Statistical Thermodynamics

Basic principles and applications

From microscopic interactions to macroscopic quantities.

http://www.biochem.oulu.fi/Biocomputing/juffer/Teaching/Biocomputing/

Thermodynamics

First Law of Thermodynamics: The energy *U* of an isolated system is constant.

$$dU = dq + dw$$

$$\Delta U = \Delta w + \Delta q$$

Amount of heat supplied to the system.

$$dq = C_V dT$$

At constant V

$$dq = C_p dT$$

At constant p

Amount of work done on the system, e.g:

$$dw = -p dV$$

Reversible *pV*-work

Mechanical work

Thermodynamics

Types of mechanical work

$p\,dV$: Change of volume (dV)

$\gamma\, d\sigma$: Change of surface area $(d\sigma)$

$f\,dl$: Change of length (dl)

$\phi\, dq$: Change of charge (dq)

γ : Surface tension

l : Length

ϕ : Electrostatic potential

Thermodynamics

The temperature *T* of a system of *N* particles is a quantity related to the averaged kinetic energy of the disordered motion of the particle in the C-frame of reference.

$$T \propto E_{k,ave} = \frac{1}{N}\sum_i \frac{1}{2} m_i v_i^2$$

Mass of particle *i*

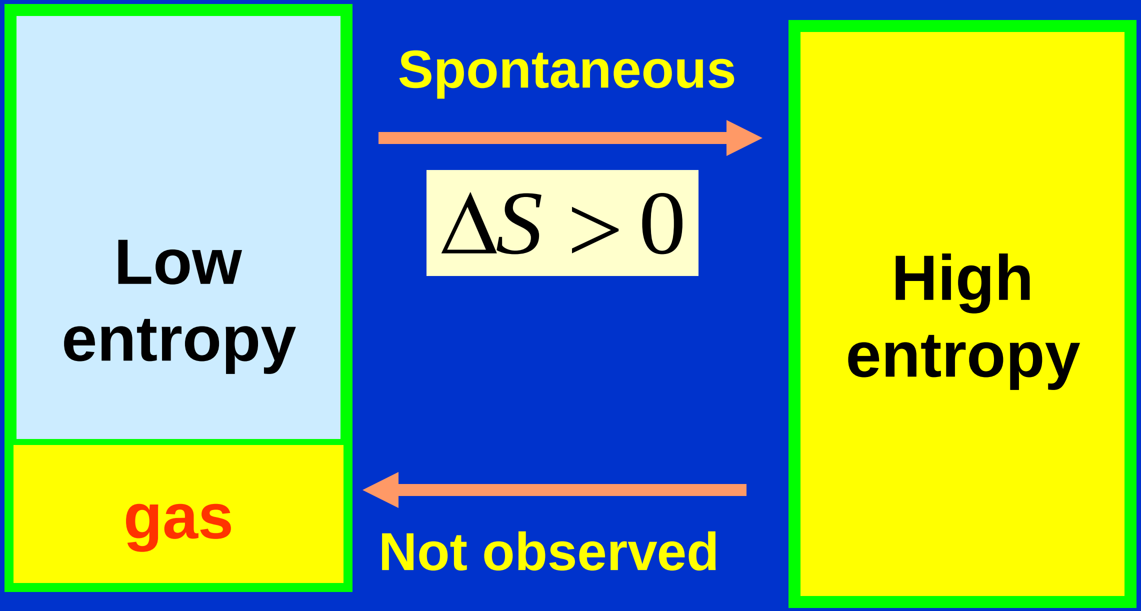
Velocity of particle *i*

Thermal equilibrium:

Average kinetic energy is the same in all regions of the system

Thermodynamics

Second Law of Thermodynamics: The entropy *S* of an isolated system increases during any spontaneous change.



Low entropy

gas

Spontaneous

$$\Delta S > 0$$

Not observed

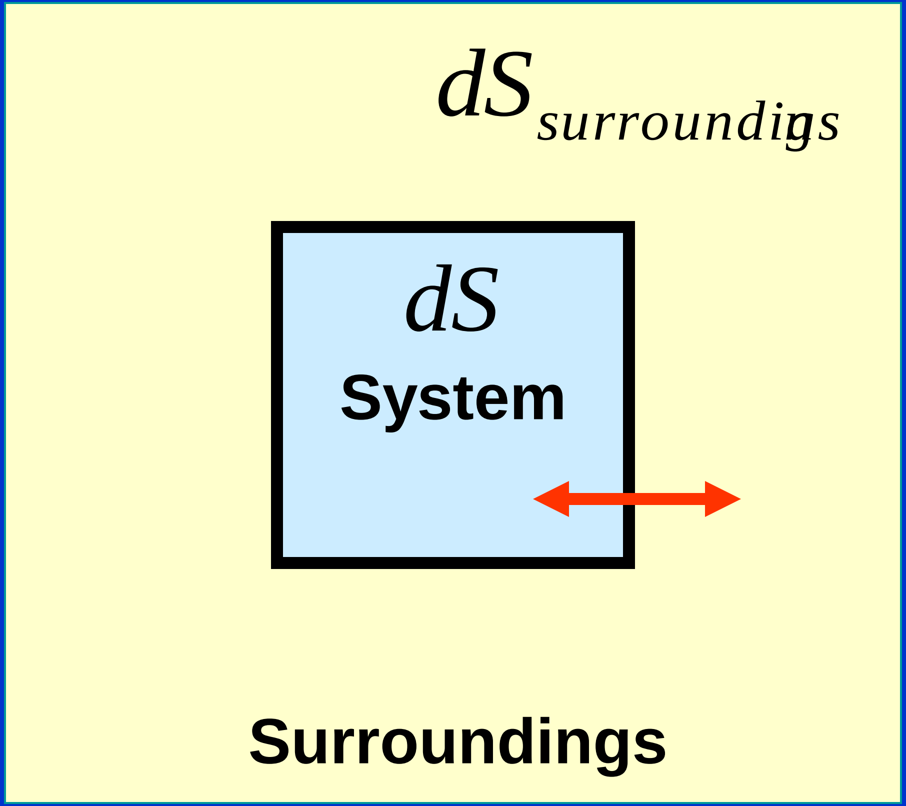
High entropy

Thermodynamics

- Only irreversible processes generate entropy.
- The entropy change of reversible process is exactly zero.
- Most basic irreversible process is the generation of heat:

$$dS = \frac{dq}{T}$$

Thermodynamics



$dS_{surroundigs}$

dS

System

Surroundings

$$dS_{universe} = dS + dS_{surroundigs}$$

$$dS_{universe} \geq 0$$

Heat: $\frac{dq_{surroundigs}}{T}$

$$dS_{universe} = 0$$

For an equilibrium process

System + Surroundings = Universe

The universe seeks higher entropy

Overall entropy production

Thermodynamics

Concentrate on the system:

$$dS - \frac{dq}{T} \geq 0$$

dq : heat supplied to the system
dS : Change of entropy of system due to internal processes.

At Constant *V*
no *pV*-work
dw=0

$$dU = dq$$
$$dS - \frac{dU}{T} \geq 0$$
$$dU - TdS \leq 0$$
$$dA \leq 0$$

At constant pressure
No non-*pV* work
dp=0

$$dq = dH$$
$$dS - \frac{dH}{T} \geq 0$$
$$dH - TdS \leq 0$$
$$dG \leq 0$$

$$\begin{aligned} H &= U + pV \\ dH &= dU + pdV + Vdp \\ &= dq - pdV + pdV + Vdp \\ &= dq + Vdp \end{aligned}$$

$$dU = dq + dw$$

Thermodynamics

$A = U - TS$ Helmholtz free energy

$G = H - TS$ Gibbs free energy

$$\Delta G = \Delta H - T\Delta S$$

$$-\frac{\Delta G}{T} = -\frac{\Delta H}{T} + \Delta S$$

ΔS : Entropy of the system

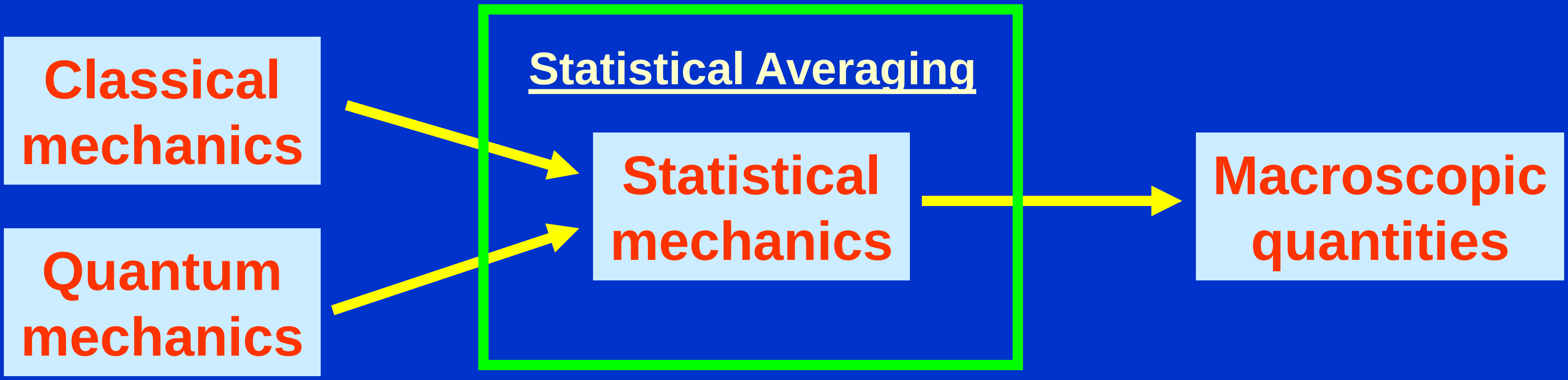
$-\frac{\Delta H}{T}$: Entropy of the surroundings

$-\frac{\Delta G}{T}$: Total entropy of the universe

$$\Delta G < 0 \Leftrightarrow -\frac{\Delta G}{T} > 0$$

For a natural or spontaneous change.

Microscopic / Macroscopic World



Classical mechanics

Quantum mechanics

Statistical Averaging

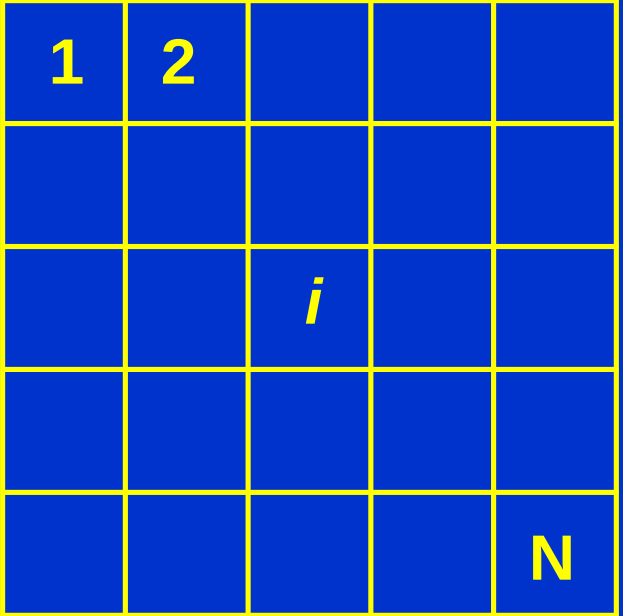
Statistical mechanics

Macroscopic quantities

Microscopic
Interactions
Phase space
Wave function

Observables:
Dynamic and
Thermodynamic
quantities

Ensemble



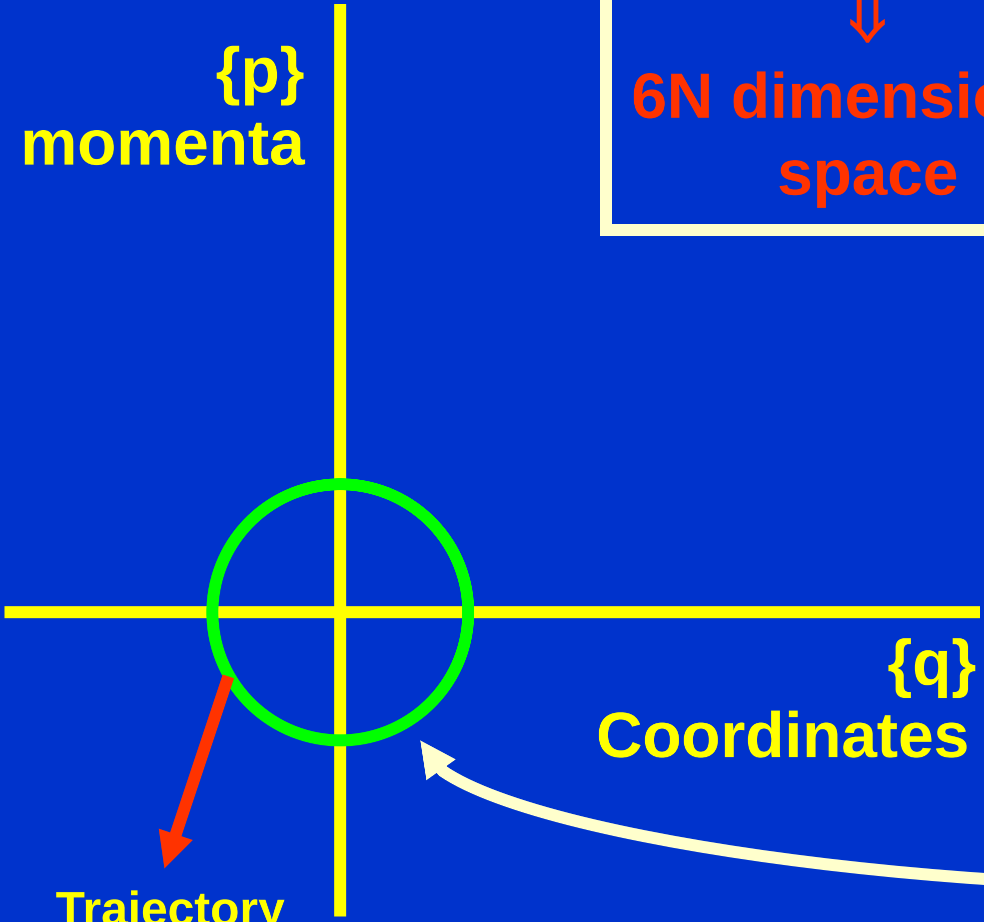
$$\langle M \rangle = \sum_i P_i M_i$$

P_i is probability of state *i*.

- Members of the ensemble represents a state of a system in accordance with external macroscopic parameters (e.g. *N, V, T*).
- A state is either defined classically (a point in phase space) or quantum mechanically (quantum numbers).
- Mechanical quantities *M* are averages over the ensemble:
  - Pressure, volume, energy, …..
  - But not entropy *S* and free energies (*A, G*).

Phase space

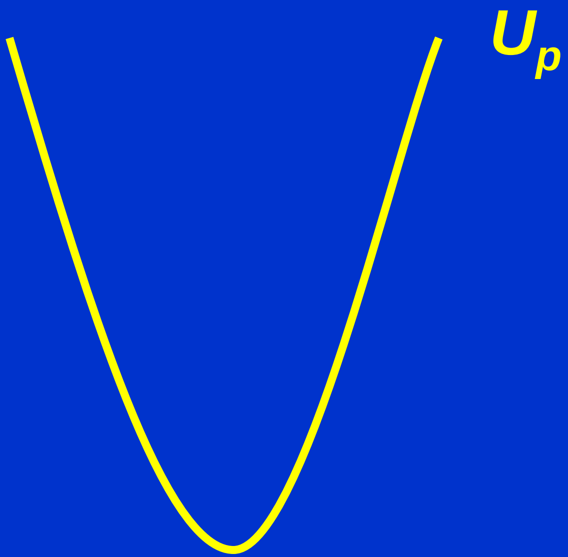
N particles
⇓
6N dimensional space



{p}
momenta

{q}
Coordinates

Trajectory



U_p

One-dimensional harmonic oscillator ⇒ 2N dimensional phase space

Quantum Numbers

- The state of the system is fully described by the wave function.
- The state of the system is fully described by a set of quantum numbers (*n*, *m*, *l*, …..).
- The total energy of the system is given from Schrödinger equation. An observable such as the energy *E* corresponds to an operator such as *H*.

$$\Psi\left(\mathbf{r}_1, \mathbf{r}_2, \ldots, t\right) \qquad H\Psi = E\Psi$$

Probability of State *i*

(quantum version)

$$\langle M \rangle = \sum_i P_i M_i$$

Average of quantum (discrete) states: Probability *P_i* depends on the type of ensemble.

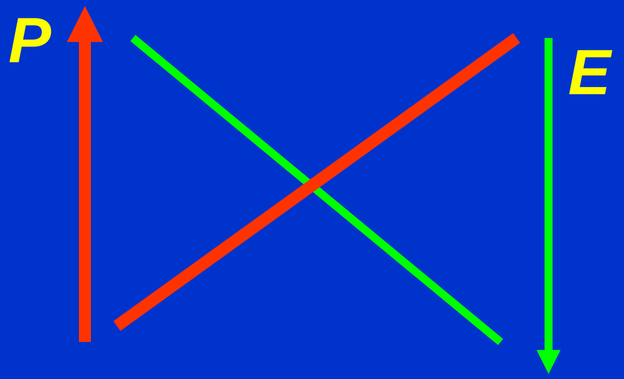
$$P_i(N,V,T) = \frac{1}{Q(N,V,T)} e^{-\beta E_i}$$

Boltzmann factor

$$Q = \sum_i e^{-\beta E_i}$$

Partition function

$$\langle M \rangle = \frac{\sum_i M_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$



Canonical ensemble (*N,V,T*)

(*E*, *p*, … fluctuating)

$$\beta = \frac{1}{kT}$$

k: Boltzmann's constant

T: Temperature

Free Energy and Entropy

Partition function plays central in equilibrium statistical thermodynamics

$$A = -kT\ln Q$$

Helmholtz free energy.

$$S = -k\sum_i P_i \ln P_i = kT\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k\ln Q$$

Entropy

$$TS = U + A$$

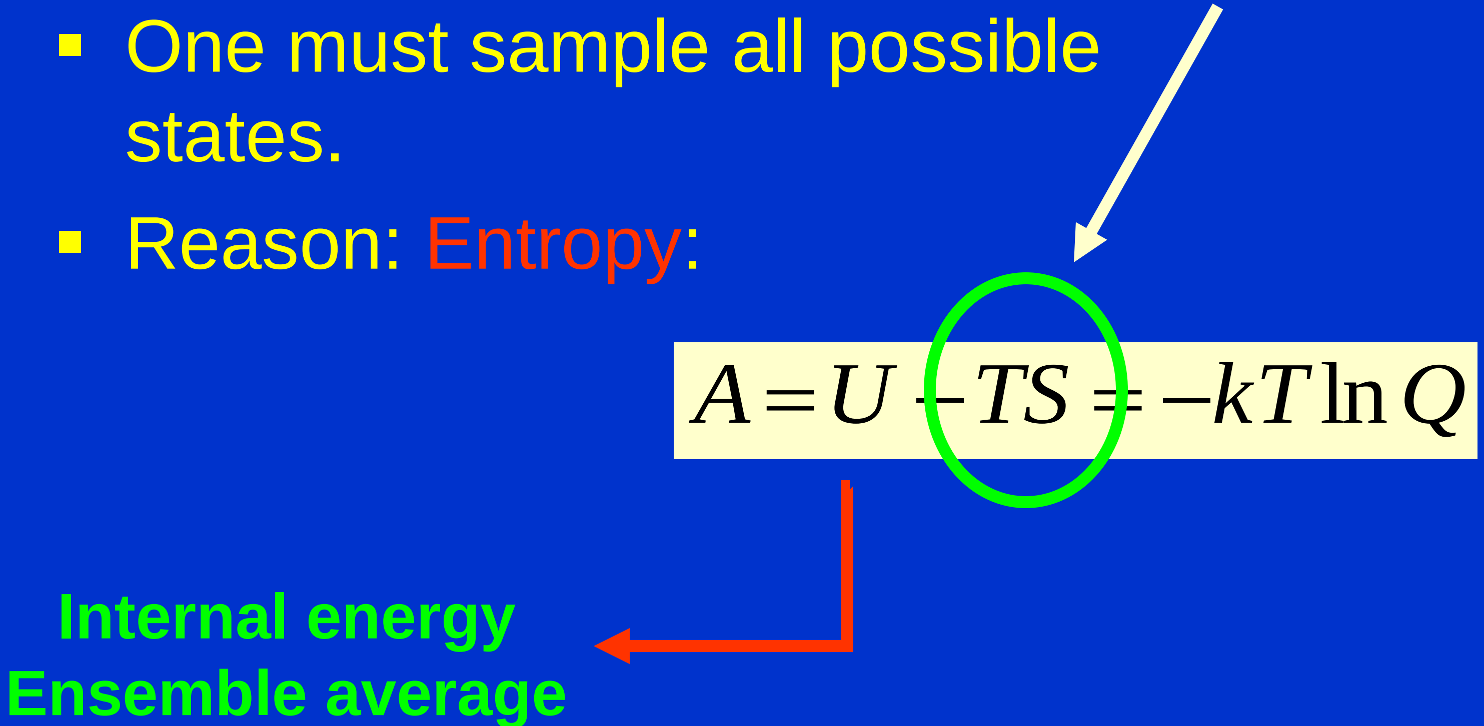
$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = \frac{\sum_i p_i e^{-\beta E}}{\sum_i e^{-\beta E_i}}$$

Pressure

$$Q = \sum_i e^{-\beta E_i}$$

Free Energy and Entropy

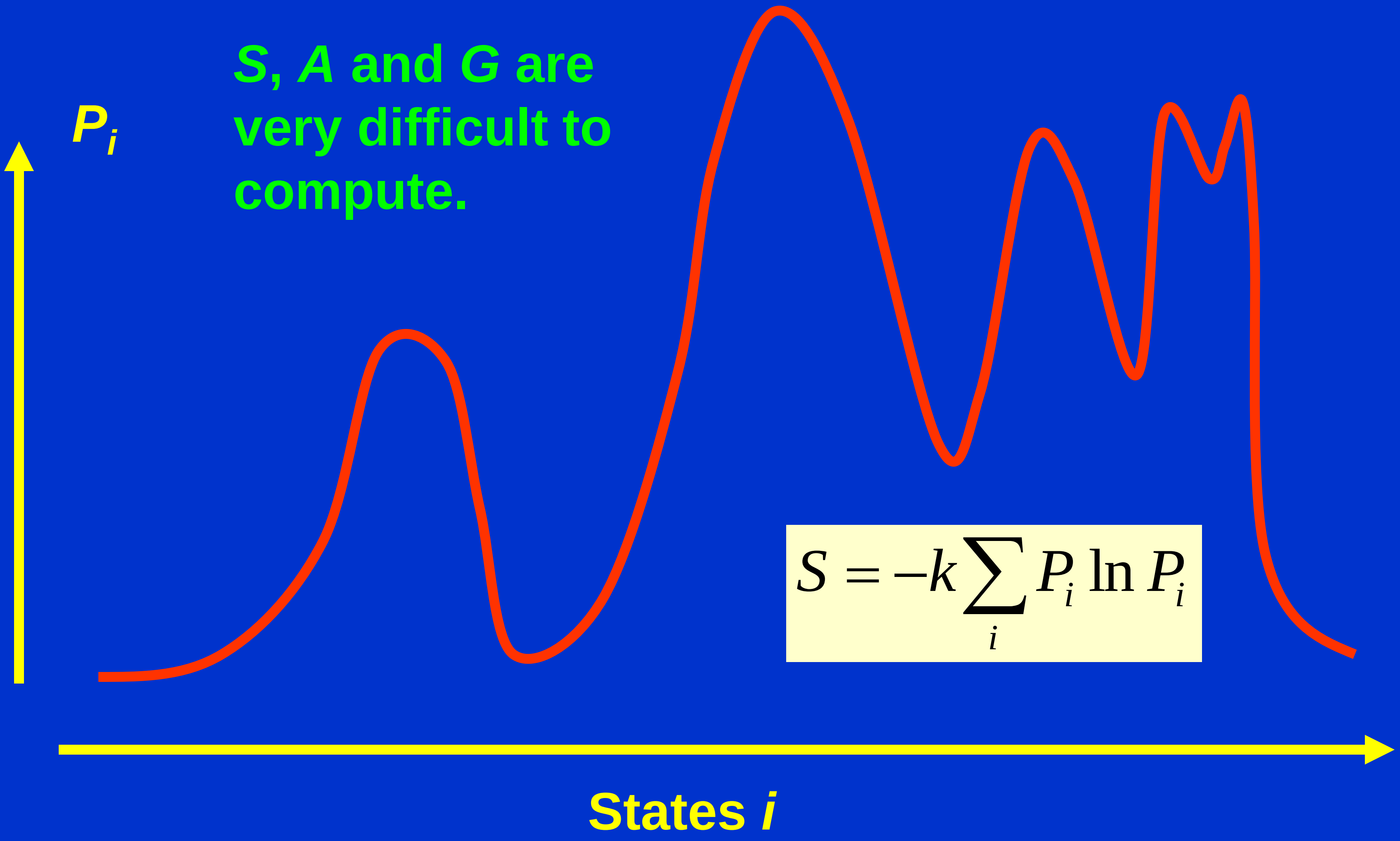
- Both entropy and free energy depend on the full phase space, or:
- One must sample all possible states.
- Reason: Entropy:



$$A = U - TS = -kT\ln Q$$

Internal energy
Ensemble average

Free Energy and Entropy



S, A and G are very difficult to compute.

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

The Solute Chemical Potential

Solute in a solvent

$$\mu = \mu^{\Theta} + kT \ln a$$

Standard chemical potential (reference state)

$$a = \gamma \frac{m}{m^{\Theta}}$$

Activity

γ : Activity coefficient
m : Molality (molarity)
mol/kg (mol/m^3)
m^{Θ}=1 mol/kg

The Solute Chemical Potential

Solute in a solvent

$$\mu = \mu^{\Theta} + kT \ln \frac{m}{m^{\Theta}} + kT \ln \gamma$$

$$kT \ln \frac{m}{m^{\Theta}}$$

Measures the deviation from standard molality (molarity).

$$kT \ln \gamma$$

Measures the deviation from ideality:
Interactions between solute molecules.
$\gamma \to 1$ if $m \to 0$ ⇔ At very low concentration (dilute).

Equilibrium Constant

Chemical equilibrium condition

$$A + B \leftrightarrow AB$$

$$\Delta G = 0$$

$$\mu_A + \mu_B = \mu_{AB}$$

$$\Delta G^{\Theta} = \mu_{AB}^{\Theta} - \mu_A^{\Theta} - \mu_B^{\Theta} = -kT \ln K$$

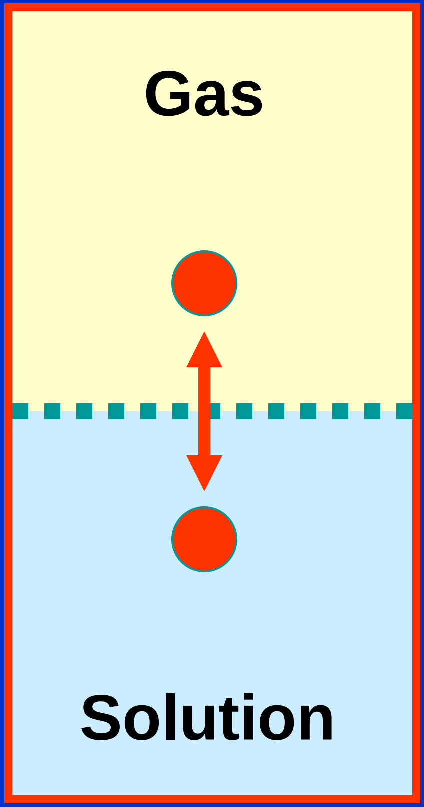
$$K = \frac{a_{AB}}{a_A a_B} = \frac{m_{AB}}{m_A m_B} \times \left(\frac{\gamma_{AB}}{\gamma_A \gamma_B} \frac{m^{\Theta} m^{\Theta}}{m^{\Theta}} \right)$$

$$\Delta G^{\Theta} = -kT \ln \frac{m_{AB}}{m_A m_B} - kT \ln \left(\frac{\gamma_{AB}}{\gamma_A \gamma_B} \frac{m^{\Theta} m^{\Theta}}{m^{\Theta}} \right)$$

K is dimensionless

Experimentally: Measurement of concentrations provides K only if it is assumed that $\gamma = 1$ for all reactants.

Equilibrium Constant



Transfer of solute from one phase to another phase:

$$A_{\mathrm{sol}} \leftrightarrow A_{\mathrm{gas}}$$

$$\Delta G_{\mathrm{t}}^{\Theta} = -kT\ln\frac{pm^{\Theta}}{p^{\Theta}m} - kT\ln f + kT\ln\gamma$$

Real gas

$$\mu_g = \mu_g^{\Theta} + kT\ln\frac{p}{p^{\Theta}} + kT\ln f$$

Equilibrium Constant

- Previous formulation for ΔG^{Θ} (or K) is not suitable for computational purposes.
- Instead what is required are expressions for:
  - Standard chemical potential or some related quantity.
  - Activity coefficients, for low or moderate to high concentrated solutions.