భారతీయ సాంకేతిక విజ్ఞాన సంస్థ హైదరాబాద్
भारतीय प्रौद्योगिकी संस्थान हैदराबाद
Indian Institute of Technology Hyderabad

Biomolecular Simulation BT2123

Lecture 6 : Laws of Thermodynamics

Himanshu Joshi 6 Feb 2024

ভারতীয় সাংকেতিক ...

Course contents

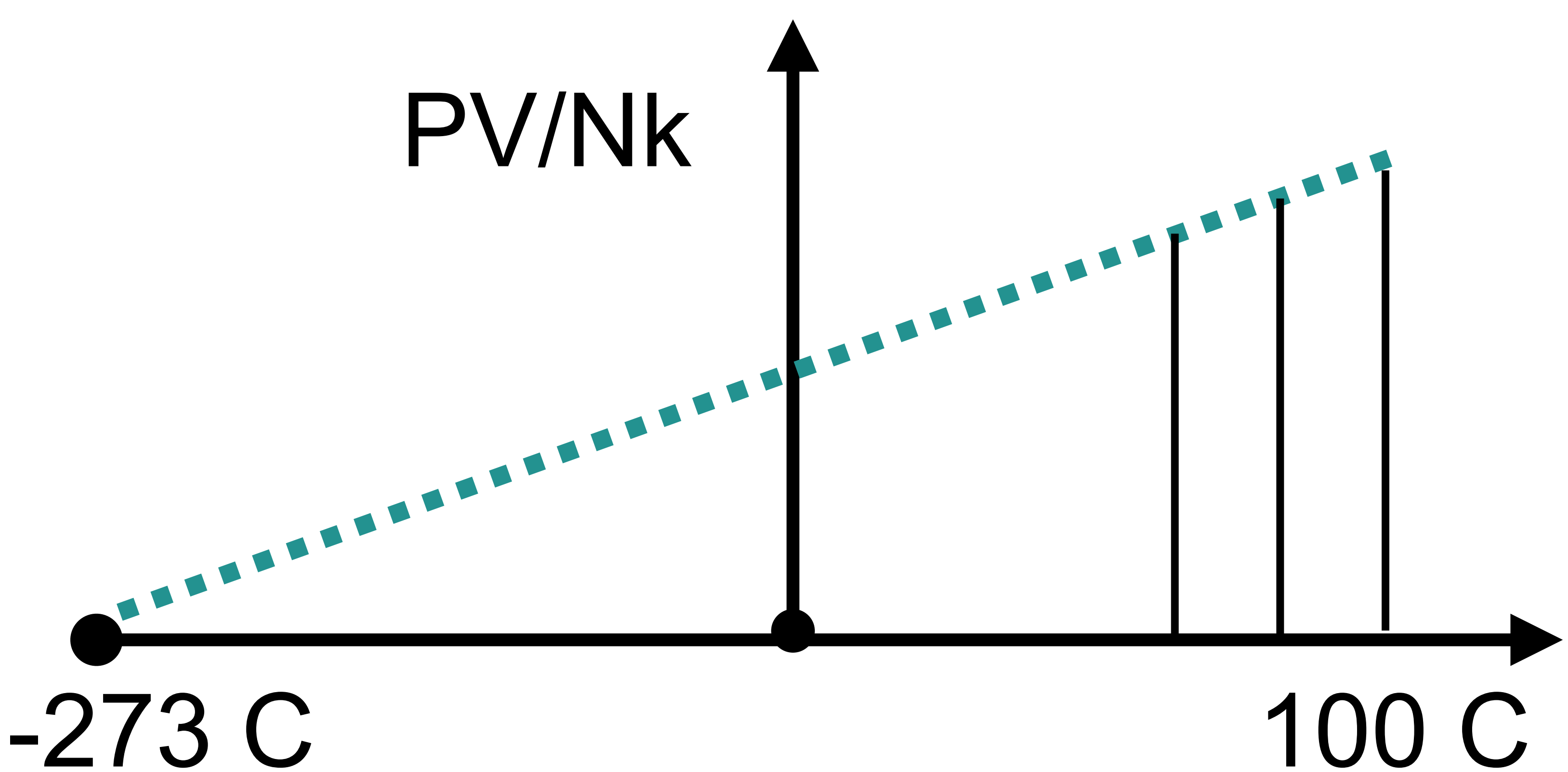
- Historical perspective
- Foundations of Molecular Mechanics (MM)
- **Statistical ensembles**
- Quantum Mechanics (QM)
- Introduction molecular dynamics simulations
- Equation of motion,
- Force-fields, Scheme of integrations,
- Langevin Dynamics,
- Non-bonded Computations,
- Brownian Dynamics,
- Monte Carlo Techniques,
- Coarse Graining Models

Equation of state: $f(P, V, T) = 0$

Relationship between theromdynamic parameters

Ideal gas $PV = NK_bT$

Definition of Temperature using ideal gas law



Intensive quantities P, T,

Extensive quantities S, U, V E

Thermodynamics

- Thermodynamics is a phenomenological theory.
- It is valid in macroscopic worlds and will inevitably fails at the atomic level.
- Laws of thermodynamics are mathematical axioms defining a mathematical model

First law of Thermodynamics

Conservation of energy

$$\Delta U = \Delta Q - \Delta W$$

Second law of Thermodynamics

Every process that conserve energy does not take place

Kelvin statement:

It is impossible to devise a heat engine that takes heat from the hot reservoir and converts all the energy into useful external work without losing heat to the cold reservoir.

Clausius statement

It is impossible to design a device which works on a cycle and produces no effect other than heat transfer from a cold body to a hot body.

$$\int_O^A \frac{dQ}{T} = S(A) \qquad\qquad dS = \frac{dQ}{T}$$

Third law of Thermodynamics

The entropy change associated with any condensed system undergoing a reversible isothermal process approaches zero as the temperature at which it is performed approaches 0 K

Nernst 1905

Entropy

The entropy is, according to Boltzmann, proportional to the logarithm of the number of available states, as measured by the phase space volume

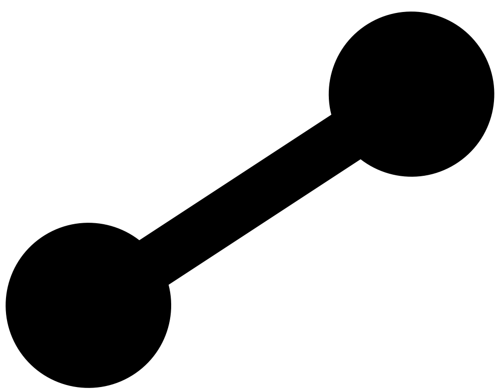
$$S = k_B \ln \left(\frac{\Gamma(E,V,N)}{\Gamma_0(N)} \right)$$

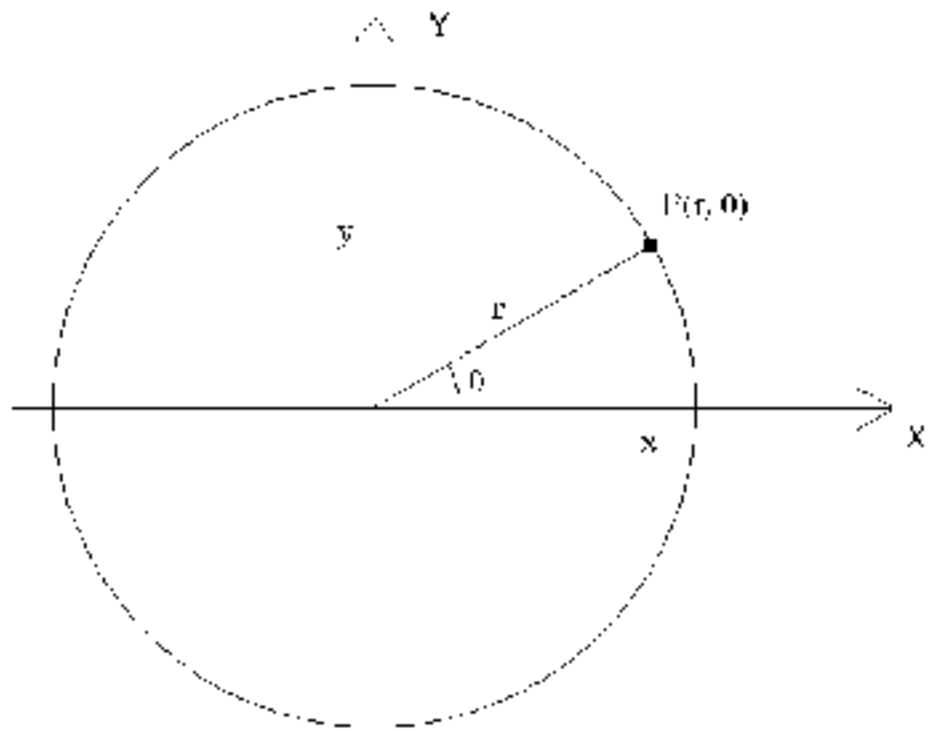
$$\Gamma(E,V,N) \; :$$

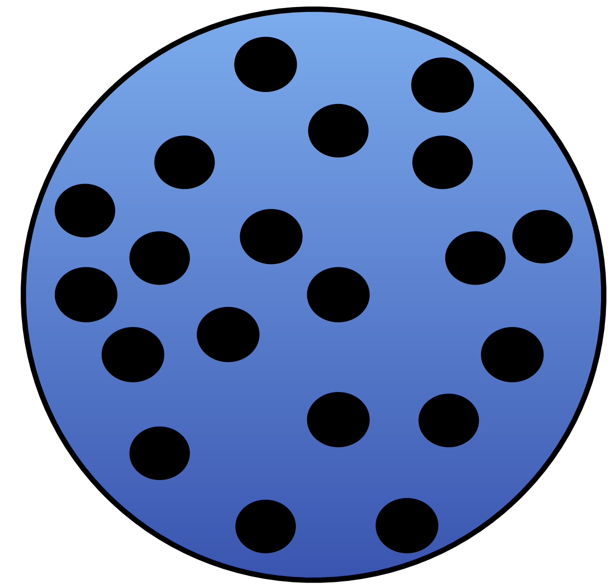
Total number of micro states available to the system

Lagrangian Mechanics

Generalized coordinate = Degree of freedom - constraints







Rigid body
N particles

Ref:
www.quora.com/What-is-the-comparison-among-Newtonian-Lagrangian-Hamiltonian-and-quantum-mechanics

Lagrangian Mechanics

$$L(q_1, q_2...., q_N, \dot{q}_1, \dot{q}_2...., \dot{q}_N)$$

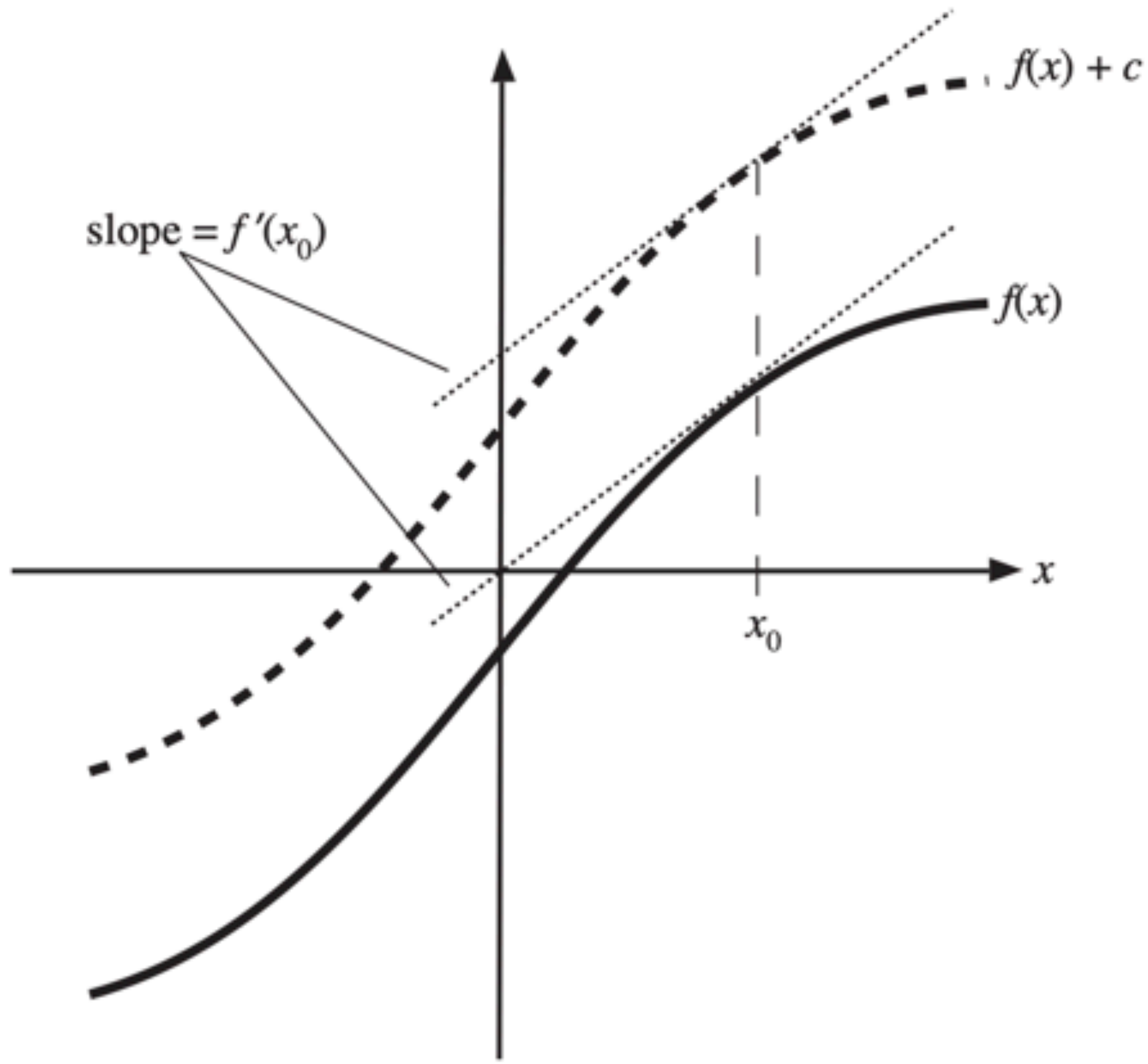
$$= \qquad K(\dot{q}_1, \dot{q}_2...., \dot{q}_N) - U(q_1, q_2.., q_N)$$

$$S = \int_{t1}^{t2} L(q_i, \dot{q}_i, t)\, dt$$

Euler Lagrange equation

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0$$

Legendre transform



Reference:
https://www.aapt.org/docdirectory/meetingpresentations/sm14/mungan-poster.pdf

Hamiltonian Mechanics

Set of coordinates q_i and p_i which makes the conserved quantities clear immediately

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

$$-\dot{p}_i = \frac{\partial H}{\partial q_i}.$$

Quantum Mechanics

In the beginning, it was formulated as an extension of Hamiltonian mechanics but it failed at small scale

Position and momenta are not quantities but operators

When they apply on the wavefunction you get the eigenvalues

$$\frac{\partial \Psi}{\partial t} = \frac{1}{i\hbar}\hat{H}\Psi$$

Entropy

The entropy is, according to Boltzmann, proportional to the logarithm of the number of available states, as measured by the phase space volume

$$S = k_B \ln \left(\frac{\Gamma(E,V,N)}{\Gamma_0(N)} \right)$$

$$\Gamma(E,V,N) :$$

Total number of micro states available to the system

Microcanonical ensemble

Microcanonical ensemble pertains to a collection of system in isolation obeying the Hamiltonian dynamics

Microcanonical ensemble

$$\Omega_{3N}(\sqrt{2mE}) \;=\; (2mE)^{3N/2}\,\Omega_{3N}(1),$$

$$\Omega_{3N}(1) \;=\; \frac{\pi^{3N/2}}{(3N/2)\,\Gamma(3N/2)}\;,$$

$$\Gamma(z) = \int_0^\infty t^{z-1}e^{-t}\,dt$$