Lecture 8, Sep 26, 2022

Molecular Definition of Entropy

- Consider a rigid, insulated box divided into two parts: one with gas, the other with vacuum
  - When the partition is removed, the gas will expand and the pressure equalizes
  - This is accompanied by an increase in entropy
  - But why do the molecules spread out evenly?
- A *microstate* is a combination of the exact states of molecules (we cannot directly measure this); a *macrostate* is some kind of an average (we can measure this in terms of e.g. pressure)
- Divide the boxes into left and right, and consider if there were just 2 particles in the left box
  - We can either have both on one side and one on each side
  - Consider all the possibilities (*microstates*): LL, LR, RL and RR; in terms of *macrostates* (averages), the macrostate with an even distribution is more likely than all the molecules to one side
- If there are instead 4 particles, then there are 5 macrostates (4 left, 3 left + 1 right, etc)
  - The probability of all the particles being on one side is even smaller
- A probability distribution of the percentage of particles on one side would follow a Gaussian
  - The probability of having everything on one side decreases as the number of particles increases
  - The total number of states is 2^n, but there is only one state corresponding to all particles on one side
  - For a large number of particles the distribution is extremely sharp and essentially all cases are at equilibrium
- The equilibrium macrostate is the one that has the largest number of microstates (and thus the highest probability)
  - This leads us to define molecular entropy in terms of the number of microstates that correspond to each macrostate, so that as the system moves toward equilibrium, it increases
- For a very large number of particles, $S_{eq} = \Omega_{total}$
- But note entropy is an extensive property, i.e. if we have two systems with entropies S_1 and S_2, the entropy of the combined system should be $S_1 + S_2$
  - Consider if each system had N particles, then the combined system has $2N$ particles, so the number of microstates would be 2^{2N}
  - This prompts us to use logarithms

Equilibrium in a Gas

- Consider a gas in an isolated system
  - Constant mass defined by n, number of molecules
  - Constant energy determined by U, the internal energy
    - Note the energies of the molecules are not continuous but occupy discrete levels
- $n = \sum_i n_i$ where n_i is the number of molecules with energy ε_i
  - The total energy is $U = \sum_i \varepsilon_i n_i$
- Any arrangement of molecules that satisfies these constraints is a microstate
- At equilibrium the molecules will be in a *Maxwell-Boltzmann distribution*

- As the temperature goes up, the peak of the distribution moves to the right; more energy levels become available, and the distribution flattens out
- If Ω is the number of microstates that correspond to equilibrium state

Definition

$S = k \ln \Omega$, where Ω is the number of microstates of the system, and k is the Boltzmann constant, $k = 1.38 \times 10^{-23}$ J/K

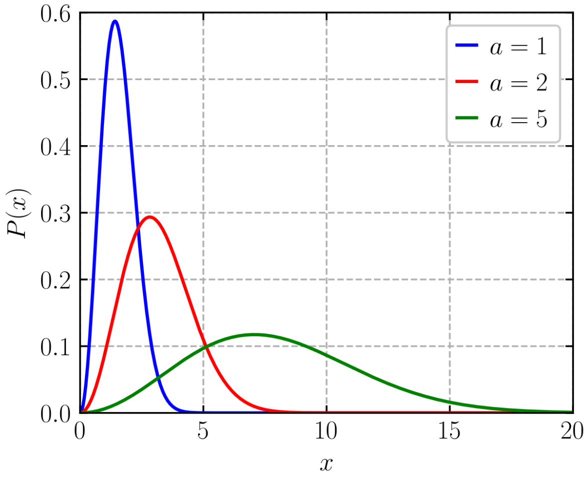

Figure 1: Maxwell-Boltzmann distribution plotted as a function of energy

- The Boltzmann constant makes this definition consistent with the Clausius definition based on heat transfer
- Consider the example at the beginning; we had Ω_i microstates before the partition was opened and Ω_f after the partition was opened ($\Omega f \gg \Omega i$)
  - This represents a positive entropy change of $\Delta S = k \ln \left(\frac{\Omega_f}{\Omega_i}\right)$
- To calculate Ω, we need to solve Schrödinger's Equation
- For a monoatomic ideal gas, with n molecules, volume of V and energy U, then $\Omega(U, V, n) = f(n)V^n U^{\frac{3}{2}n}$
  - Thus $S(U, V, n) = nk \ln V + \frac{3}{2} nk \ln U + k \ln f(n)$
  - $\Delta S = nk \left(\ln \frac{V_2}{V_1} + \frac{3}{2} \ln \frac{U_2}{U_1}\right)$
  - Recall $nk = NR_u = mR$ and $U \propto T$, therefore $\Delta S = mR \left(\ln \frac{V_2}{V_1} + \frac{3}{2} \ln \frac{T_2}{T_1}\right)$

Important

For a monoatomic ideal gas, $\Delta S = mR \left(\ln \frac{V_2}{V_1} + \frac{3}{2} \ln \frac{T_2}{T_1}\right)$