Equilibrium and non-equilibrium thermodynamics of small systems with emergent structures

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29th May 2020

Introduction

- L. Boltzmann defined entropy as the logarithm of state multiplicity: $S = k_B \log W$
- When multiplicity is a multinomial factor $W = \frac{n!}{\prod_{i=1}^{m} n_i!}$
  - we get *Boltzmann-Gibbs entropy* $S = -\sum_{i=1}^{m} p_i \log p_i$
  - *sample space* grows exponentially

$$W(n) = \sum_{\sum_{i=1}^{m} n_i = n} \frac{n!}{\prod_{i=1}^{m} n_i!} = m^n$$

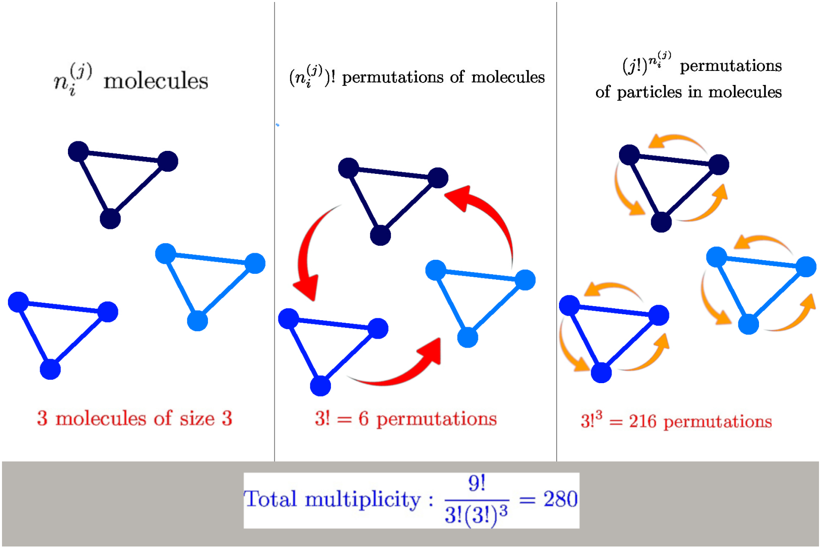
- Sample space of *complex systems* typically does not grow exponentially due to e.g., correlations (sub-exponential growth)
- Also we get super-exponential growth for systems with emergent structures - e.g., molecules

Multiplicity of a system with molecules

- Let us consider a system of n particles
- particles can have states $\{s_1^{(1)}, \ldots, s_{m_1}^{(1)}\}$
- Moreover, particles can form molecules
  - molecules of 2 particles have states $\{s_1^{(2)}, \ldots, s_{m_2}^{(2)}\}$
  - ...
  - molecules of j particles have states $\{s_1^{(j)}, \ldots, s_{m_j}^{(j)}\}$
- Maximum size of molecules - $m \quad (\leq n)$.
- There are $n_i^{(j)}$ molecules of size j and state $s_i^{(j)}$
- Altogether we have $\sum_{j=1}^{m} jn_j = n$ particles

Multiplicity of a system with molecules

- Entropy is given by the Boltzmann formula $S(\{n_i^{(j)}\}) = \log W(\{n_i^{(j)}\})$
- Let us focus on the multiplicity of state $\{n_i^{(j)}\}$
- Number of all configurations is $n!$
- Many of these configurations correspond to the same microstate
- For the case of single particles, all permutations of $n_i^{(1)}$ particles in the state $s_i^{(1)}$ correspond to the same state- this is $(n_i^{(1)})!$ states
- We will show that for molecules each state corresponds to $(n_i^{(j)})!(j!)^{n_i^{(j)}}$ permutations


$n_i^{(j)}$ molecules
$(n_i^{(j)})!$ permutations of molecules
$(j!)^{n_i^{(j)}}$ permutations
of particles in molecules
3 molecules of size 3
$3! = 6$ permutations
$3!^3 = 216$ permutations
Total multiplicity : $\frac{9!}{3!(3!)^3} = 280$

Entropy of a system with molecules

- Total multiplicity is therefore

$$W(\{n_i^{(j)}\}) = \frac{n!}{\prod_{ij} n_i^{(j)}!(j)!^{n_i^{(j)}}}$$

- Entropy can be expressed as (using Stirling's approximation)

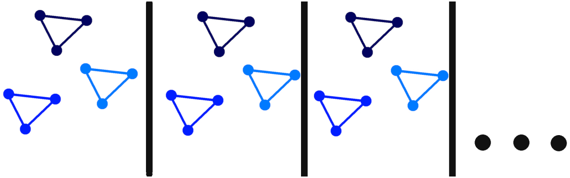
$$S = n \log n - \sum_{ij} n_i^{(j)} \log n_i^{(j)} - \sum_{ij} n_i^{(j)} \log j!$$

- Defining $p_i^{(j)} = n_i^{(j)}/n$, we end with

$$S/n = -\sum_{ij} p_i^{(j)} \log p_i^{(j)} - \sum_{ij} p_i^{(j)} \log \frac{j!}{n^{j-1}}$$

Finite range interaction

- Until now, we allowed all particles to form molecules
- Real systems have finite interaction range
- simple model - consider b boxes



- Particles can form molecules only in boxes
- Resulting entropy

$$S/n = -\sum_{ij} p_i^{(j)} \log p_i^{(j)} - \sum_{ij} p_i^{(j)} \log \frac{j!}{c^{j-1}}$$

where $c = n/b$ is "concentration" of particles

MaxEnt distribution

- Consider a Hamiltonian $H = \sum_{ij} \epsilon_i^{(j)} p_i^{(j)}$
- Maximize Lagrange functional

$$L = S/n - \alpha \left(\sum_{ij} j p_i^{(j)} - 1 \right) - \beta \left(\sum_{ij} \epsilon_i^{(j)} p_i^{(j)} - U \right)$$

- MaxEnt distribution can be found in the following form

$$\hat{p}_i^{(j)} = \frac{c^{j-1}}{j!} \exp\left(-j\alpha - 1 - \beta \epsilon_i^{(j)} \right)$$

- α is calculated from normalization condition $\sum_{ij} j p_i^{(j)} = 1$ as

$$\sum_j \left[\frac{c^{j-1}}{e(j-1)!} \sum_i e^{-\beta \epsilon_i^{(j)}} \right] \left(e^{-\alpha} \right)^j = 1$$

Thermodynamics

- We obtain thermodynamics from the following relation

$$S = \alpha + \beta U + \sum_{ij} p_i^{(j)}$$

- Helmholtz free energy

$$F = U - TS = -\frac{\alpha}{\beta} - \frac{\sum_{ij} p_i^{(j)}}{\beta}$$

- Key quantity: $M = \sum_{ij} p_i^{(j)}$ number of molecules per particle

Non-equilibrium thermodynamics

- Let us consider a general linear Markovian evolution given by master equation

$$\dot{p}_i^{(j)}(t) = \sum_{kl} \left(w_{ik}^{jl} p_k^{(l)}(t) - w_{ki}^{lj} p_i^{(j)}(t) \right)$$

- We consider detailed balance for equilibrium distribution

$$\frac{w_{ik}^{jl}}{w_{ki}^{lj}} = \frac{j!}{l!} c^{l-j} \exp\left[\alpha(l-j) + \beta \left(\epsilon_k^{(l)} - \epsilon_i^{(j)} \right) \right]$$

2nd law of thermodynamics

- Time derivative of entropy can be expressed as

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\sum_{ij} \dot{p}_i^{(j)} \log p_i^{(j)} - \sum_{ij} \dot{p}_i^{(j)} - \sum_{ij} \dot{p}_i^{(j)} \log \left(\frac{j!}{c^{j-1}} \right)$$

- The second term does not vanish. It is equal to $\dot{M}$.
- After a straightforward calculation, we obtain that

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\frac{\mathrm{d}M}{\mathrm{d}t} + \beta \dot{Q} + \dot{S}_i$$

Fluctuation theorems for molecule systems

- Time derivative of free energy is therefore

$$\dot{F} = \dot{U} - T\dot{S} = \dot{W} + \cancel{\dot{Q}} + T\dot{M} - \cancel{\dot{Q}} - T\dot{S}_i$$

- Thus, entropy production is equal to

$$\Delta S_i = \beta(W - \Delta F) + \Delta M$$

- From this, we directly obtain Crooks' fluctuation theorem

$$\frac{P(W)}{\tilde{P}(\tilde{W})} = \exp\left(\beta(W - \Delta F) + \Delta M\right)$$

and Jarzynski equality

$$\langle \exp(-\beta W) \rangle = \exp(-\beta \Delta F + \Delta M)$$

Perspectives

- Thermodynamics of small closed chemical networks
- Critical phenomena for systems with emergent structures
  - First step - fully connected Ising model with molecule states
  - Next steps - applications of information geometry
- Reference: J. Korbel, S. D. Lindner, R. Hanel and S. Thurner, arXiv:2004.06491