# MATH327: StatMech and Thermo

Tuesday, 10 February 2026

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**Something to consider**

A micro-canonical system in thermodynamic equilibrium adopts all possible micro-states with equal probability.

How can this explain the smooth and stable distribution of the $\sim 10^{25}$ molecules that compose the air in this room?

Recap

Statistical ensembles

↳ Stochastically sampling micro-states $\omega_i$ with prob $p_i$

Conserve $E$, $N$ → micro-canonical ensemble

"First law"

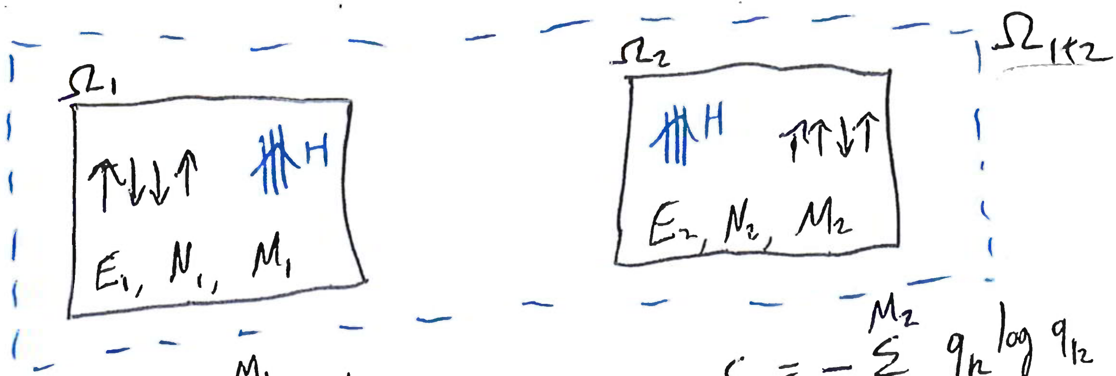
Entropy $S = -\sum_{i=1}^{M} p_i \log p_i$

Thermodynamic equilibrium

↳ Micro-canonical all $p_i$ equal → $S = \log M$

Today

Second law → generalize therm equil. based on entropy




$$S_1 = -\sum_{i=1}^{M_1} p_i \log p_i \qquad S_2 = -\sum_{k=1}^{M_2} q_k \log q_k$$

What is $S_{1+2}$?

For each $\underset{p_i}{w_i} \in \Omega_1$, $M_2$ micro-states from $\Omega_2$ ($q_k$)

$\therefore$ $M_{1+2} = M_1 M_2$ micro-states with prob. $p_i q_k$

Sanity check: $\sum_{M_{1+2}} p_i q_k = \sum_{i=1}^{M_1}\sum_{k=1}^{M_2} p_i q_k = \Big(\underbrace{\sum_i p_i}_{1}\Big)\Big(\underbrace{\sum_k q_k}_{1}\Big) = 1$ ✓

$$\boxed{\begin{aligned} S_{1+2} &= -\sum_{i,k} p_i q_k \log(p_i q_k) = \sum_{i,k} p_i q_k \left(\log p_i + \log q_k\right) \\ &= -\sum_i p_i \log p_i \Big(\underbrace{\sum_k q_k}_{1}\Big) - \Big(\underbrace{\sum_i p_i}_{1}\Big) \sum_k q_k \log q_k = S_1 + S_2 \end{aligned}}$$

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Extensive quantity adds up across independent subsystems

$S_{1+2} = S_1 + S_2 \qquad N_{1+2} = N_1 + N_2 \qquad E_{1+2} = E_1 + E_2$

<u>Intensive</u> quantity independent of extent of system
temperature, pressure, density

$M_{1+2} = M_1 M_2$ neither intensive nor extensive

If each of $\Omega_1$, $\Omega_2$ in therm. equil.

$p_i = \frac{1}{M_1}$ $\qquad$ $q_k = \frac{1}{M_2}$

$S_1 = \log M_1$ $\qquad$ $S_2 = \log M_2$

$p_i q_k = \frac{1}{M_1} \cdot \frac{1}{M_2} = \frac{1}{M_{1+2}}$ → also in equil.

$S_{1+2} = \log M_{1+2} = \log M_1 + \log M_2 = S_1 + S_2$ ✓

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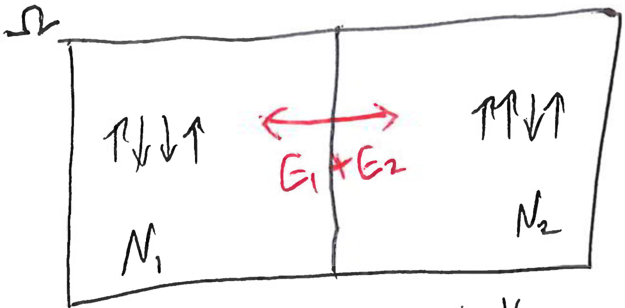
Now put subsystems in <u>thermal contact</u>
└ exchange energy, not particle




wait for equilibrium

Total $E = E_1 + E_2$ still conserved → $\Omega$ is micro-canonical
subsystems are not

How many micro-states $M$ for overall $\Omega$?

Use energy conservation: $\left.\begin{array}{r} e_1 \text{ from } N_1 \\ E - e_1 \text{ from } N_2 \end{array}\right\}$ $M_{e_1} = M^{(1)}_{e_1} M^{(2)}_{E-e_1}$

Overall $M = \sum_{e_1} M^{(1)}_{e_1} M^{(2)}_{E-e_1}$

└ $e_1 = E_1$ accounts for all $M_{1+2} = M_1 M_2 = M^{(1)}_{E_1} M^{(2)}_{E_2}$

$$M = M_{1+2} + \sum_{e_1 \neq E_1} M^{(1)}_{e_1} M^{(2)}_{E-e_1} \geq M_{1+2}$$

$\rightarrow M > M_{1+2}$ unless $\{E_1, E_2\}$ only possible distribution
very special case

Result $S = \log M \geq \log(M_{1+2}) = S_{1+2} = S_1 + S_2$

Second law of thermodynamics

When isolated subsystems in therm. equil.
are brought into thermal contact
entropy $S \geq S_1 + S_2$ can never decrease

Increases except in very special cases

More generally, entropy never decreases as time passes
(generally increases)

$\rightarrow$ System (with finite $M$) is in
thermodynamic equilibrium
if its entropy is maximal

Holds for any stat. ensemble

Let's check micro-canonical

Maximize $S = -\sum_i p_i \log p_i$ with conserved $E, N$
and $\sum_i p_i = 1$

Use Lagrange multiplier

$$\bar{S}(\lambda) = S + \lambda\left(\sum_i p_i - 1\right) = -\sum_i p_i \log p_i + \lambda\left(\sum_i p_i - 1\right)$$

1) Maximize $\bar{S}(\lambda)$ w.r.t. $p_k$

2) Impose $\sum_i p_i = 1 \rightarrow \frac{\partial \bar{S}}{\partial \lambda} = 0$ so $\max \bar{S} \leftrightarrow \max S$

$\bar{S}(\lambda = 0)$

$$\frac{\partial S}{\partial p_k} = 0 = \frac{\partial}{\partial p_k}\left[ - \sum_i p_i \log p_i + \lambda \left( \sum_i p_i - 1 \right) \right]$$

$$= - \log p_k - \underbrace{\frac{\cancel{p_k}}{\cancel{p_k}}}_{1} + \lambda$$

$$\log p_k = \lambda - 1 \quad \rightarrow \quad p_k = \exp(\lambda - 1) = \text{const.} = \frac{1}{M} \quad \checkmark$$

$$S = \log M$$

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Derived micro-canonical def. of therm. equil. from entropy maximization