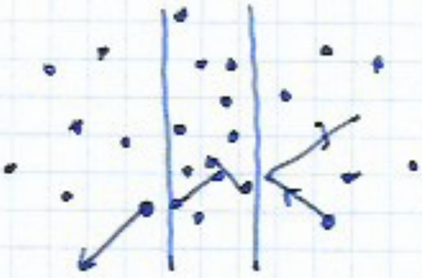


$U = U_1 + U_2$
$V = V_1 + V_2$
$N = N_1 + N_2$

Assume that V_1 = const., V_2 = const.
N_1 = const., N_2 = const.

but the partition can exchange energy between one and two

partition/wall



microscopically

thermal contact
thermal interaction

U_1 and U_2 are random/fluctuating variables such that

$$U = U_1 + U_2 \quad \text{is fixed}$$

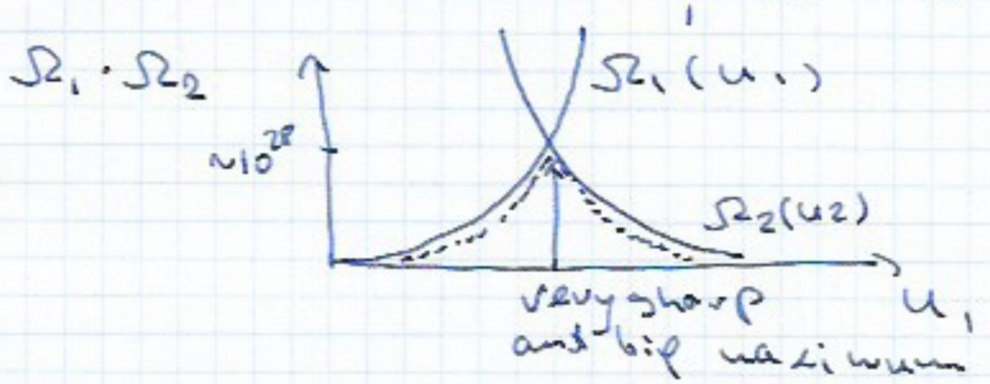
The total number of states is given by

$$\Omega(U,V,N) = \sum_{U_1 \le U} \underbrace{\Omega_1(U_1,V_1,N_1)}_{\#\text{ of states in ①}} \underbrace{\Omega_2(\underbrace{U-U_1}_{U_2},V_2,N_2)}_{\#\text{ of states in ②}}$$

sum over all possible energy U_1 (U_2)

As we discussed Ω as well as Γ are increasing functions of U. From examples we've seen that they are <u>rapidly</u> changing

$$\Gamma \sim U^{3N/2} \qquad \Omega \sim U^{\frac{3N}{2}-1} \qquad N \sim 10^{23}$$



The sum over U_1 is dominated by the largest term. So <u>the most probable</u> distribution of U_1 and U_2 is such that

$\Omega_1(U_1)\,\Omega_2(U-U_1)$ has <u>a maximum</u>

In other words, approaching the thermal equilibrium, a system evolves to the most probable state.

we maximize $\Omega(U, V, N)$

$$d\Omega = \left(\frac{\partial \Omega_1}{\partial U_1}\right)_{V_1,N_1} \Omega_2 \, dU_1 + \left(\frac{\partial \Omega_2}{\partial U_2}\right)_{V_2,N_2} \Omega_1 \, dU_2 = 0$$

with a constrain

$$0 = dU = dU_1 + dU_2 \rightarrow dU_2 = -dU_1$$

Hence, the equilibrium condition is

$$\boxed{\frac{1}{\Omega_1}\left(\frac{\partial \Omega_1}{\partial U_1}\right)_{V_1,N_1} = \frac{1}{\Omega_2}\left(\frac{\partial \Omega_2}{\partial U_2}\right)_{V_2,N_2}}$$

In equilibrium there is a physical quantity that is the same in both subsystem → <u>temperature</u> (?)

We define a <u>Boltzmann entropy</u> (*)

$$\boxed{S = k_B \ln \Omega(U, V, N)}$$

$$\boxed{k_B = 1{,}380\,649 \cdot 10^{-23} \; J \cdot K^{-1}}$$

<u>SI, 2019</u>

Boltzmann constant

(*) In thermodynamics the entropy was <u>a state function</u> ~~of state~~ depending on $U, V, N, \ldots$.
and not on the whole process like a heat Q or a work W, with
Additive, Monotonic, Analytic, Extensive, $\Delta S \geq 0$

Then the equilibrium condition is written as

$$\boxed{\left(\frac{\partial S_1(U_1, V_1, N_1)}{\partial U_1}\right)_{V_1,N_1} = \left(\frac{\partial S_2(U_2, V_2, N_2)}{\partial U_2}\right)_{V_2,N_2}}$$

thermal equilibrium condition means equality of temperatures (zero-th thermodynamic law)

$T_1 = T_2$

where

def

$$\boxed{\frac{1}{T} = \left(\frac{\partial S(U,V,N)}{\partial U}\right)_{V,N}} \qquad \left[\frac{\partial S}{\partial U}\right] = \left[\frac{J \cdot K^{-1}}{J} = \frac{1}{K}\right]$$

is a temperature!(*)

We introduced the entropy

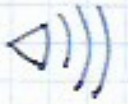
$$\boxed{S = k_B \ln \Omega}$$

as a logarithm of the configuration number for a given macrostate. The more available microstates the larger is the entropy of that macrostate.

(*) In thermodynamics $S = S(U, V, N)$ and

$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$ is an absolute temperature

Some other entropy - information theory



a source of a message $\{m_k\}_{k=1..d}$ with probability $\{p_k\}$

if $p_k = 1 \to$ no information

if $p_k \ll 1 \to$ a lot of information

Df. a measure of information (surprise)

$$I(m_k) := -\log_2 p_k$$

$$0 \leq I(m_k)$$

The average information (information entropy)

$$I = \langle I(m_k) \rangle := \sum_{k=1}^{d} p_k I(m_k) = -\sum_{k=1}^{d} p_k \log_2 p_k$$

I is maximal if $p_k = \frac{1}{d} \ \forall k$

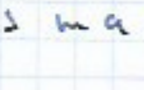
$$0 \leq I \leq \log_2 d = I_{max}$$

In statistical physics all probabilities are equal

$p_k = \frac{1}{\Omega(U,V,N)}$ then

$$S = -k_B \langle \ln p_m \rangle = -k_B \underbrace{\sum_m \frac{1}{\Omega}}_{1} \ln \frac{1}{\Omega} = k_B \ln \Omega(U,V,N)$$

e) Some other properties of information entropy



m_k, p_k

two independent sources

$\{m_k\} \cap \{n_k\} = \emptyset$

n_k, q_k

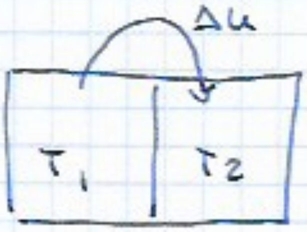
$$p(m_k, n_k) = p_k q_k$$

$$I(m_k, n_k) = -\log_2 p_k q_k = -\log_2 p_k - \log_2 q_k$$

$$\boxed{I = \langle I(m_k, n_l) \rangle = -\sum_{kl} p_k q_l \log_2 p_k q_l = -\sum_k p_k \log_2 p_k - \sum_l q_l \log_2 q_l = I_1 + I_2}$$

info. entropy is additive

What will happen with the entropy when an energy ΔU is transfered from 1 to 2 subsystem?



$T_1 > T_2$ → energy is transfered from ① → ②

$$\Delta S = \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1 N_1} (-\Delta U) + \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2 N_2} \Delta U =$$

$$= \left(-\frac{1}{T_1} + \frac{1}{T_2}\right) \Delta U > 0$$

The energy is transfered from a system with higher temperature to a system with lower temperature until the temperatures are the same – entropy increases!

The final state is the most probable.

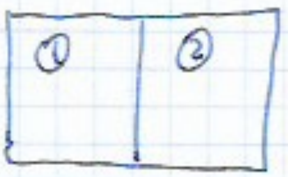
Second law of thermodynamics

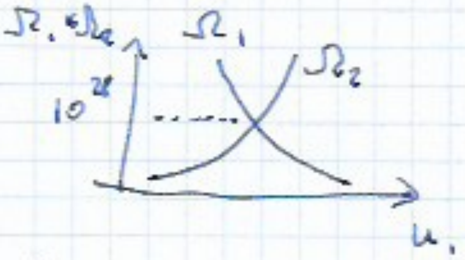
Entropy of an isolated system increases in spontenous processes.

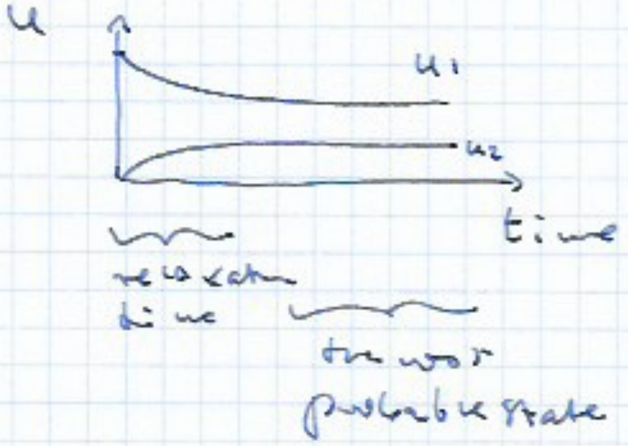
$$\Updownarrow$$

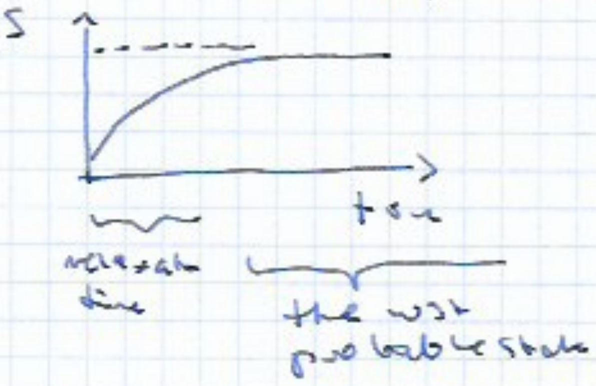
Microscopically – an isolated system spontenously evolves toward a more probable state

In our example

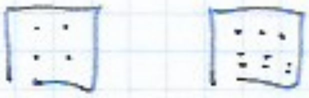






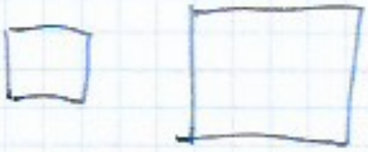


Typical processes ~~th~~ increasing entropy



adding particles

adding energy



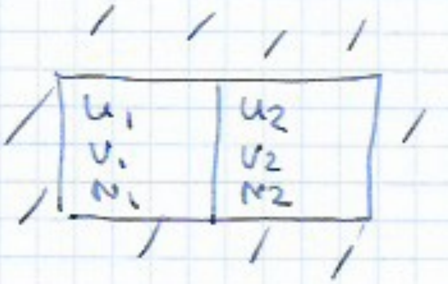
increasing volume

decay of particles

folding a (linear) polimer

A general partition can exchange

1) energy
2) volume
3) particles



thermal interaction

mechanical interaction

chemical interaction

Random variables U_i, V_i, N_i $i=1,2$ with constrains

$$U = U_1 + U_2$$

$$V = V_1 + V_2$$

$$N = N_1 + N_2$$

Entropy $S = k_B \ln \Omega(U, V, N)$

Temperature $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$

Pressure $\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}$

Chemical potential $-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{U,V}$

Equilibrium conditions

$$T_1 = T_2$$

$$P_1 = P_2$$

$$\mu_1 = \mu_2$$