3.020 Lecture 28

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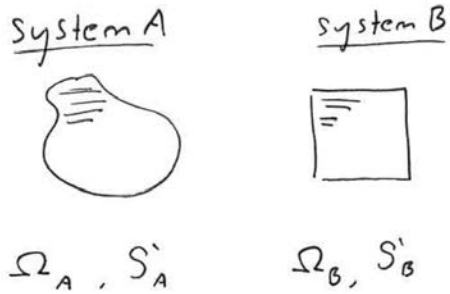
1 Boltzmann hypothesis

Preamble: Ω describes the stability of a macrostate.
The state with maximum Ω will appear to be the most stable in time.

Hypothesis: $S = f(\Omega)$
Entropy is a monotonically rising function of Ω

- Consider two isolated systems



$$\begin{aligned} S' &= S'_A + S'_B && \textbf{– extensive} \\ \Omega &= \Omega_A \cdot \Omega_B && \textbf{– combinatorics} \\ f(\Omega) &= f(\Omega_A \Omega_B) \\ &= f(\Omega_A) + f(\Omega_B) \\ &\Downarrow \end{aligned}$$

$$f(\Omega) = S = k_B \ln \Omega$$

Boltzmann entropy formula

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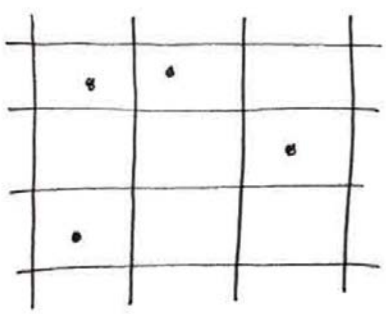
2 Configurational entropy



\# ways to put n molecules into r boxes.
boxes sufficiently small such that no box has more than 1 molecule

$$\Omega = \binom{r}{n} = \frac{r!}{r!\,(r-n)!}$$

- Let $r = \frac{V'}{b}$. V': total volume; b: voxel, take to be volume of a molecule
- Can show that $\ln \binom{r}{n} \approx n \ln r$ for $r >> n$

- Now let system expand from V' to $2V'$

$$\Delta S' = k_B\ n\ (\ln(\frac{2V'}{b}) - \ln\frac{V'}{b}) = k_B\ n \ln(\frac{2V'}{V'}) = k_B\ n\ \ln 2$$

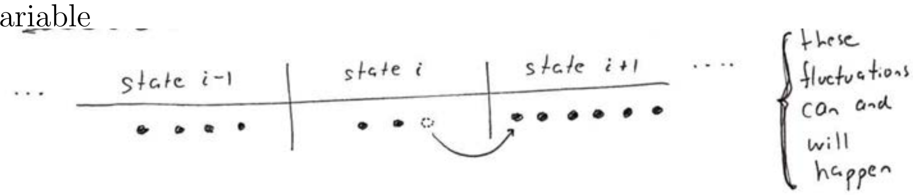
- Same as classical result for isothermal expansion of ideal gas
- $k_B n = R$ for $n = N_A$

3 Maximum entropy condition and the Boltzmann distribution

- Consider n_{TOT} particles distributed among r states according to occupation numbers $n_i = n_1, n_2, \ldots, n_r$

$$\begin{aligned} S' &= k_B \ln\left(\frac{n_{TOT}\ !}{\Pi_i\ n_i!}\right) \\ &= k_B\Big(n_{TOT}\ \ln n_{TOT} - n_{TOT} - \sum_i n_i \ln n_i + \sum_i n_i\Big) \quad \leftarrow \textbf{Using Stirling's approx.} \\ &= k_B\Big(n_{TOT} \ln n_{TOT} - \sum_i n_i \ln n_i\Big) \qquad \textbf{using} \quad \sum_i n_i = n_{TOT} \\ &= -k_B \sum_i n_i \ln\left(\frac{n_i}{n_{TOT}}\right) \end{aligned}$$

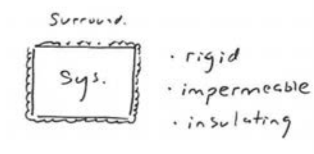
- The distribution of occupation numbers n_i is an <u>unconstrained</u> internal variable



- The maximum entropy condition $S = S_{MAX}$ requires that S is stationary w.r.t. all such unconstrained internal processes

$$dS' = -k_B \sum_i \Big(\ln n_i \; dn_i + \frac{n_i}{n_i} \; dn_i - \ln n_{TOT} \; dn_i - \frac{n_i}{n_{TOT}} \; dn_{TOT} \Big)$$
$$= -k_B \sum_i \; \ln \Big(\frac{n_i}{n_{TOT}} \Big) \; dn_i$$

- Isolation constraints
  - let ϵ_i be the energy per particle in state i



$$U' = \sum_i \epsilon_i \; n_i \quad \longrightarrow \quad dU = \sum_i \epsilon_i \; dn_i = 0 \qquad \textbf{conservation of energy}$$
$$n_{TOT} = \sum_i n_i \quad \longrightarrow \quad dn_{TOT} = \sum_i dn_i = 0 \qquad \textbf{conservation of mass}$$

Note: Conservation of volume connected to the $\epsilon_i' s$ being constants

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- Constrained optimization: Want to optimize S' subject to constraints that U', n_{TOT} are fixed

Method of Lagrange multipliers

$$\underline{\nabla} S' + \alpha \underline{\nabla} n_{TOT} + \beta \; \underline{\nabla} U' = 0 \qquad \textbf{as in calculus textbooks}$$
$$dS + \alpha \; dn_{TOT} + \beta \; dU' = 0$$

α, β: Lagrange multipliers

- Substitute expressions for dS, dU', dn_{TOT} and collect terms

$$\sum_i \underbrace{\Big(-k_B \ln \Big(\frac{n_i}{n_{TOT}} + \alpha + \beta \; \epsilon_i \Big) \Big)}_{\textbf{set each coefficient to zero}} \quad \underbrace{dn_i}_{\textbf{unconstrained}} \quad = 0$$

$$\Downarrow$$

$$-k_B \ln \Big(\frac{n_i}{n_{TOT}} \Big) + \alpha + \beta \; \epsilon_i = 0$$
$$\frac{n_i}{n_{TOT}} = e^{\alpha/k_B} \; e^{\beta \; \epsilon_i/k_B} \qquad \textbf{for each } i = 1, 2, \ldots, r$$

- Determine α by normalization

$$\sum_i \frac{n_i}{n_{TOT}} = 1$$

$$e^{\alpha/k_B} = \frac{1}{\sum_i e^{\beta \ \epsilon_i/k_B}} = \frac{1}{Q}$$

$$Q = \sum_i e^{\beta\epsilon_i/k_B} \qquad \textbf{partition function}$$

- Partition function normalizes the distribution function

$$\frac{n_i}{n_{TOT}} = \frac{e^{\beta\epsilon_i/k_B}}{Q}$$

$$\frac{n_i}{n_{TOT}} = \frac{e^{\beta\epsilon_i/k_B}}{Q}$$

The fraction of molecules in state i depends on energy ϵ_i