Macrostates and microstates

$V$: volume

$N$: identical particles.

$N \sim 10^{23}$

Thermodynamic limit: $N \to \infty$, $V \to \infty$

but $n = \frac{N}{V} = \text{constant}$

Density.

Extensive properties:

- Increase proportionally to $V$ and $N$.
  - Energy
  - Mass
  - Entropy

Intensive properties: independent of $V$ and $N$.

$n$, $T$, $p$, $c$ (specific heat).
Energy: (consider non-interacting particles).

\[ E = \sum_i n_i \varepsilon_i \]

- one of many possible values of the energy that one particle can have.

\[ N = \sum_i n_i \]

Stat. Mech. can be applied to either quantum or classical systems.

Quantum mechanically \( \varepsilon_i \) are discrete and \( E \) is discrete but \( \Delta E < \varepsilon_i \) then \( E \) usually can be seen as continuous.
Quantum particle in a box with $\psi = 0$ at the boundaries.

1D \[ \epsilon_n = \frac{n^2 \hbar^2}{8 \pi mL^2} \quad n = 1, 2, \ldots \]

3D \[ V = L^3 \quad \epsilon_n = \epsilon_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \quad n = 1, 2, \ldots \]

Microstate: a particular state with a given $\{m_i\}$ and $\{\ell_i\}$ each is identified by $\psi (r_1, \ldots, r_n)$ which is a solution of the Schrödinger eq.
Example: system of 3 spins in H field.

\[ H \uparrow \uparrow + + - \quad E = -\mu H \quad N = 3 \]

Macrostate: \( N, V, \) and \( E \)

are all the microstates compatible with the external parameters.

Example: 3 spins, \( E = -\mu H \)

\[ H \uparrow \uparrow + + - \]
\[ + + + \quad + - + \quad - + + \quad - + + \]

3 microstates constitute the macrostate.
Equal a-priori probability postulate:

At any time $t$, a system is equally likely to be in any of the microstates consistent with its macrostate.

Key issue in Stat Mech is to be able to calculate $\Omega(N, V, E)$ which is the number of microstates for the macrostate with $E, V, N$. 
Statistics and Thermodynamics.

Physical meaning of \( \Omega (N, V, E) \).

Only \( E \) can be exchanged.

\[ A^{(0)} \begin{cases} A_1 & A_2 \\ N_1, V_1, E_1 & N_2, V_2, E_2 \end{cases} \]

\[ \Omega_2 (N_2, V_2, E_2) \]

\[ \Omega_1 (N_1, V_1, E_1) \]

\[ \Omega_0 (N^0, V^0, E^0) = \Omega_1 \Omega_2 \]

\[ E^{(0)} = \bar{E}_1 + \bar{E}_2 = \text{constant} \]

\[ A^{(0)} = A_1 + A_2 \quad \text{(no interaction energy)} \]

\( A_1 \) and \( A_2 \) are separately in equilibrium. We need to find the value of \( \Omega_1 \) and \( \Omega_2 \) when they reach equilibrium with each other.
\[ \Omega (\epsilon^*) = \Omega_1 (\epsilon_1) \Omega_2 (\epsilon_2) = \Omega_1 (\epsilon_1) \Omega_2 (\epsilon^{(0)} - \epsilon_1) \]

\[ = \Omega^{(0)}(\epsilon^{(0)}, \epsilon_1) \]

For what value of $\epsilon_1$, the system $A^0$ reaches equilibrium?

We need to find the value of $\epsilon_1$, that maximizes $\Omega^{(0)}$ so that the system spends all its time in the large number of microstates compatible with $\epsilon^{*}_1$.

$\epsilon^{*}_1$ is the value of $\epsilon_1$, that maximizes $\Omega^{(0)}$. 
Example:
\[ E_0 = 15 \]

\[
\begin{array}{cccccccccccc}
A_1 & A_2 & E_1 & E_2 & \Omega_1(E_1) & \Omega_2(E_2) & \Omega_{12} \\
M_1 & E_1 & m_2 & E_2 & 4 & 11 & 2 & 90 & 80 \\
2 & 4 & 3 & 7 & 5 & 10 & 5 & 26 & 130 \\
5 & 5 & 8 & 8 & 6 & 9 & 10 & 16 & 160 \\
10 & 6 & 14 & 9 & 17 & 8 & 17 & 8 & 136 \\
17 & 7 & 26 & 10 & 18 & 7 & 25 & 3 & 75 \\
25 & 8 & 40 & 11 & & & & & \\
\end{array}
\]

\[ E_1^* = c \]
\[
\frac{\partial \Omega^{(0)}}{\partial E_1} \bigg|_{E_1 = E_1^*} = \frac{\partial \Omega_1(E_1)}{\partial E_1} \bigg|_{E_1 = E_1^*} + \Omega_2(E_2^*),
\]

\[
+ \Omega_1(E_1^*) \frac{\partial \Omega_2(E_2^*)}{\partial E_2} \bigg|_{E_2 = E_2^*} \frac{\partial E_2}{\partial E_1} = 0
\]

\[
E_2 = E^0 - E_1 = 0 \quad \frac{\partial E_2}{\partial E_1} = -1
\]

Then
\[
\frac{\partial \Omega_1(E_1)}{\partial E_1} \bigg|_{E_1 = E_1^*} \Omega_2(E_2^*) = \frac{\partial \Omega_2(E_2^*)}{\partial E_2} \bigg|_{E_2 = E_2^*} \Omega_1(E_1^*)
\]
\[
\frac{1}{\delta_1} \frac{\partial \Omega_1}{\partial \varepsilon_1} \bigg|_{\varepsilon_1 = \varepsilon_1^*} = \frac{1}{\delta_2} \frac{\partial \Omega_2}{\partial \varepsilon_2} \bigg|_{\varepsilon_2 = \varepsilon_2^*}
\]

or
\[
\frac{\partial \ln \Omega_1(\varepsilon_1)}{\partial \varepsilon_1} \bigg|_{\varepsilon_1 = \varepsilon_1^*} = \frac{\partial \ln \Omega_2(\varepsilon_2)}{\partial \varepsilon_2} \bigg|_{\varepsilon_2 = \varepsilon_2^*}
\]

Define
\[
\beta = \frac{\partial \ln \Omega(\varepsilon)}{\partial \varepsilon} \bigg|_{\varepsilon = \varepsilon^*, N, \nu}
\]

Then at equilibrium between \( A' \) and \( A^2 \): \( \beta_1 = \beta_2 \).
Zeroth law of thermodynamics: a common parameter T that characterizes 2 or more systems in thermal equilibrium.

Then we expect that p and T (temperature) will be related.

From thermodynamics we know that

\[ dE = T \, ds - P \, dV + \mu \, dN \]

\[ E = E(s, v, N) \]

Then

\[ \frac{\partial E}{\partial s} \bigg|_{v, N} = T = 0 \left[ \frac{\partial s}{\partial E} \right]_{v, N} = \frac{1}{T} \]
Compare:
\[ \frac{\partial \ln \mathcal{R}}{\partial E} = \beta \]

with
\[ \frac{\partial S}{\partial E} \bigg|_{n, \nu} = \frac{1}{\nu} \]

So
\[ \ln \mathcal{R} \Rightarrow S = C \ln \mathcal{R} \]

and
\[ \frac{1}{\nu} \propto \beta \]

or
\[ \frac{\Delta S}{\Delta (\ln \mathcal{R})} = \frac{1}{\rho \nu} \]

\[ \frac{1}{\nu} = \frac{1}{\rho} \]
Boltzmann noticed this and defined
\[ S = k \ln \Omega(N, V, T) \]  \( \text{(i)} \)

Then
\[ k = \frac{1}{\beta T} \Rightarrow \beta = \frac{1}{kT} \]  \( \text{\( \text{(ii)} \)} \)

(1) determines the absolute value of the entropy \( S \) in terms of the \# of microstates.
We see that if \( S = 0 \), then \( S = 0 \).

\( S = 1 \) single microstate it happens when the system at \( T = 0 \) is in its ground state.

Third law of thermodynamics: if \( T \to 0 \) then \( S \to 0 \).

(or \( S \) very small in case of degenerate ground state).

Second law: the energy available in the universe becomes less and less available to be transformed into work = \( S \) measures disorder or chaos in a system.
S always increases or stays the same.

Then the largest $S$ is the most important the system is and the least information we have about it.

More relations shift.

Assume that the wall between $A_1$ and $A_2$ can move. Then $V_1 + V_2 = V_0 = \text{constant.}$

Find maximum of $S$ with respect to the volume $V_1$, then you will find that
The maximum occurs when

\[ \frac{\partial \mu}{\partial V_1} \bigg|_{n_1, \epsilon, \nu_1 = \nu_1^*} = \frac{\partial \mu}{\partial V_2} \bigg|_{n_2, \epsilon, \nu_2 = \nu_2^*} \]

Define

\[ \gamma = \frac{\partial \mu}{\partial V} \bigg|_{n_1, \epsilon, \nu = \nu^*} \]

then \( \gamma_1 = \gamma_2 \) in equilibrium.
If the barrier now allows particles to go through we have \( N_1 + N_2 = N^* = \text{constant} \) and \( \Delta S^* \) will have a maximum at \( N_1 = N_1^* \).

\[
\frac{\partial \ln \mathcal{Z}}{\partial N_1} \bigg|_{v_1, E, N_1 = N_1^*} = \frac{\partial \ln \mathcal{Z}}{\partial N_2} \bigg|_{v_2, E_2, N_2 = N_2^*}
\]

Define

\[
\xi = \frac{\partial \ln \mathcal{Z}}{\partial N} \bigg|_{v_1, E, N = N^*}
\]

\( \xi_1 = \xi_2 \) at equilibrium.