Chapter 2:

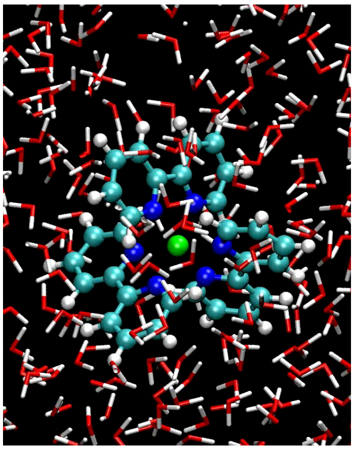
Statistical Mechanics in a Nutshell

Checklist

- Thermodynamic ensembles
  - microcanonical, canonical, isobaric-isothermal, grand-canonical ensembles
- Microstate
- Statistical mechanics definitions of entropy, free energy
- fundamental postulates of statistical mechanics
- Boltzmann distribution
- Maxwell-Boltzmann distribution
- Partition function
- Ensemble averages
- microscopic definitions of temperature, pressure
- Phase space – phase space integral
- Configuration space – configuration space integral
- ergodicity and ergodic theorem

Link between microscopic <-> macroscopic systems

Ru-tris(bipy) in water



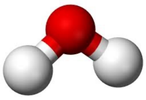
10^2-10^5 atoms

Macroscopic sample

Avogadro number 10^{23} of particles

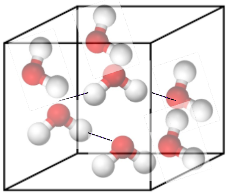
Link between microscopic <-> macroscopic systems

Single molecule



1 H_2O, gas phase

simulation system



macroscopic system

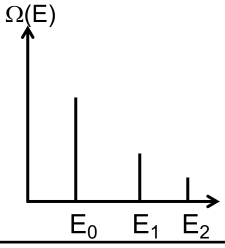
microcanonical ens ⟷ N, V, E

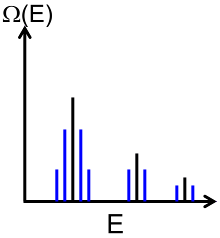
canonical ensemble ⟷ N, V, T

Isobaric-isothermal ⟷ N, p, T

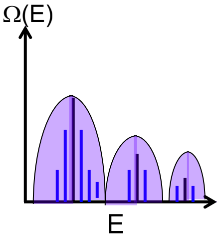
grand canonical ens ⟷ μ, V, T

Many possible microscopic realizations
Every realisation: microstate
All microstates: ensemble





quasi continuous spectrum
-> classical SM



Probability distribution

What is the probability of finding the system in a certain microstate for a given ensemble?

What is the most likely energy distribution?

How can we calculate ensemble properties?

Quiz II: Throwing Dice

1) You are throwing two (ideal) dice. Which total sum is the most likely outcome?

Statistical Mechanics definition of entropy

⇒Every realization corresponds to one microstate of the system
⇒There is a total of 36 microstates
⇒ the number of microstates associated with a given outcome determines its probability!

⇒ The number of possible realization/microstates is a crucial property!!
⇒ Measure for the number of microstates Ω

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

Entropy
k: Boltzmann constant
1.38×10^{-23} J/K

⇒Measure for the number of microstates
⇒measure for probability/uncertainty!

SM definition of entropy

⇒Every realisation is one microstate
⇒There is a total of 36 microstates
⇒ the number of microstates associated with a given outcome determines its probability!

⇒ The number of possible realisation/microstates is a decisive property!!
⇒ Measure for the number of microstates Ω

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

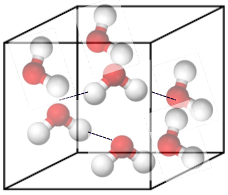
Entropy
k: Boltzmann constant
1.38×10^{-23} J/K

⇒Measure for the number of microstates
⇒measure for probability/uncertainty!

Corresponding definition of the free energy

$\boxed{F = U - TS = U - kT \ln \Omega = - kT \ln Q}$ Helmholtz free energy

Fundamental Postulates of SM



1^{st} postulate of SM

The result of a measurement of an observable in a macroscopic system is the ensemble average of such an observable.

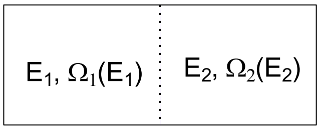
2^{nd} postulate of SM

For an isolated macroscopic system with a constant total energy, particle number and volume (i.e. an isolated system) every microstate is equally probable.

2^{nd} law of thermodynamics:
- nonequilibrium systems always evolve towards the state with highest entropy: A -> B $\Delta S_{AB} > 0$
- In an equilibrium system S is constant and has reached a maximum value

Entropy is a measure of the number of microstates Ω and the probability is given by Ω_1/Ω_{tot} => entropy is a measure of probability => 2^{nd} law of thermodynamics states that a process always occurs in the direction of the more likely state, i.e. the one with the highest entropy

What is the most probable energy distribution?



E = constant = $E_1 + E_2$

What is the most likely energy partitioning E_1,E_2?

$\Omega(E) = \Omega(E_1,E_2) = \Omega(E_1,E-E_1) = \Omega_1(E_1)\,\Omega_2(E-E_1)$
$\ln \Omega(E,E-E_1) = \ln \Omega_1(E_1) + \ln \Omega_2(E-E_1)$

The number of total microstates is maximal for:

$$\frac{\partial \ln \Omega\left(E_1, E-E_1\right)}{\partial E_1} = 0 \qquad \frac{\partial \ln \Omega_1\left(E_1\right)}{\partial E_1} + \frac{\partial \ln \Omega_2\left(E-E_1\right)}{\partial E_1} = 0$$

$$E_2 = E - E_1$$
$$\partial E_1 = -\partial E_2$$

$$\frac{\partial \ln \Omega_1\left(E_1\right)}{\partial E_1} = \frac{\partial \ln \Omega_2\left(E_2\right)}{\partial E_2} \qquad \boxed{\beta = \frac{\partial \ln \Omega}{\partial E}}$$

$$\beta_1 = \beta_2$$

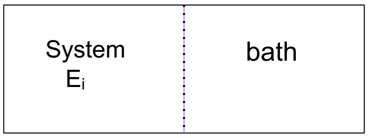
$$S = k_B \ln \Omega\left(N,V,E\right)$$

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T} = k_B \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} = k_B \beta$$

$$\boxed{\beta = \frac{1}{k_B T}}$$ Inverse temperature

For the most probable partitioning $T_1 = T_2$ => system is in thermal equilibrium!

What is the probability distribution in the canonical ensemble?



E= const = $E_i + E_B \approx E_B$

Probability $p(E_i)$?

$$p_i\left(E_i\right) = \frac{\Omega_B\left(E-E_i\right)}{\sum_j \Omega_B\left(E-E_j\right)}$$

Taylor expansion of $\ln\Omega_B(E-E_i)$ around E:

$$\ln\Omega_B\left(E-E_i\right) = \ln\Omega_B\left(E\right) - E_i\frac{\partial \ln\Omega_B\left(E\right)}{\partial E} + \vartheta\left(E_i^2\right)$$

$$\frac{\partial \ln\Omega_B\left(E\right)}{\partial E} = \beta = \frac{1}{k_B T}$$

$$\ln\Omega_B\left(E-E_i\right) = \ln\Omega_B\left(E\right) - E_i / k_B T$$

$$\Omega_B\left(E-E_i\right) = \Omega_B\left(E\right)e^{-E_i/k_B T}$$

$$p_i\left(E_i\right) = \frac{\Omega_B\left(E\right)e^{-E_i/k_B T}}{\Omega_B\left(E\right)\sum_j e^{-E_j/k_B T}}$$

$$\boxed{p_i\left(E_i\right) = \frac{e^{-E_i/k_B T}}{\sum_j e^{-E_j/k_B T}}}$$ Boltzmann Distribution

$$\boxed{Q = \sum_j e^{-E_j/k_B T}}$$ Canonical Partition Function

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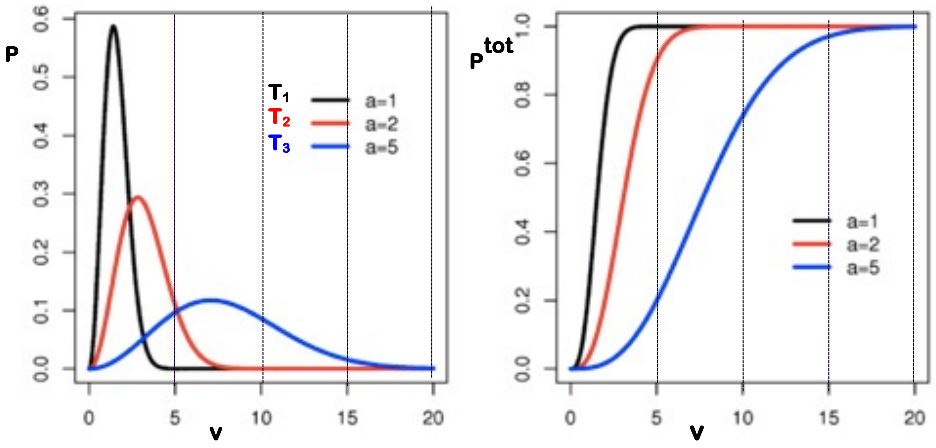
Quiz III: Boltzmann Distribution

1) The Boltzmann distribution refers to a system of classical particles. What are the corresponding distributions for a system of quantum particles with a) fermions or b) bosons?

2) What is the probability $P\left(\vec{p}\right)$ to find a particle with momentum $\vec{p}$ in a system of classical particles (no quantum effects) with only kinetic energy (E_{pot} = 0) at temperature T (canonical ensemble)? $\beta = 1/k_B T$
Help:

$$\boxed{\int_{-\infty}^{+\infty} e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}}$$

Maxwell-Boltzmann Distribution



Probability distribution in different ensembles

Microcanonical ensemble (NVE)

$$\boxed{p_i\left(E_i\right) = const}$$

Canonical ensemble (NVT)

$$\boxed{p_i\left(E_i\right) = \frac{e^{-E_i/k_B T}}{\sum_j e^{-E_j/k_B T}}}$$

Isobaric-isothermal ensemble (NpT)

$$\boxed{p_i\left(E_i\right) = \frac{e^{-H_i/k_B T}}{\sum_j e^{-H_j/k_B T}}}$$

Enthalpy H

$$\boxed{H = E + pV}$$

Grand potential Z

$$\boxed{Z = E - \mu N}$$

Grand canonical ensemble (μVT)

$$\boxed{p_i\left(E_i\right) = \frac{e^{-Z_i/k_B T}}{\sum_j e^{-Z_j/k_B T}}}$$

$$\boxed{\mu = \left(\frac{\partial E}{\partial N}\right)}$$

Simulation results from one ensemble can be converted to another!

Evaluation of Ensemble Properties

Properties of thermodynamic ensembles:

$$\boxed{\langle A\rangle = \sum_{i=1}^{N_{tot}} w_i A_i}$$

w_i: probability of finding system in configuration i
$w_i = N_i/N_{tot}$

All possible states of a classical system are defined by $(\mathbf{r}^N, \mathbf{p}^N)$ with $\mathbf{r}^N$: $\mathbf{r}_1 \ldots \mathbf{r}_N$, $\mathbf{p}^N$: $\mathbf{p}_1..\mathbf{p}_N$, the space spanned by all possible $(\mathbf{r}^N, \mathbf{p}^N)$ is called the phase space.

[Quantum analogon: Hilbert space]

Ensembles properties have to be evaluated as integrals over all possible states
=> evaluate 6N dimensional phase space integrals

$$\boxed{\langle A\rangle = \int \ldots \int d\vec{r}^{\,N}\, d\vec{p}^{\,N}\, w(\vec{r}^{\,N}, \vec{p}^{\,N}) A(\vec{r}^{\,N}, \vec{p}^{\,N})}$$

S is given by the accessed phase space volume!

For the **canonical** ((NVT) ensemble:

$$\boxed{w\left(\vec{r}^{\,N}, \vec{p}^{\,N}\right) = \frac{e^{-E_{tot}\left(\vec{r}^{\,N}, \vec{p}^{\,N}\right)/k_B T}}{\int \ldots \int d\vec{r}^{\,N}\, d\vec{p}^{\,N}\, e^{-E_{tot}\left(\vec{r}^{\,N}, \vec{p}^{\,N}\right)/k_B T}}}$$

Boltzmann factor

← Partition function

Phase Space and Configuration Space

Canonical ensemble average:

$$\boxed{\langle A\rangle = \frac{\int \ldots \int d\vec{r}^{\,N}\, d\vec{p}^{\,N}\, A\left(\vec{r}^{\,N}, \vec{p}^{\,N}\right) e^{-E_{tot}\left(\vec{r}^{\,N}, \vec{p}^{\,N}\right)/k_B T}}{\int \ldots \int d\vec{r}^{\,N}\, d\vec{p}^{\,N}\, e^{-E_{tot}\left(\vec{r}^{\,N}, \vec{p}^{\,N}\right)/k_B T}}}$$

6N dimensional integral

$$\boxed{E_{tot}\left(\vec{r}^{\,N}, \vec{p}^{\,N}\right) = E_{pot}\left(\vec{r}^{\,N}\right) + E_{kin}\left(\vec{p}^{\,N}\right)}$$

(conservative forces)

Momentum part simple quadratic dependence on *p*
⇒ analytic evaluation possible (remember: Maxwell-Boltzmann distribution)

Potential energy part more complex => evaluated numerically via computer simulations
=> 3N dimensional configurational space integral

$$\boxed{\langle A\rangle = \frac{\int \ldots \int d\vec{r}^{\,N}\, A\left(\vec{r}^{\,N}\right) e^{-E_{pot}\left(\vec{r}^{\,N}\right)/k_B T}}{\int \ldots \int d\vec{r}^{\,N}\, e^{-E_{pot}\left(\vec{r}^{\,N}\right)/k_B T}}}$$

QM analogon:

$$\boxed{\langle A\rangle = \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\int \ldots \int d\vec{r}^{\,N}\, \Psi^* A \Psi}{\int \ldots \int d\vec{r}^{\,N}\, \Psi^* \Psi}}$$

Sampling thermodynamic ensembles

$$\boxed{\langle A\rangle = \frac{\int\ldots\int d\vec{r}^{\,N}\, d\vec{p}^{\,N}\, A\left(\vec{r}^{\,N},\vec{p}^{\,N}\right) e^{-E_{tot}\left(\vec{r}^{\,N},\vec{p}^{\,N}\right)/k_BT}}{\int\ldots\int d\vec{r}^{\,N}\, d\vec{p}^{\,N}\, e^{-E_{tot}\left(\vec{r}^{\,N},\vec{p}^{\,N}\right)/k_BT}}} \qquad \boxed{\langle A\rangle = \sum_{i=1}^{N_{tot}} w_i A_i}$$

Monte Carlo simulations: stochastic sampling of configurational space

Molecular dynamics simulations: time average

Ergodicity:
a dynamical system that has the same behavior averaged over space as averaged over time

All molecular dynamics simulations are based on the ergodic hypothesis:

$$\boxed{\langle A\rangle_{ensemble} = \langle A\rangle_{time}}$$

Assumes that for a sufficiently long time trajectory the system visits all the configurations that are accessible at a given temperature
Not necessarily true!

Microscopic Definitions of T and p

Temperature

$$\boxed{E_{kin} = \frac{1}{2}\sum_I M_I v_I^2} \qquad \boxed{T = \frac{2}{3}\frac{E_{kin}}{N^{DOF} k_B}}$$

N^{DOF}: number of degrees of freedom (3N)
k_B: Boltzmann constant

Pressure

$$\boxed{p = \frac{Nk_BT}{V} + \frac{1}{3V}\sum_i \vec{r}_i \cdot \vec{f}_i}$$

Ideal gas part

virial

Checklist

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- Microstate
- Stat.mech. definitions of entropy, free energy
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- Partition function
- microscopic definitions of temperature, pressure
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- ergodicity and ergodic theorem