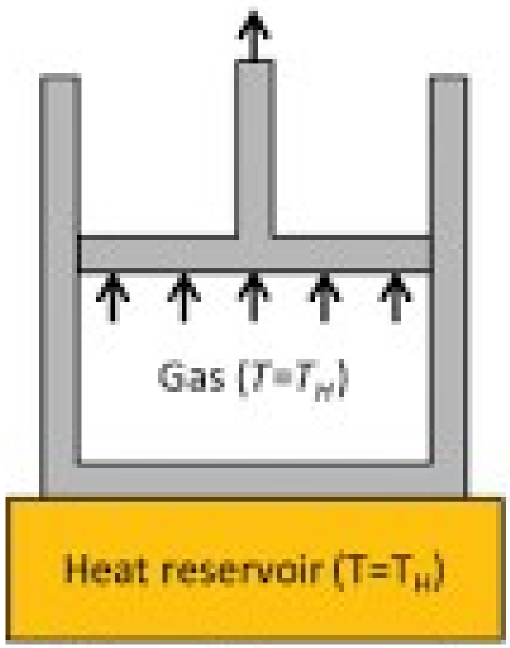
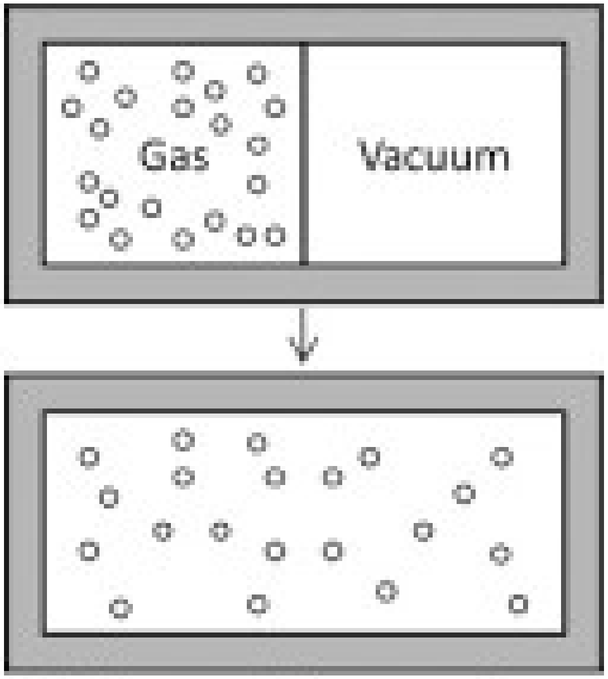
Thermodynamic Processes

<u>Reversible Process</u>→ (a) When the driving force of the process differs from the opposing force by infinitesimal amount;
(b) The process can be reversed without the aid of external agency.

<u>Irreversible Process</u> →(a) This process occurs rapidly and spontaneously & occurs against the const. external opposing force. (b) The process can not be reversed without the aid of external agency.



(a) Reversible expansion



(b) Irreversible expansion

Work: (w): When an object is displaced through a distance, dx against a force F, the work done, w=force (F) x displacement (dx) . (Realize, why it is a path function)

Types of work: (i) Mechanical work (w)=P.dv
(ii) Gravitaional work (w)=mgh
(iii) Electric work (w)=Potential energy (V)x change flowing under potential difference (Q)

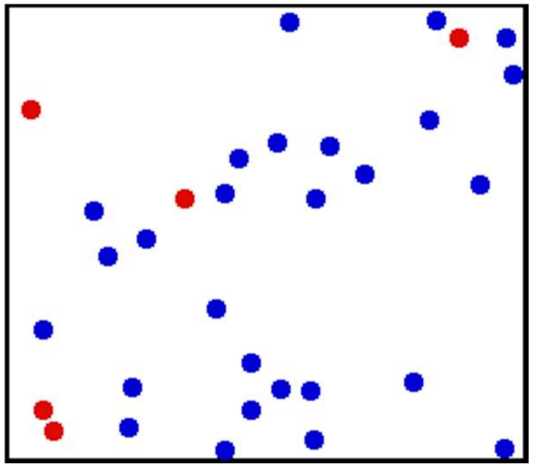
Heat (q): a form of energy. It can be produced from work or partly, converted into work. It flows from higher temp to lower temp until T becomes equal. (Realize, why it is a path function)

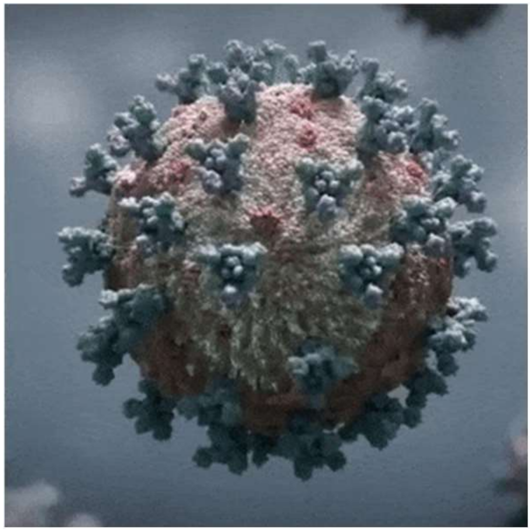
Internal energy (u): A system by virtue of its existence must posses a store of energy. Imagine a cup of hot coffee. Even when the cup is still, the coffee's molecules are constantly moving, vibrating, and interacting with other particles and walls.
Internal energy is **the total energy of these molecular motions and interactions** inside a substance. Realize, why it is a state function. It includes:

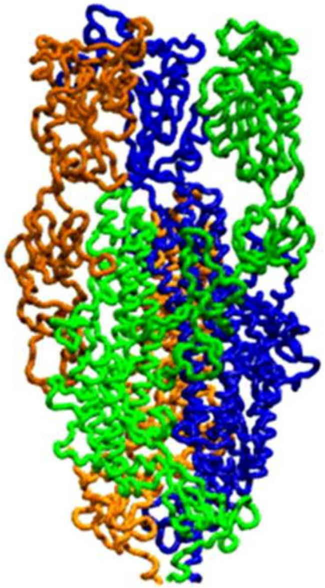
- **Kinetic energy** (due to molecular motion)
- **Potential energy** (due to molecular interactions)

So, when the coffee cools, its internal energy decreases because molecular motion slows down. U is a sensitive function of temperature: U(T)

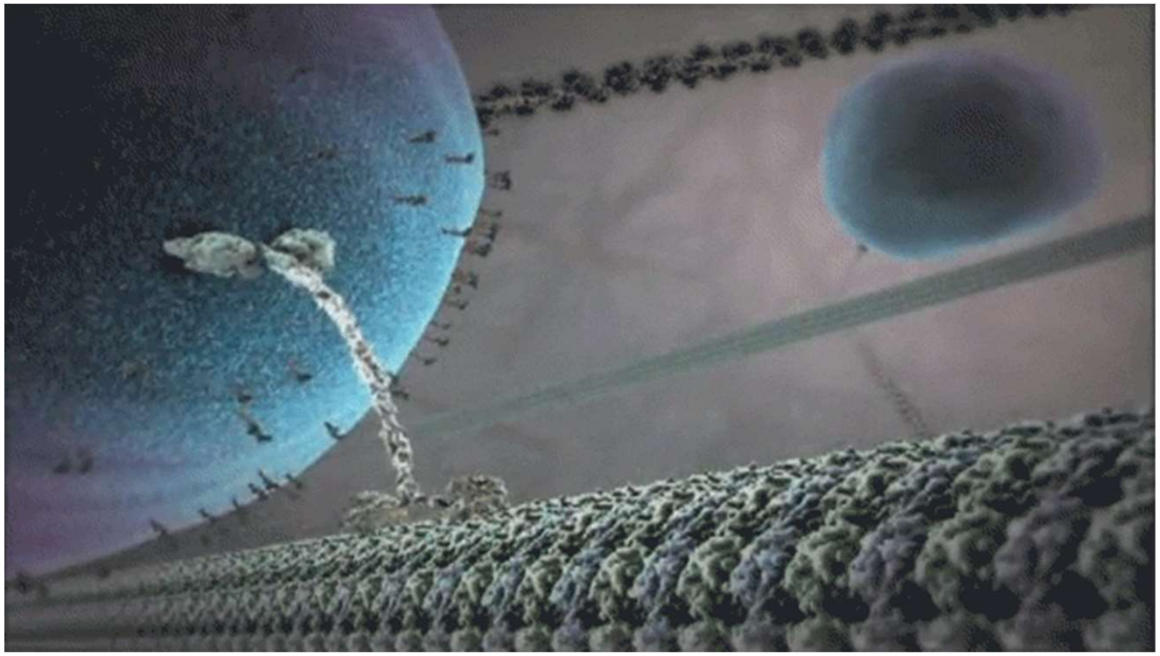
Concept of Temperature: Microscopic basis of Temperature







Roy et al. JPCL 2020

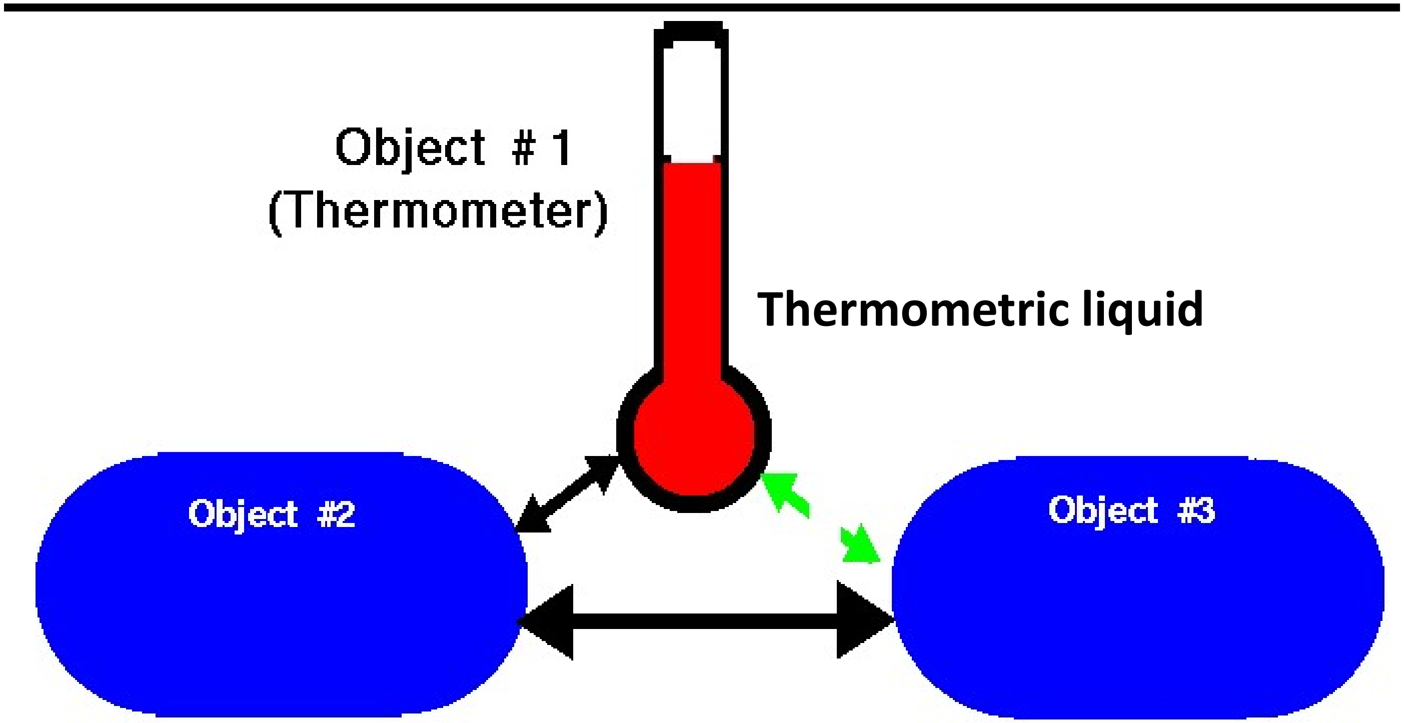


Remember our board work where we proved: Average kinetic energy ∝ Temperature

Zeroth Law Of Thermodynamics

Foundation of Thermodynamics

Definition of temperature



When two objects are separately in thermodynamic equilibrium with a third object, they are in equilibrium with each other.

Objects in thermodynamic equilibrium have the same temperature.

Realization of heat transfer

1^{st} law of Thermodynamics

Total energy of an isolated system is constant; Energy can neither be created nor be destroyed but can be transformed from one form to another.

$$\Delta U = q + w$$

- The concept of internal energy, U and enthalpy, $H = U + pV$
- During a change in state,

$$\Delta U_{universe} = \Delta U_{system} + \Delta U_{surrounding} = 0$$

(assuming the universe to be isolated and at equilibrium)

- Transfer/transformation of energy between system and surrounding, keeping the total energy fixed.

Mathematical Interlude
(Check the note)

State Function

A **state function** in thermodynamics is a property of a system that depends only on the **current state** of the system, not on the path taken to reach that state.

Key Characteristics:

- **Path-independent**: The value of a state function remains the same regardless of how the system arrived at that state.
- **Depends only on initial and final states**.
- Its differential is a **perfect (exact) differential**.

<u>Examples of State Functions:</u>

- **Internal Energy (U)**
- **Enthalpy (H)**
- **Entropy (S)**
- **Pressure (P)**
- **Temperature (T)**
- **Volume (V)**
- **Gibbs Free Energy (G)**

In contrast, **work (W) and heat (Q) are not state functions** because they depend on the process or path taken.

Path Function

A **path function** in thermodynamics is a quantity whose value depends on the **specific path** taken by a system to transition from one state to another.

Key Characteristics:

- **Path-dependent**: The value of a path function varies based on how the process occurs.
- **Cannot be described solely by the initial and final states**.

- **Not exact differentials**, meaning their integrals depend on the path.

Examples of Path Functions:

- **Work (W)**
- **Heat (Q)**

For example, the amount of heat added to a gas to increase its temperature can differ depending on whether the process is isochoric (constant volume) or isobaric (constant pressure).

Perfectly Differential Quantity

In thermodynamics, a property (X) can be referred to as perfectly differentiable quantity if it obeys the following criteria:

(i) X must be a state function and single valued
(ii) dx will be independent of the path of transformation between two specific states
(iii) $\oint dx = 0$
(iv) If $x = f(T, P)$, then it obeys Schwarz's theorem

$$\frac{\partial^2 Z}{\partial x \cdot \partial y} = \frac{\partial^2 z}{\partial y \cdot \partial x}$$ (Schwarz's theorem)

First Law of Thermodynamics

$$\Delta U = q + w$$

Process	Sign convention
Transfer of heat to the system from the surrounding	$q > 0$
Transfer of heat from the system to the surrounding	$q < 0$
Expansion of system against an external pressure	$w < 0$
Compression of system by an external pressure	$w > 0$

- For an infinitesimal change in state, $\mathrm{d}U = \partial q + \partial w$
- For an adiabatic process $\partial q = 0 \Rightarrow dU = \partial w$
- For a cyclic process $\Delta U = \oint dU = 0 \Rightarrow q + w = 0$

Class Evaluation

Post mid-sem (PM) (Syllabus: Thermodynamics)

(i) Assignment (Marks: 5)

(ii) Class test- 10 marks

End-sem: 35