# Lecture 4
# CH-4114
# Molecular Simulation

**"Everything that living things do can be understood in terms of the jigglings and wigglings of atoms."**

**- Richard P. Feynman**

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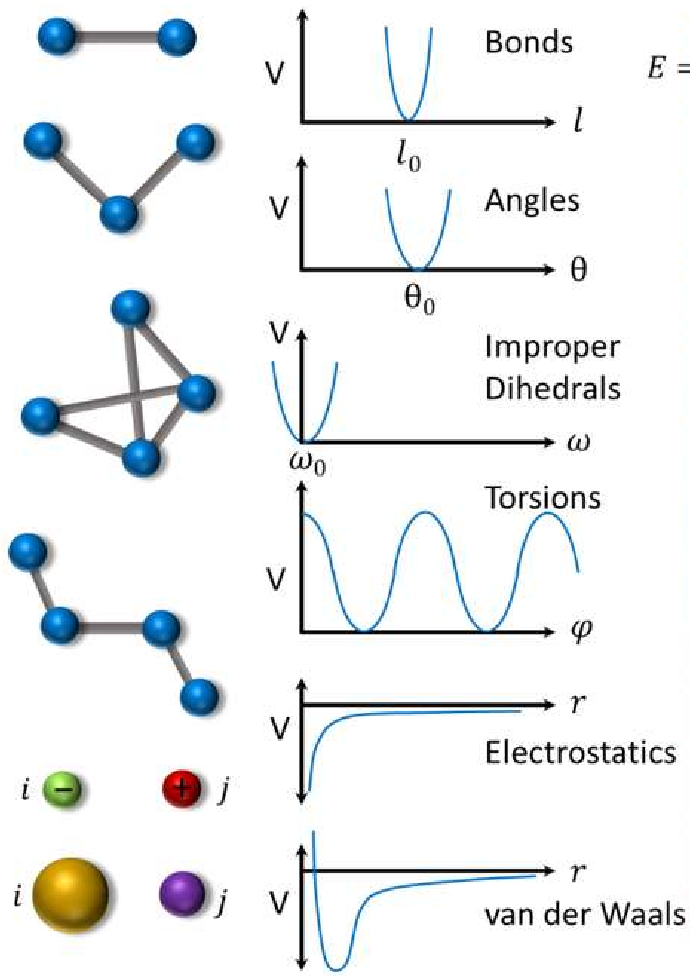
## Summary on potential accounting for relevant degrees of simple molecules

Last Week's revision




**Bonded interactions**

$$E = \sum k_l (l - l_0)^2 + \sum k_\theta (\theta - \theta_0)^2 + \sum k_\omega (\omega - \omega_0)^2 + \sum \frac{k_\varphi}{2}[1 + \cos(n\varphi - \varphi_0)]$$

**Non-bonded interactions**

$$+ \sum_i \sum_{j \neq i} \frac{q_i q_j}{\epsilon_0 \, r_{ij}} + \sum_i \sum_{j \neq i} 4\,\epsilon_{ij} \left[ \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} \right]$$

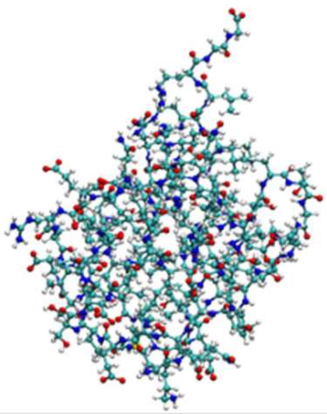
On our way to learn Molecular Dynamics Simulation: Pipeline

- Pick particles, masses and potential.
- Initialize positions and momentum. (boundary conditions in space and time)
- Solve $\mathbf{F} = m\,\mathbf{a}$ to determine $\mathbf{r}(t)$, $\mathbf{v}(t)$.

*Newton (1667-87)*

- Compute properties along the trajectory
- Estimate errors.
- Try to use the simulation to answer physical questions

Using Statistical Mechanics

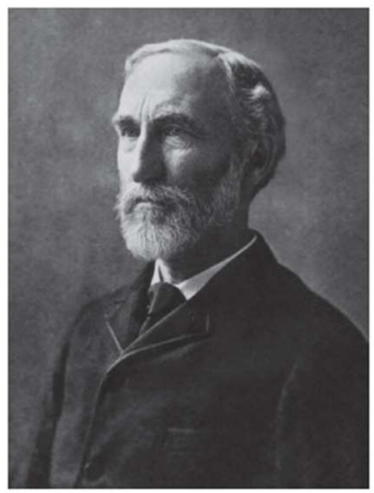


## Basic Statistical Mechanics- Microscopic and macroscopic parameters

**Statistical Mechanics**

**Equilibrium Statistical Mechanics** ⟷ **Non-equilibrium Statistical Mechanics**

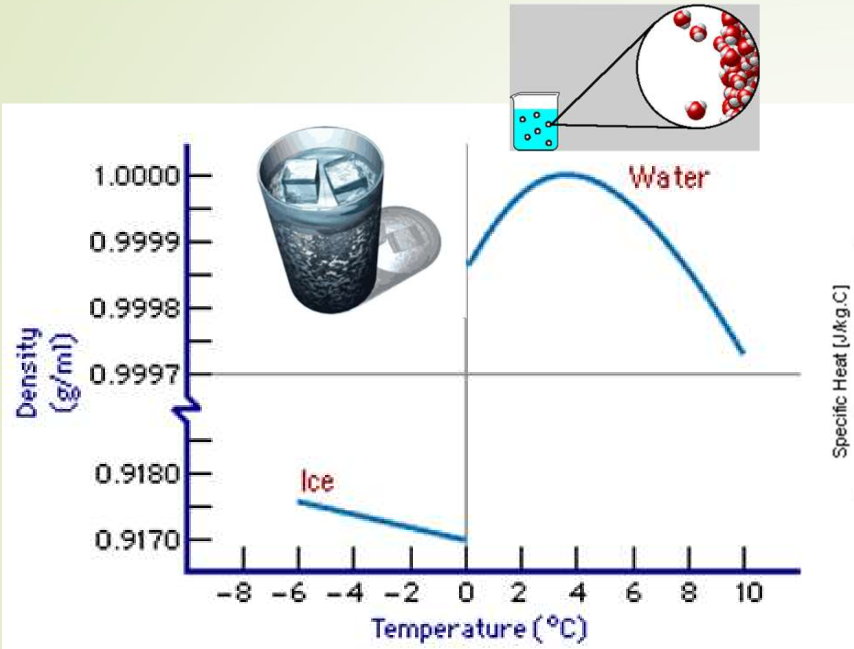
James Clerk Maxwell

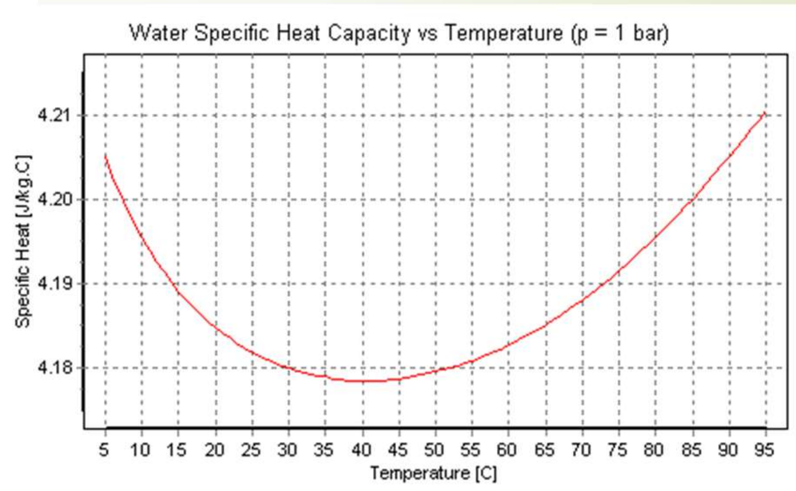


Willard Gibbs

Ludwig Boltzmann

# Classical Thermodynamics vs. Statistical Thermodynamics

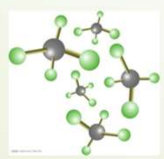



Statistical Mechanics teaches us to calculate various macroscopic properties of a system and help us to interpret/explain experimentally observed properties in connection with the molecular/atomic information of that system.

Microscopic $\xrightarrow{\text{Statistical Mechanics}}$ Macroscopic

Atom



Molecule

Thermodynamics

## Key features of classical thermodynamics

- System
  A part of the universe whose properties are being investigated
- Surrounding
  Rest of the universe
- Macroscopic dimensions
  - Length – 1 meter
  - Time – 1 minute
  - Number of particles - $6.023 \times 10^{23}$
- A system in Equilibrium
  All measurable properties are independent of time

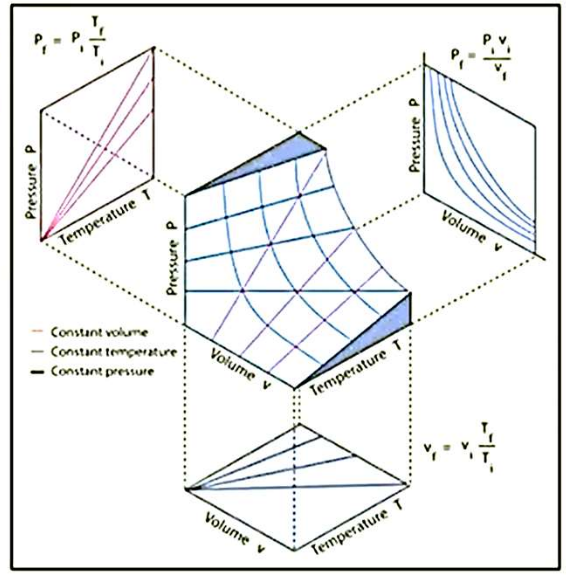
How to define a macroscopic state of a system?

Remember Natural (Independent) Variables?

# Recall

## Equation of State

This is a mathematical relationship between appropriate thermodynamic variables of a system at equilibrium




**Example**

- Ideal gas equation of state

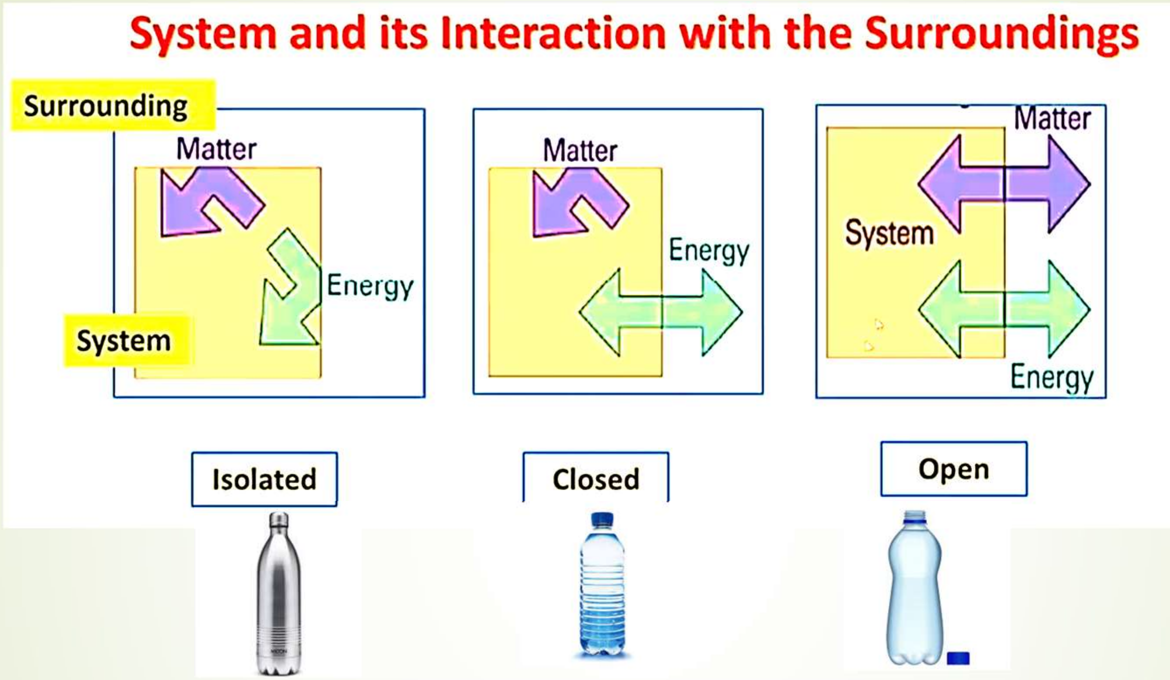
$$pV = nRT$$

- van der Waals equation of state

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/idegas.html

# System and Thermodynamic Potential

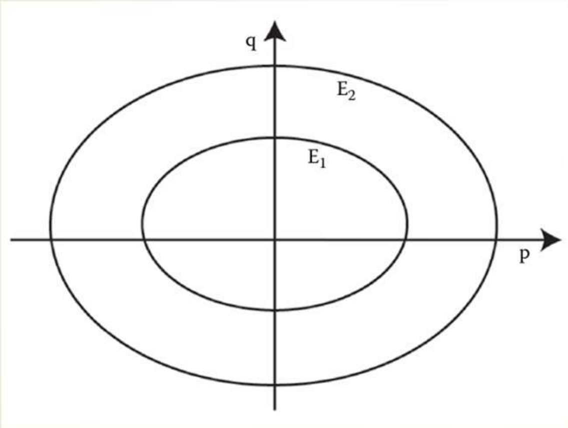



| | Thermodynamic state of system | Thermodynamic potential | Direction of spontaneous change in state | Condition of equilibrium |
|---|---|---|---|---|
| Isolated system | S, $V$, $N$<br>$U,V,N$ | $U$<br>S | Decrease in $U$<br>Increase in S | Minimization of $U$<br>Maximization of S |
| System + Thermostat | T, $V$, $N$ | $F = U - TS$ | Decrease of $F$ | Minimization of $F$ |
| System + Thermostat + Barostat | T, $p$, $N$ | $G = U - TS + pV$ | Decrease of $G$ | Minimization of $G$ |

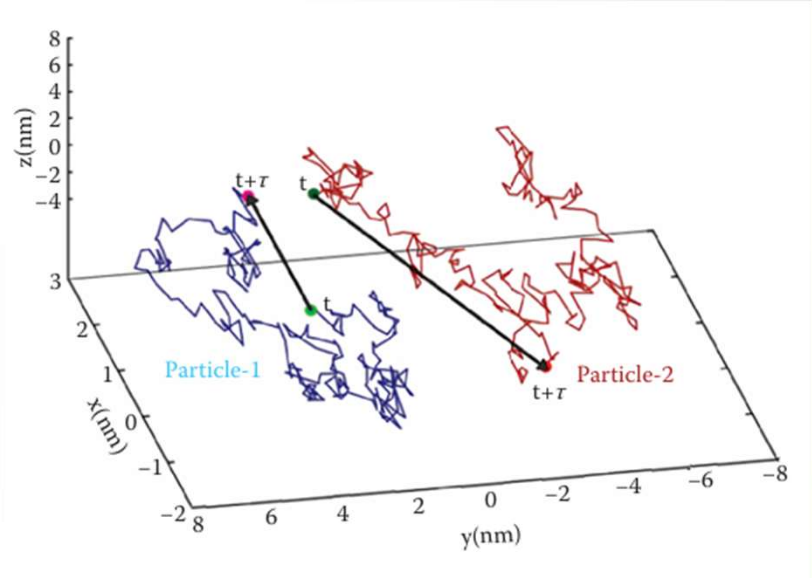
## Phase Space and Trajectory

Let us consider only one single atom in one-dimensional space at any time t = 0. To specify its future trajectory, we need time evolution of two coordinates – one position coordinate (q) and one momentum (p) coordinate – these two can be plotted against each other. This two-dimensional coordinate space spanned by p and q is called the phase space of the particle.

$$H = KE + PE = \frac{p^2}{2m} + \frac{1}{2}kq^2$$



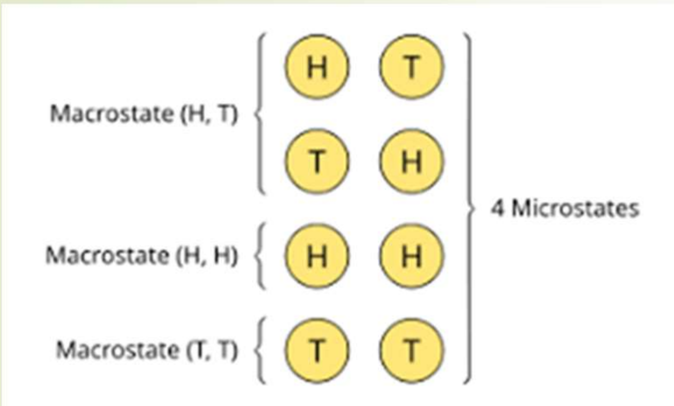

Phase space trajectories of harmonic oscillator for two constant energy values, E1 and E2



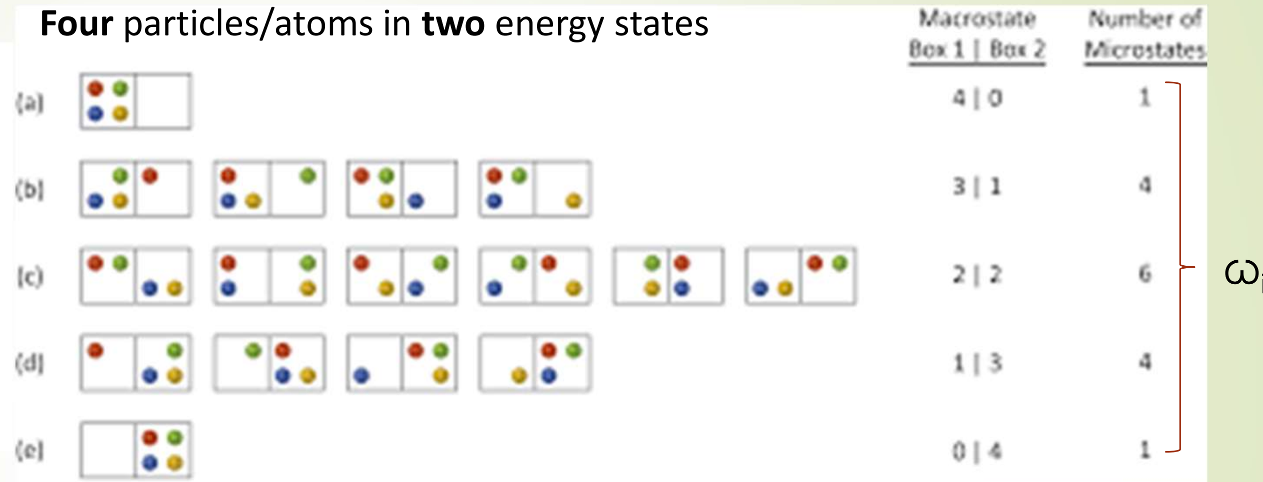

The continuous movement of the position of the particles in the configuration space is a consequence of the system’s motion in 6N-dimensional phase space.

# How do we define microstate?

10 **A state that describe microscopic length scale configuration of a system and the interaction**.




**Four** particles/atoms in **two** energy states




## How to Calculate the Number of Microstates

**Total Outcome=16**

**Number of Microstates:**

for $N = 4$ $N_1 = 3$ $w_2 = ?$ (# of microstates in the 2nd macrostate)

$$w_k = \binom{N}{N_1} = \frac{N!}{N_1!\,(N - N_1)!}$$

$N = 10$ 5H, 5T $N_1 = 5$ $w = ?$

| macro-state | macro-state specs. | | microstates | | | | thermo prob. | math prob. |
|---|---|---|---|---|---|---|---|---|
| $k$ | $N_1$ | $N_2$ | coin1 | 2 | 3 | 4 | $w_k$ | $P_k = \frac{w_k}{\Omega}$ |
| 1 | 4 | 0 | H | H | H | H | 1 | 1/16 |
| 2 | 3 | 1 | H<br>H | H<br>H | H<br>T | T<br>T | 4 | 4/16 |
| ⋮ | ⋮ | ⋮ | ⋮ | ⋮ | ⋮ | ⋮ | ⋮ | ⋮ |