# Thermostatistics - the basics -

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[1] These slides are modified from the original version of Prof. Damián Scherlis.

- The statistical sampling
- Probability density and the Boltzmann factor
- The partition function
- Molecular Dynamics
- Monte Carlo

Establish a connection between macroscopic properties (e.g. entropy, heat capacity, surface tension, etc.) and microscopic (e.g. molecular geometry, intermolecular interactions, molecular mass, etc.)

# Macrostate - Microstate

### Macroscopic state or Macrostate

The state of the system is defined by the values adopted by macroscopic variables called state functions that are related through a state equation. The state of a pure substance in equilibrium is defined by three variables, e.g. pressure, temperature and number of particles.
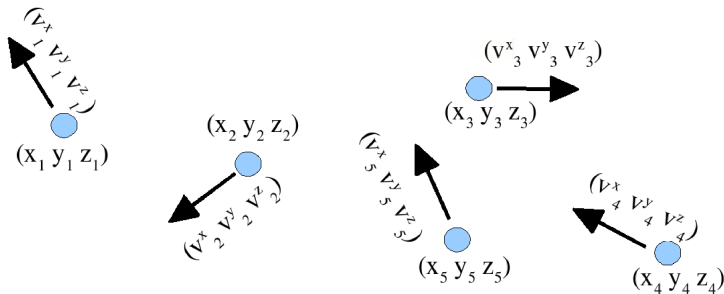
### Microscopic state or Microstate

To specify a mictrostate in the context of classical mechanics we need the coordinates and velocity of all the particles in the system, whereas in quantum mechanics we need the wavefunction of the system.

Is the set of all the possible configurations of the system

- In an *N* particle system, each configuration is determined by 3*N* spacial coordinates and 3*N* velocity components.

The instantaneous value of a given property $A(t)$ in an $N$ particle system is a function of the positions and momentum of the $N$ particles at instant $t$

$$A(\mathbf{p}^N(t), \mathbf{r}^N(t)) \equiv A(\mathbf{p_1}, \mathbf{p_2}, \cdots, \mathbf{r_1}, \mathbf{r_2}, \cdots, t)$$

The experimental measurement comes from a time average:

$$\bar{A} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau A(\mathbf{p}^N(t), \mathbf{r}^N(t)) dt$$

Alternatively, *A* can be thought of as an average over all the possible configurations. If we call $\rho(\mathbf{p}^N, \mathbf{r}^N)$ to the probability of finding a configuration with $\mathbf{p}^N$ moments and $\mathbf{r}^N$ positions then:

$$\langle A \rangle = \sum_{\mathbf{p}}^{N} \sum_{\mathbf{r}}^{N} A(\mathbf{p}^N, \mathbf{r}^N) \rho(\mathbf{p}^N, \mathbf{r}^N)$$

Ergodic Hypothesis:

$$\lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} A(\mathbf{p}^N(t), \mathbf{r}^N(t)) dt = \sum_{\mathbf{p}} \sum_{\mathbf{r}} A(\mathbf{p}^N, \mathbf{r}^N) \rho(\mathbf{p}^N, \mathbf{r}^N)$$

# The probability density

Lets consider a system described by the following variables:

$N$: number of particles in the system
$\langle E \rangle$: average value of the total energy
$n_i$: number of particles in the $i$ state
$E_i$: energy of the $i$ state

Then the following equalities are verified:

$\sum_i n_i = N$
$\sum_i P_i E_i = \langle E \rangle$    where $P_i = \frac{n_i}{N}$

The configuration of the system is determined by the $n_i$ values:
$\{n_1, n_2, \cdots, n_N\}$

A given configuration can be reached in $W$ different ways.
For example:

- $\{N, 0, 0, ...\} \rightarrow W = 1$
- $\{N - 1, 1, 0, ...\} \rightarrow W = N$
- $\{N - 2, 2, 0, ...\} \rightarrow W = \frac{1}{2}N(N - 1)$

In general $W = \frac{N!}{n_1!n_2!n_3!...}$    (**Exercise:** probe it)

The most probable distribution is the one that maximizes $W$ (or $\ln(W)$) considering the following restrictions:

- $\sum_i n_i = N$
- $\sum_i P_i E_i = \langle E \rangle$

## The probability density

These restrictions can be introduced through the Lagrange multiplier method:

$$\frac{\partial}{\partial n_i} \left[ \ln W - \alpha \left( \sum n_i - N \right) - \beta \left( \sum n_i E_i - \langle E \rangle \right) \right] = 0$$

$$\frac{\partial \ln W}{\partial n_i} - \alpha - \beta E_i = 0$$

with $\ln W = \ln N! - \ln[n_1! n_2! n_3!...]$

For $x$ sufficiently big, the following equality is verified:
$\ln x! = x \ln x - x$
Hence,

$$\ln W \approx N \ln N - N - \sum_i n_i \ln n_i + \sum_i n_i = N \ln N - \sum_i n_i \ln n_i$$

$$\frac{\partial \ln W}{\partial n_i} = -\ln n_i - 1 \Rightarrow -\ln n_i - \alpha - \beta E_i = 0 \Rightarrow n_i = e^{-\alpha - \beta E_i}$$

$n_i = e^{-\alpha} e^{-\beta E_i}$ represents the most likely pupulation of the state with $E_i$ energy.

Si $\sum_i n_i = N = \sum e^{-\alpha} e^{-\beta E_i}, \Rightarrow e^{-\alpha} = \frac{N}{\sum e^{-\beta E_i}} \Rightarrow \frac{n_i}{N} = \frac{e^{-\beta E_i}}{\sum e^{-\beta E_j}}$

Using thermodynamical argument it can e established that $\beta = 1/kT$ (**Exercise:** prove it!)

Boltzmann distribution: probability density at constant $N, V, T$

$$P(E_i) = \frac{n_i}{N} = \frac{e^{-E_i/kT}}{\sum_j e^{-E_j/kT}}$$

- $e^{-E_i/kT}$: Boltzmann Factor $\rightarrow E_i$ vs $kT$
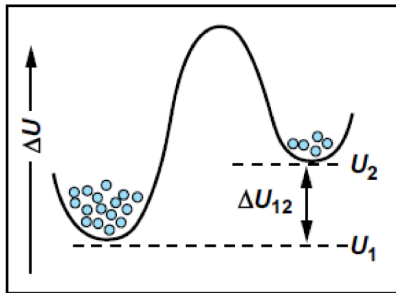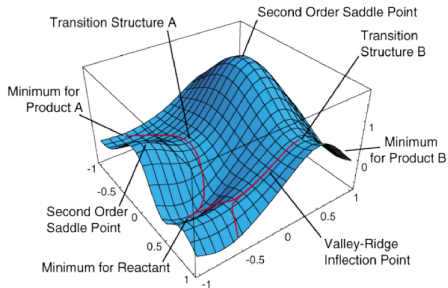- $\sum_j e^{-E_j/kT}$: Partition Function, $Q$

**Important postulate**

A thermodynamic state at equilibrium is defined by a distribution that maximizes the entropy of the system defined as:

$$S = -k \sum_i P_i ln[P_i]$$

**Exercise:** Prove that by maximizing entropy one obtains the same result as we did for $W$. What is the relation between $S$ and $W$?

The lower the energy of a state the higher the probability of visiting that state

$$Q = \sum_j e^{-E_j/kT}$$

This function contains all the thermodynamic information of a system in equilibrium. For example the total energy of the system can be calculated as the sum of the population of each state multiplied by its energy:

$$E = \sum_i E_i P(E_i) = \sum_i E_i \frac{e^{-E_i/kT}}{Q} = \frac{kT^2}{Q}\frac{\partial Q}{\partial T}$$

From $Q$ we can derive the different state functions that describe the system:

$$\textbf{Energy}\ \ E = \frac{kT^2}{Q}\frac{\partial Q}{\partial T}$$

$$\textbf{Entropy}\ \ S = k\ln W = E/T + k\ln Q$$

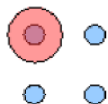$$\textbf{Free Energy}\ \ A = E - TS = -kT\ln Q$$

In the classical limit, the state distribution tends to a continuous and the sum can be replaced by an integral over all the positions and momenta of the $N$ particles:

$$\langle A \rangle = \int d\mathbf{p}^N d\mathbf{r}^N A(\mathbf{p}^N, \mathbf{r}^N) \rho(\mathbf{p}^N, \mathbf{r}^N)$$
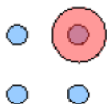
At constant $N$, $V$ and $T$, the probability density $\rho(\mathbf{p}^N, \mathbf{r}^N)$ is the Boltzmann distribution expressed in the continuum:

$$\rho(\mathbf{p}^N, \mathbf{r}^N) = \frac{e^{-E(\mathbf{p}^N, \mathbf{r}^N)/kT}}{\int d\mathbf{p}^N d\mathbf{r}^N e^{-E(\mathbf{p}^N, \mathbf{r}^N)/kT}}$$

T1      T2      T3      T4      H

$$\mathbf{E(T1) = E(T2) = E(T3) = E(T4) = E(T) \neq E(H)}$$

$$P(T) = \frac{4 \times e^{-E(T)/kT}}{4 \times e^{-E(T)/kT} + e^{-E(H)/kT}}$$

$$P(H) = \frac{e^{-E(H)/kT}}{4 \times e^{-E(T)/kT} + e^{-E(H)/kT}}$$

$$\langle E \rangle = \sum_i E(i)P(i) = \frac{4 \times E(T) \times e^{-E(T)/kT} + E(H) \times e^{-E(H)/kT}}{4 \times e^{-E(T)/kT} + e^{-E(H)/kT}}$$

## Ergodic Hypothesis

$$\lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau A(\mathbf{p}^N(t), \mathbf{r}^N(t)) dt = \int d\mathbf{p}^N d\mathbf{r}^N A(\mathbf{p}^N, \mathbf{r}^N) \rho(\mathbf{p}^N, \mathbf{r}^N)$$

### Two approximations to the problem:

- $\bar{A} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau A(\mathbf{p}^N(t), \mathbf{r}^N(t)) dt$   Molecular Dynamics

- $\langle A \rangle = \int d\mathbf{p}^N d\mathbf{r}^N A(\mathbf{p}^N, \mathbf{r}^N) \rho(\mathbf{p}^N, \mathbf{r}^N)$   Monte Carlo

Molecular dynamics consists on evolving in time the positions of the particles according to the forces

$$\mathbf{F}_I = -\frac{\partial E(\mathbf{R}_I)}{\partial \mathbf{R}_I} = m\mathbf{a}$$

The positions can be evolved according to their Taylor expansion in $t \pm \Delta t$:

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \Delta t \mathbf{v}(t) + \frac{1}{2}\Delta t^2 \mathbf{a}(t) + \cdots$$

$$\mathbf{r}(t - \Delta t) = \mathbf{r}(t) - \Delta t \mathbf{v}(t) + \frac{1}{2}\Delta t^2 \mathbf{a}(t) + \cdots$$

Adding these expressions we obtain the Verlet algoritm that allows to calculate the coordinates of the particles step by step from the acceleration $\mathbf{a}$:

$$\mathbf{r}(t + \Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \Delta t) + \frac{1}{2}\Delta t^2 \mathbf{a}(t)$$

# Temperature and Ensambles

$E$, $V$ and $N$ constant: microcanonical ensemble.

The instantaneous temperature $T(t)$ depends on the kinetic energy of the particles in the system:

$$E_c = \frac{3}{2}NkT = \frac{1}{2}\sum_{i=1}^{N} m_i \langle v_i^2 \rangle \Rightarrow T(t) = \frac{1}{3Nk}\sum_{i=1}^{N} m_i \langle v_i(t)^2 \rangle$$

If instead of the total energy we fix the temperature (this is usually achieved in molecular dynamics with an algorithm called thermostat that modifies the total energy but produces trajectories at constant $T$). Hence, this leads to a $T$, $V$ and $N$ ensamble called canonical ensemble.

Another important ensamble is the one with $T$, $P$ y $N$ constant: isothermic—isobaric ensamble

An alternative approach to the time domain propagation is to evaluate $\langle A \rangle$ as an average over all the microstates of the system:

$$\langle A \rangle = \frac{\int d\mathbf{p}^N d\mathbf{r}^N A(\mathbf{r}^N) e^{-E(\mathbf{p}^N, \mathbf{r}^N)/kT}}{\int d\mathbf{p}^N d\mathbf{r}^N e^{-E(\mathbf{p}^N, \mathbf{r}^N)/kT}}$$
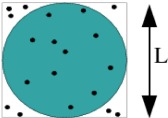
Now, if we separate the kinetic and potential (**Exercise:** when is this possible?):

$$E(\mathbf{p}^N, \mathbf{r}^N) = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m} + E(\mathbf{r}^N)$$

$$\langle A \rangle = \frac{\int d\mathbf{p}^N e^{-E(\mathbf{p}^N)/kT} \int d\mathbf{r}^N A(\mathbf{r}^N) e^{-E(\mathbf{r}^N)/kT}}{\int d\mathbf{p}^N e^{-E(\mathbf{p}^N)/kT} \int d\mathbf{r}^N e^{-E(\mathbf{r}^N)/kT}} = \frac{\int d\mathbf{r}^N A(\mathbf{r}^N) e^{-E(\mathbf{r}^N)/kT}}{\int d\mathbf{r}^N e^{-E(\mathbf{r}^N)/kT}}$$

$$A_{circulo} = \frac{n_{dentro}}{n_{dentro} + n_{fuera}} \times L^2$$



$$\langle A \rangle = \frac{\int d\mathbf{r}^N A(\mathbf{r}^N) e^{-E(\mathbf{r}^N)/kT}}{\int d\mathbf{r}^N e^{-E(\mathbf{r}^N)/kT}}$$

$$\approx \frac{E(\mathbf{r_1}^N) e^{-E(\mathbf{r_1}^N)/kT} + E(\mathbf{r_2}^N) e^{-E(\mathbf{r_2}^N)/kT} + E(\mathbf{r_3}^N) e^{-E(\mathbf{r_3}^N)/kT} + \cdots}{e^{-E(\mathbf{r_1}^N)/kT} + e^{-E(\mathbf{r_2}^N)/kT} + e^{-E(\mathbf{r_3}^N)/kT} + \cdots}$$

where $\mathbf{r_i}^N$ represents each one of the randomly generated configurations. For a system of $N$ particles with $m$ points in each direction the number of terms is $m^{3N}$

**The random selection of $\mathbf{r_i}^N$ is very inefficient because — in general — most of the terms contribute with a negligible Boltzmann factor**

The goal is to generate the configurations $\mathbf{r_i}^N$ whose probabilities are proportional to $e^{-E(\mathbf{r_i}^N)/kT}$

Metropolis Algorithm:

1) Evaluation of $E(\mathbf{r}_i^N)$, the energy of the $i$ configuration

2) Generation of $\mathbf{r}_{i+1}^N$ by a random displacement of a particle

3) Evaluation of $E(\mathbf{r}_{i+1}^N)$

- $E(\mathbf{r}_{i+1}^N) \leq E(\mathbf{r}_i^N) \Rightarrow$ the new configuration is accepted
- $E(\mathbf{r}_{i+1}^N) > E(\mathbf{r}_i^N) \Rightarrow$ the new configuration is accepted only if $e^{-\Delta E/kT} \geq rand(0,1)$