Lecture 9, Sep 27, 2022

More on Entropy

- Suppose we have a pure substance at absolute zero; all the molecules go to their lowest energy state
  - This means we only have 1 microstate, so $S = k \ln \Omega = 0$
- Entropy, unlike energy, has an absolute zero value
- At the molecular level this can be derived; but on a macroscopic level it needs to be a postulate

Definition

The Third Law of Thermodynamics: The entropy of a pure substance in thermodynamic equilibrium is zero at a temperature of 0K

The State Postulate

- How much information is contained in the state of a system? Is there a minimum list of variables from which you can calculate everything else?
  - We need mass of the system and its energy
  - We need one property for each mode of work (e.g. boundary work is specified by the volume; spring work is specified by the spring compression, etc)
    - *Simple compressible systems* are systems where the only mode of work is boundary work; for these we only need the volume
  - We need heat transfer, which can be specified by the internal energy U (since we already have work)

Definition

The State Postulate: The equilibrium state of a pure, simple compressible system is completely described by its: mass m, volume V and internal energy U

- Since entropy is a property this means $S = S(U, V, m)$
- Define the *specific entropy* $s = \dfrac{S}{m}$, which is a function of volume and energy: $s = s(u, v)$
  - Or $u = u(s, v)$ or $v = v(u, s)$
- In general to fix the state of a pure, simple compressible system, we need two independent intensive properties
- These 4 postulates are all we need to develop thermodynamics

Entropy Changes With Heat and Work

- Transfer of heat creates entropy, but work does not, why?
- Consider the energy levels ε_i each with n_i molecules: $U = \sum\limits_i n_i \varepsilon_i \implies \mathrm{d}U = \sum\limits_i \varepsilon_i \mathrm{d}n_i + \sum\limits_i n_i \mathrm{d}\varepsilon_i$
  - $\mathrm{d}n_i$ is a change in the number of molecules in each level – the rearrangement of molecules in energy levels
    - This would correspond to heating up the gas to shift the peak of the Maxwell-Boltzmann distribution to the right
    - The shifting of the distribution means now there are new energy states occupied, increasing the number of microstates
  - $\mathrm{d}\varepsilon_i$ is a change of the energy of the energy levels
    - This would correspond to lifting up the gas so every energy state now has more potential energy (the entire distribution gets shifted evenly)
    - This does not occupy new energy states, so the number of microstates stays the same

    - $\delta W = \sum_i n_i \mathrm{d}\varepsilon_i, \delta Q = \sum_i \varepsilon_i \mathrm{d}n_i \implies \mathrm{d}U + \delta W + \delta Q$

Reversible and Irreversible Processes

- A process that produces no entropy is reversible; conversely a process that process entropy is irreversible
    - e.g. in a rapid compression the molecules near the piston are compressed more than the others, which increases their energy by a greater amount; some molecules are shifted into higher energy states and entropy increases
    - On the other hand a quasi-static process has all the molecules compressed the same amount, moving the energies up but not redistributing them, so no entropy is created
- In reality all real processes are irreversible and generate entropy
- The universe is an isolated system, so $\Delta S > 0$
    - Initially all mass and energy is concentrated in a single point, which has very low entropy; after the big bang energy and mass are dispersing and energy increases
    - The universe tends to equilibrium, where all mass and energy are evenly distributed; at this point there is no more energy and mass gradient, so no work can be done and no processes happen

"Order" and "Disorder"

- When we say something is "orderly" and "disorderly", how do we actually define this?
    - e.g. a deck of hards has 52! of shuffling, and every combination has a probability of 1/52! but why do we think some are more "orderly" than others?
- We would need to define our microstates and macrostates
    - Microstates in this case is every combination of the cards
    - Microstates need to be changing randomly
    - The macrostate can be any macroscopic property, e.g. the number of black cards in the top half of the deck divided by 26
- Correct statement: *Isolated* systems that are *randomly alternating between microstates* go spontaneously from a macrostate that corresponds to a smaller number of microstates to a macrostate with a larger number of microstates
    - It's incorrect to say that systems simply go from being highly organized to being disorganized

Summary

The Postulates of Classical Thermodynamics

The Fundamental Concepts:

- Mass m
- Volume V
- Energy U
- Entropy S

The Four Postulates:

- First Law: $Q + W + \Delta E$
- Second Law: $\Delta S \geq 0$ for an isolated system
- Third Law: $S = 0$ for a pure substance at absolute zero
- State Postulate: $S = S(U, V, m)$

From these fundamental concepts and postulates, we can define everything else.