

Thermodynamics

Introduction



Thermal Physics: why?

- In science and technology we very often want to **describe/explain/predict** the properties of **macroscopic** objects **containing unimaginably large numbers of particles** (eg $\sim 10^{23}$ atoms in a typical “lump” of solid material)
- In this context, we can think of *macroscopic* as meaning “big enough to be seen with a microscope” (rough definition!)
- We know, pretty well, how **individual** particles behave (classical/quantum mechanics) so can we understand properties of macroscopic objects by solving equations of motion for all the constituent particles???
- **NO!!** there are just far, far, too many.....

Thermal Physics: why?

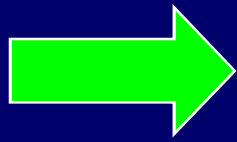
- ❑ The **macroscopic description** of a system of $\sim 10^{23}$ particles may involve only a few variables!

“**Simple systems**”: Macroscopically homogeneous, isotropic, uncharged, large enough that surface effects can be neglected, not acted upon by electric, magnetic, or gravitational fields.

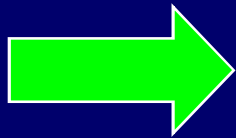
- ❑ **Only those few particular combinations** of atomic coordinates that are essentially time-independent are macroscopically observable. Such quantities are **the energy, momentum, angular momentum, etc.**
- ❑ There are “**thermodynamic**” variables in addition to the standard “mechanical” variables.

Thermal Physics: how?

- Two approaches:



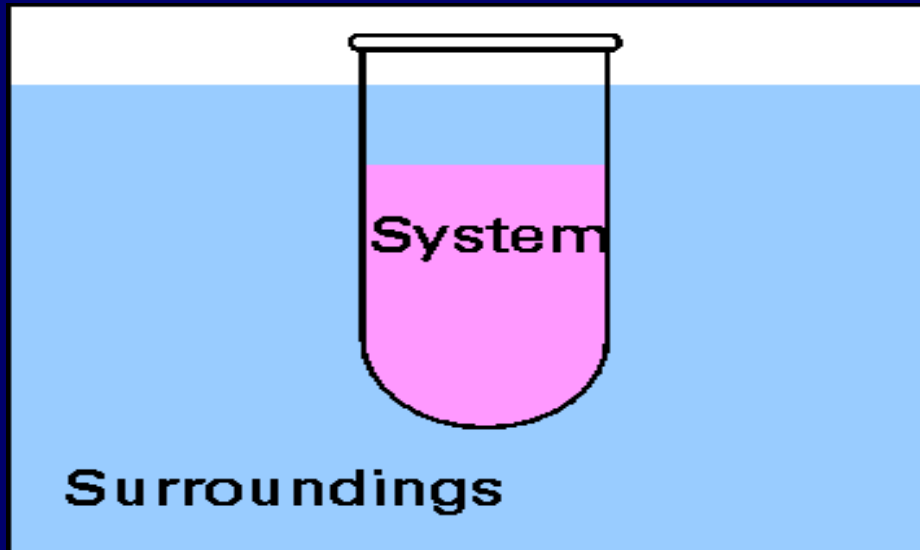
Not to worry about “microscopic” behaviour, just consider relationships between macroscopic variables.....Thermodynamics



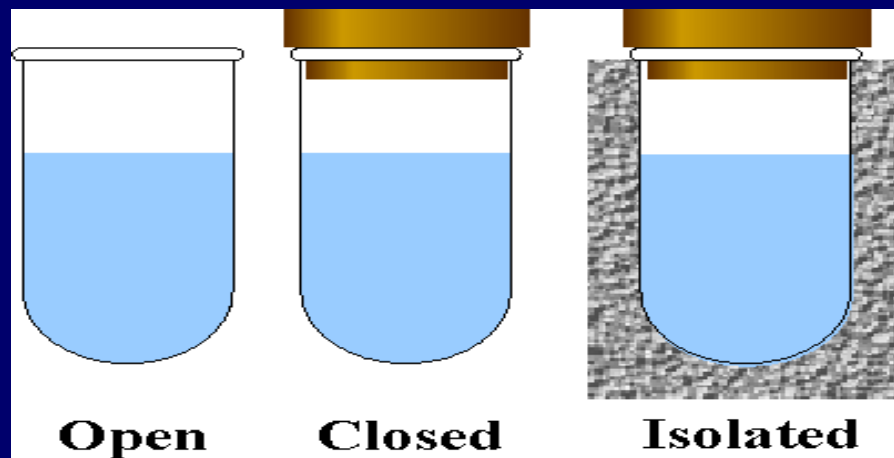
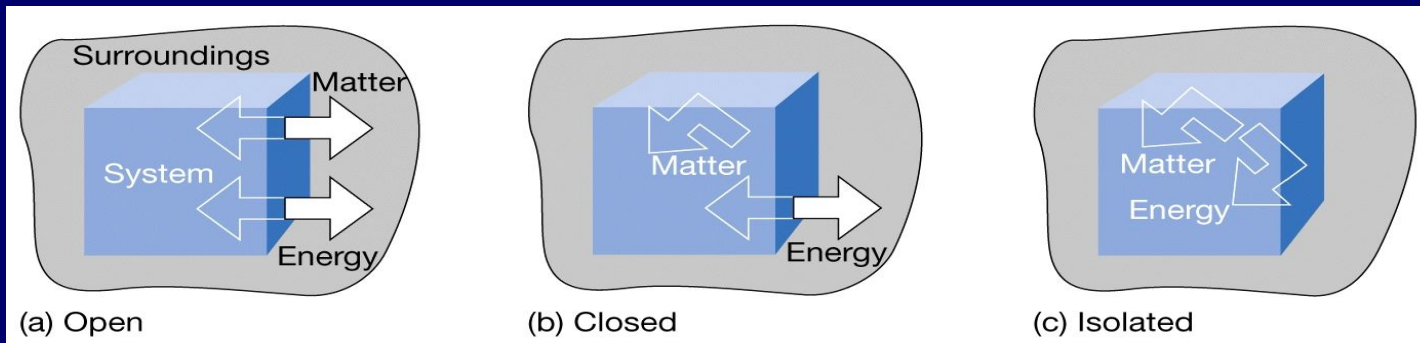
Try to understand macroscopic behaviour on the basis of the “averaged” microscopic behaviour of the particles, using the laws of statistics.....Statistical Mechanics

(But you should think of these as complementary, rather than competing approaches: see later)

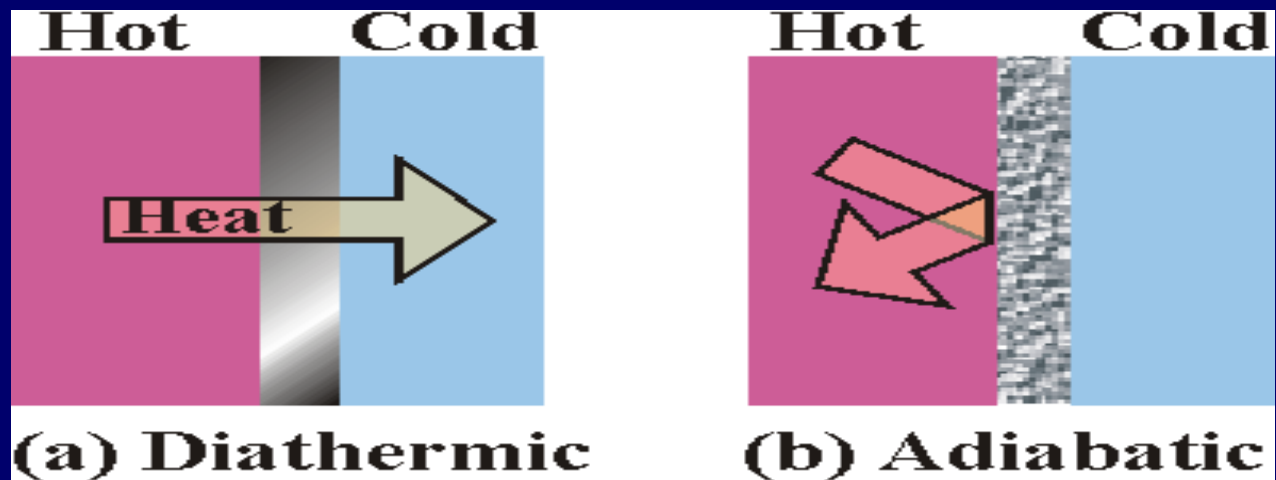
A thermodynamic *system* is that portion of the Universe that we have selected for investigation



The *surroundings* are everything outside the system. •



The *boundary* separates the system from the surroundings



The **STATE** of a system (whatever we are looking at) is uniquely defined in terms of a few variables e.g. for a gas: amount of substance (n), temperature (T) and pressure (p). Alternatively, mass (m), volume (V) and p ; or m , V & T etc.

More than three variables are unnecessary for a gas because they are not all independent: they are linked by an **EQUATION OF STATE**.

A system is in thermodynamic **EQUILIBRIUM** if there is no change with time in any of the system's macroscopic properties.

Thermodynamic Equilibrium

In all systems there is a tendency to evolve toward states whose properties are determined by intrinsic factors and not by previously applied external influences. Such simple states are, by definition, time-independent. They are called **equilibrium states**.

Thermodynamics describes these simple static equilibrium states.

Postulate:

There exist particular states (**called equilibrium states**) of simple systems that, macroscopically, are characterized completely by the **internal energy U , the volume V , and the mole numbers N_1, \dots, N_r** of the chemical components.

Thermodynamic Equilibrium

- Suppose we allow 2 or more objects or systems to interact with each other. In general, the interaction will cause the “properties” of the objects to change.
- After a sufficiently long time, the properties will stop changing
- We then say that the objects are in **equilibrium**

THERMAL EQUILIBRIUM: temperature of each object remains constant

MECHANICAL EQUILIBRIUM: volume of each object remains constant

DIFFUSIVE EQUILIBRIUM: number of particles in each object remains constant

The central problem of thermodynamics is the determination of the equilibrium state that is eventually attained after the removal of internal constraints in a closed, composite system.

➤ **Laws of Thermodynamics**

Quasistatic processes

- In thermal physics courses we almost always deal with systems assumed to be in equilibrium (**non-equilibrium thermodynamics = v. hard!**)
- So, whenever a system we are investigate undergoes a **change of state**, we assume that **the system remains in equilibrium throughout the process**
- We say that the system passes through a series of equilibrium states (ie the change occurs slowly compared with the “response time” of the system)
- Such a change is known as a **QUASISTATIC** process

Reversible processes

- A reversible process as an idealised one, whose direction can be reversed with an *infinitesimal* change in conditions
- For a process to be reversible it must be **quasistatic** and there must be **no hysteresis** (internal/external “friction”)
- A reversible process produces no change in the entropy of the **universe** ($\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$): entropy of system can change, but entropy of surroundings must change by an equal and opposite amount

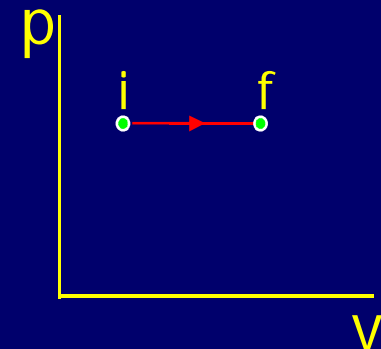
Important types of process

- *Isothermal* : occurs at constant_temperature
- *Isobaric* : occurs at constant_pressure
- *Isovolumic* : occurs at constant_volume
- *Adiabatic* : occurs without transfer_of_heat

NB, even there is no heat transfer, you can't assume that there is no temperature change.

An adiabatic process is not necessarily (or even usually isothermal

Isobaric process



Isovolumic process

