MSE-421 Statistical Mechanics

Exercise Session 2

Kevin Kazuki Huguenin-Dumittan

EPFL, Switzerland

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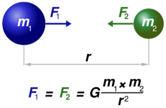
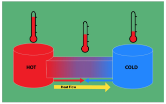
Goal of Statistical Mechanics:

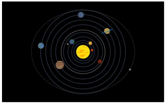


Classical Mechanics

StatMech ⟷

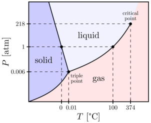
Thermo-dynamics



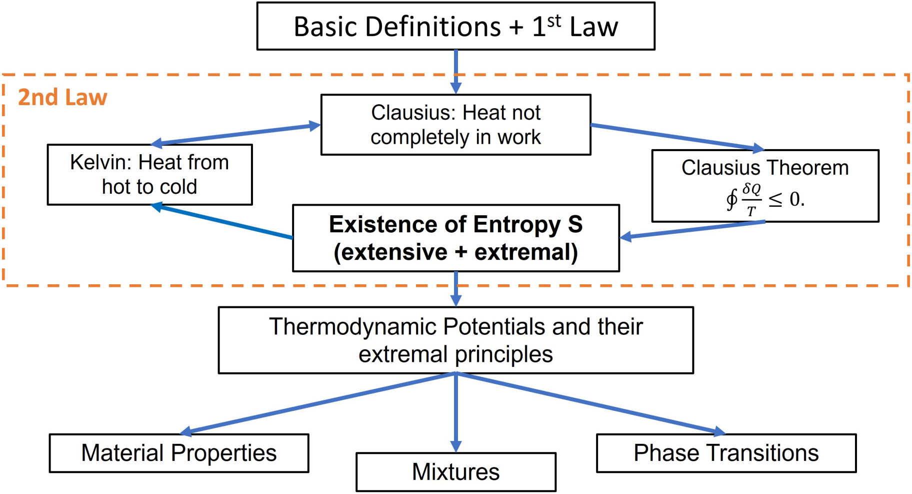


- Particles
- Forces
- Everything is Continuous
- Reversible time evolution

- Macroscopic Bodies
- Temperature
- Entropy
- Phase Transitions
- Irreversible Processes



Logical Structure of Thermodynamics



Basic Definitions + 1^{st} Law

2nd Law

Clausius: Heat not completely in work

Kelvin: Heat from hot to cold

Clausius Theorem $\oint \frac{\delta Q}{T} \leq 0.$

Existence of Entropy S (extensive + extremal)

Thermodynamic Potentials and their extremal principles

Material Properties

Mixtures

Phase Transitions

Key concept: Change of variables.
Example: Ideal gas law

$$pV = Nk_B T \tag{1}$$

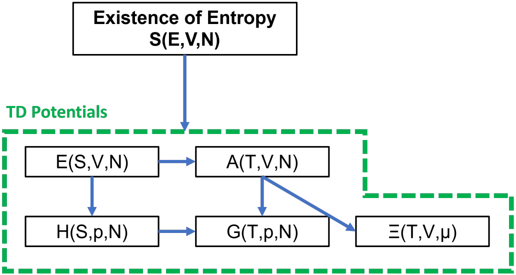
Describe system using (T, p, N):

$$V = V(T, p, N) = \frac{Nk_B T}{p} \tag{2}$$

or using (T, V, N):

$$p = p(T, V, N) = \frac{Nk_B T}{V} \tag{3}$$

Thermodynamic Potentials



Existence of Entropy
S(E,V,N)

TD Potentials

E(S,V,N)

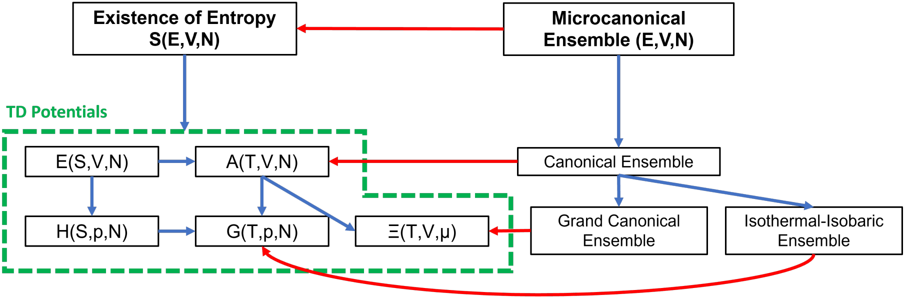
A(T,V,N)

H(S,p,N)

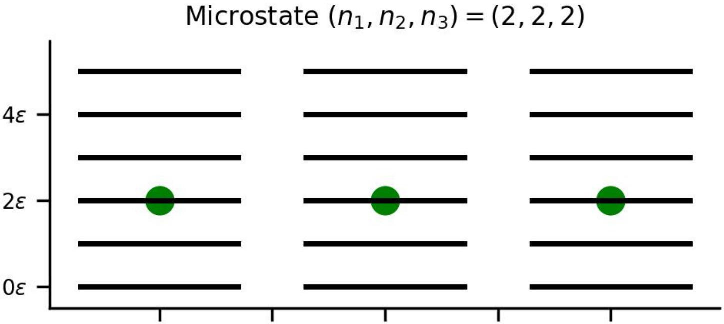
G(T,p,N)

Ξ(T,V,μ)

Thermodynamic Potentials



Example: Macrostate $(N, E) = (3, 6\epsilon)$, where $E = E_1 + E_2 + E_3$. Microstate determined by three numbers (n_1, n_2, n_3).



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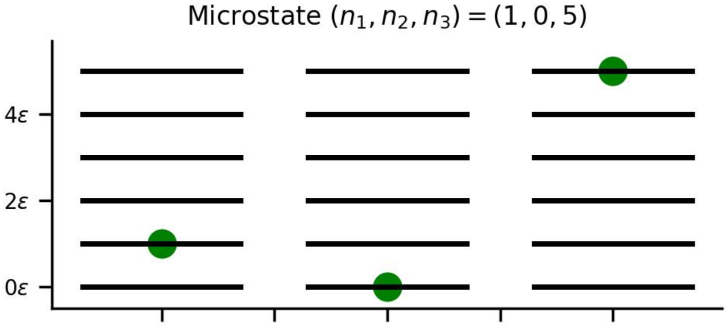

Microcanonical ensemble:

Given: (E, V, N)

$$P(\nu) \propto \begin{cases} 1 & \text{if} \quad E_\nu = E \\ 0 & \text{else} \end{cases} \tag{4}$$

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Normalization:

$$P(\nu) = \begin{cases} \frac{1}{\Omega} & \text{if} \quad E_\nu = E \\ 0 & \text{else} \end{cases} \tag{5}$$

with $\Omega =$ number of microstates ν having the energy E

Canonical ensemble

Given: (T, V, N)

$$P(\nu) \propto e^{-E_\nu/k_B T} = e^{-\beta E_\nu} \tag{6}$$

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Normalization:

$$P(\nu) = \frac{e^{-E_\nu/k_B T}}{Q} = \frac{e^{-\beta E_\nu}}{Q} \tag{7}$$

with $Q = \sum_{\nu \in \text{microstates}} e^{-E_\nu/k_B T} = \sum_{\nu \in \text{microstates}} e^{-\beta E_\nu}$.

Boltzmann vs Gibbs Entropy

Microcanonical Ensemble: Boltzmann Entropy

$$S_{\mathrm{Boltzmann}}(N, E) = k_B \log \Omega(N, E). \tag{8}$$

Canonical Ensemble (and others): Gibbs Entropy

$$S_{\mathrm{Gibbs}}[P] = -k_B \sum_{\nu} P(\nu) \log(P(\nu)) = -k_B \langle \log P \rangle. \tag{9}$$

Theorem: Boltzmann entropy is a special case of Gibbs entropy in the special case of uniform probability.
Example: Dice roll with $\nu = 1, 2, \ldots, 6 = \Omega$ outcomes with the same probability $P(\nu) = 1/6$. Then:

$$S_{\mathrm{Boltzmann}} = k_B \log \Omega = k_B \log 6 \tag{10}$$

agrees with

$$S_{\mathrm{Gibbs}} = -k_B \sum_{\nu=1}^{6} P(\nu) \log(P(\nu)) = -k_B \sum_{\nu=1}^{6} \frac{1}{6} \log \frac{1}{6} \tag{11}$$

$$= -k_B \cdot 6 \cdot \left(\frac{1}{6} \log \frac{1}{6} \right) = -k_B \log \frac{1}{6} = +k_B \log 6. \tag{12}$$

Example: Alice and Bob want to calculate the energy, temperature and entropy of a solid using (for example) the classical Einstein model.

- Alice uses the microcanonical ensemble (E, N)
- Bob uses the canonical ensemble (T, N)

Microcanonical ensemble:

What does Alice do?

1. Fix the variables (E, N).
2. Count the number of states $\Omega(E, N)$.
3. Boltzmann entropy $S(E, N) = k_B \log \Omega(E, N)$
4. Temperature from $\frac{1}{T(E,N)} = \frac{\partial S}{\partial E}$.

For the classical Einstein model, she gets

$$T = \frac{E}{3Nk_B}. \tag{13}$$

Thus, starting from $E = 200\mathrm{J}$, she obtains $T = 350\mathrm{K}, S = 400\mathrm{J/K}$ etc.

Canonical ensemble:

What does Bob do?

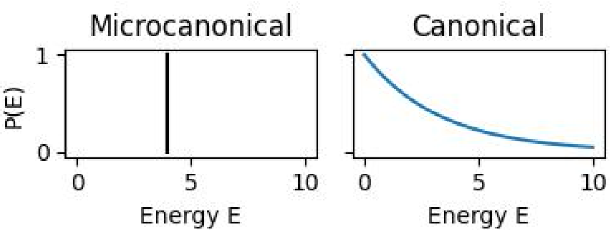
1. Fix the variables (T, N).
2. Compute the Partition function $Q(T, N)$.
3. Internal energy $E(T, N) = -\frac{\partial \log Q}{\partial \beta}$
4. Entropy $S = -k_B \langle \log P \rangle$

For the classical Einstein model, he gets

$$E = 3Nk_B T. \tag{14}$$

Thus, starting from $T = 350\mathrm{K}$, he obtains $E = 200\mathrm{J}, S = 400\mathrm{J}/\mathrm{K}$ etc.

Quantity	Alice (micro, E)	Bob (canon, T)
E	**200J**	200J
T	350K	**350K**
S	$400\mathrm{J}/\mathrm{K}$	$400\mathrm{J}/\mathrm{K}$
$P(\nu)$	$P(\nu) = \begin{cases} \frac{1}{\Omega} & \text{if} \quad E_\nu = E \\ 0 & \text{else} \end{cases}$	$P(\nu) = \frac{e^{-\beta E_\nu}}{Q}$



Recall: In the **thermodynamic limit** $N \to \infty$, probabilistic predictions become exact! This will also be our savior to the inconsistencies!

Today: 3 Exercises

1. Boltzmann vs Gibbs Entropy
2. Microcanonical vs Canonical Ensemble
3. (optional): understand the solution to inconsistencies

Three key concepts to understand StatMech:

1. Nature tries to minimize the (Helmholtz) free energy

$$A = E - TS \tag{15}$$

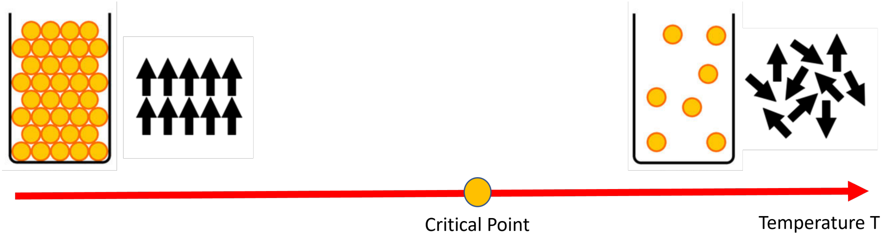
2. The Boltzmann (Planck) entropy formula

$$S = k_B \log \Omega \tag{16}$$

3. The canonical probability measure

$$P(\nu) \propto e^{-\frac{E_\nu}{k_B T}} \tag{17}$$

Minimization of the free energy: $A = E - TS$



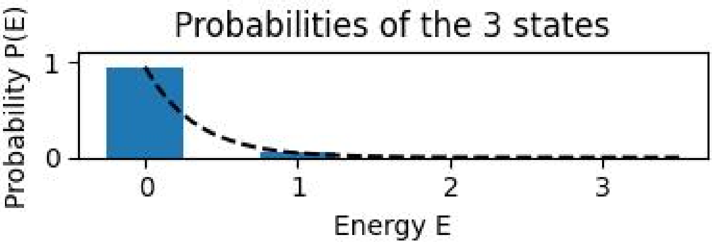
Critical Point

Temperature T

Example: 3 level system. $E_1 = 0, E_2 = 1, E_3 = 3$.
As $T \to 0$: Entire probability concentrated in ground state

$$P(1) = 1, \quad P(2) = 0, \quad P(3) = 0 \tag{18}$$

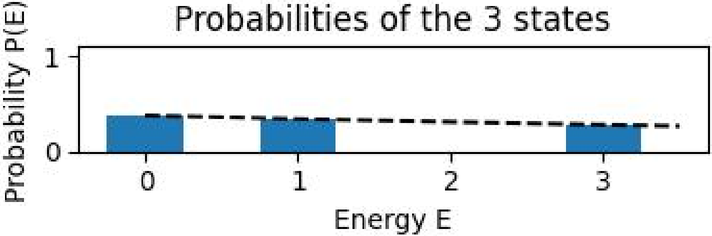
$$E \to 0, \quad S \to k_B \log \Omega = k_B \log 1 = 0. \tag{19}$$



Example: 3 level system. $E_1 = 0, E_2 = 1, E_3 = 3$.
As $T \to \infty$: All three states have equal probability.

$$P(1) = \frac{1}{3}, \quad P(2) = \frac{1}{3}, \quad P(3) = \frac{1}{3} \tag{20}$$

$$E \to \frac{E_1 + E_2 + E_3}{3} = \frac{4}{3}, \quad S \to k_B \log \Omega = k_B \log 3 \tag{21}$$



In reality, we have N independent and identical particles. What then are the energies and entropies as $T \to 0, \infty$? Due to independence:

$$E = N \cdot E_{\mathrm{single}}, \quad S = N \cdot S_{\mathrm{single}} \tag{22}$$

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$$E = N \cdot E_{\text{single}}, \quad S = N \cdot S_{\text{single}} \tag{22}$$

- As $T \to 0$:

$$E \to 0 \quad S \to 0 \tag{23}$$

- As $T \to \infty$:

$$E \to \frac{4}{3}N, \quad S \to Nk_B \log 3 \tag{24}$$

Calculation tricks using the Stirling approximation for $N \to \infty$

$$\log N! \sim N \log N - N \tag{25}$$

Application to combinatorial expressions:

$$\log \begin{pmatrix} n \\ k \end{pmatrix} = \log({}_nC_k) = \log \frac{n!}{k!(n-k)!} \tag{26}$$

$$= \log n! - \log k! - \log(n-k)! \tag{27}$$

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Application to combinatorial expressions:

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$$= \log n! - \log k! - \log(n-k)! \tag{27}$$

reduces to only 3 terms

$$\log \binom{n}{k} \sim n \log n - k \log k - (n-k) \log(n-k) \tag{28}$$

→ just use $\log N! \approx N \log N$ without the "$-N$" part (these cancel).

Let us take derivatives of

$$\log \left(\begin{array}{c} n \\ k \end{array} \right) \sim n \log n - k \log k - (n-k) \log(n-k) \tag{29}$$

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$$\log \binom{n}{k} \sim n \log n - k \log k - (n-k) \log(n-k) \tag{29}$$

A similar cancellation yields:

$$\frac{\partial}{\partial n} \log \binom{n}{k} = \log n - \log(n-k) = \log\left(\frac{n}{n-k}\right) \tag{30}$$

$$\frac{\partial}{\partial k} \log \binom{n}{k} = \log(n-k) - \log k = \log\left(\frac{n-k}{k}\right). \tag{31}$$

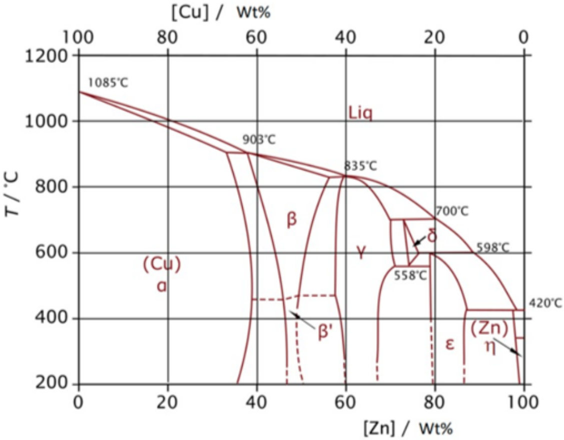
Cheat sheet for exercise session 2:

- Boltzmann entropy $S_{\mathrm{Boltzmann}} = k_B \log \Omega(N, E)$
- Gibbs entropy $S_{\mathrm{Gibbs}}[P] = -k_B \sum_\nu P(\nu) \log(P(\nu))$
- Temperature from entropy: $\frac{1}{T} = \frac{\partial S}{\partial E}$
- Stirling approximation $\log N! \sim N \log N - N$
- Shortcut for combinatorial expressions of the form $\begin{pmatrix} n \\ k \end{pmatrix}$:

  Just use $\log N! \sim N \log N$ (the other term cancels)
- For equations like $\log x - \log y = E$, write $\log \frac{x}{y} = E$ and thus $\frac{x}{y} = e^E$ (fraction form is simpler).
  On the other hand, if you need to take derivatives (e.g. with respect to x or y), keep it as $\log x - \log y$.

Boltzmann vs Gibbs Entropy:

Phase diagram of brass:



Given $N = 10^{24}$ total atoms and a desired composition for β brass. How do we compute the entropy (of mixing) for this system?

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Alice (fixed M): For a composition of $p = 0.5 = 50\%$, I assume that the number of Zn atoms is exactly $M = N/2 = 5 \cdot 10^{23}$. Then:

$$S_{\text{Boltzmann}} = k_B \log \binom{N}{M} . \tag{32}$$

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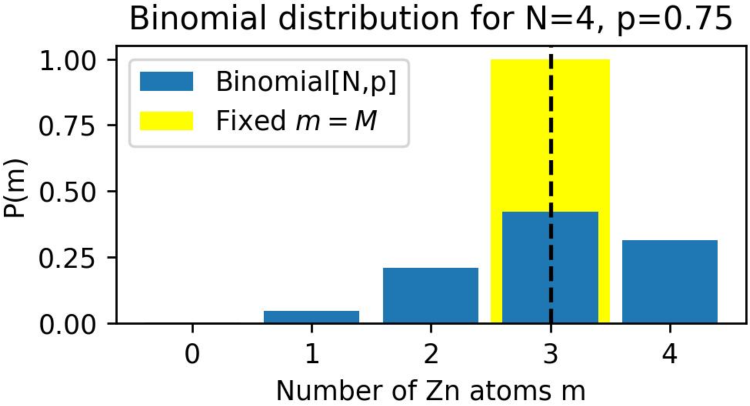
$$S_{\mathrm{Boltzmann}} = k_B \log \binom{N}{M} . \tag{32}$$

Bob (fixed p): For a composition of $p = 0.5$, I will assume that each position in the lattice is occupied by a Zn atom with a probability of p. Thus:

$$S_{\mathrm{Gibbs}} = -Nk_B \left[p \log p + (1-p) \log(1-p) \right] . \tag{33}$$

Boltzmann vs Gibbs entropies: Comparison of probability distributions at fixed M with $\binom{N}{M}$ states vs fixed $p = \frac{M}{N}$.



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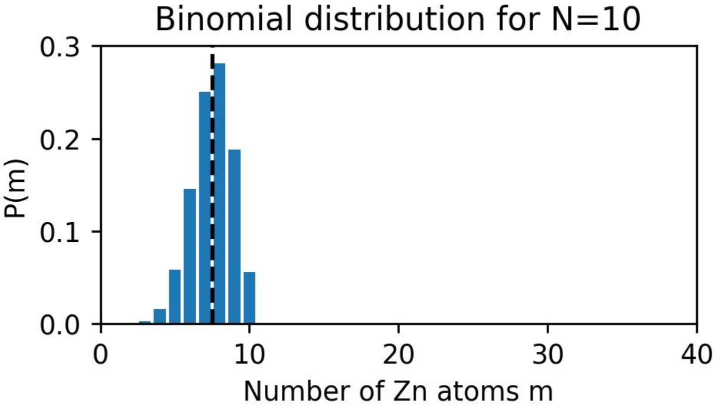

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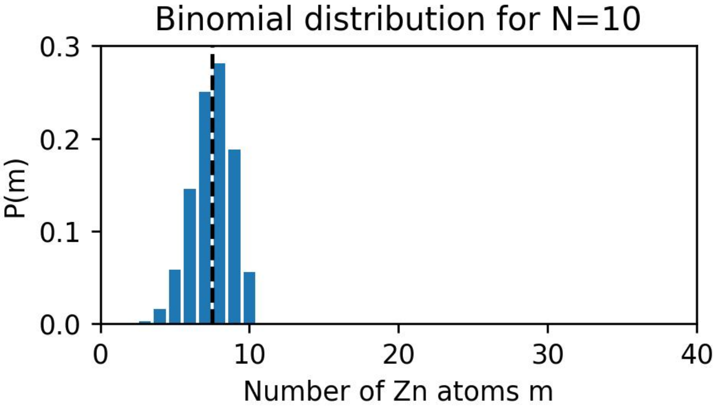

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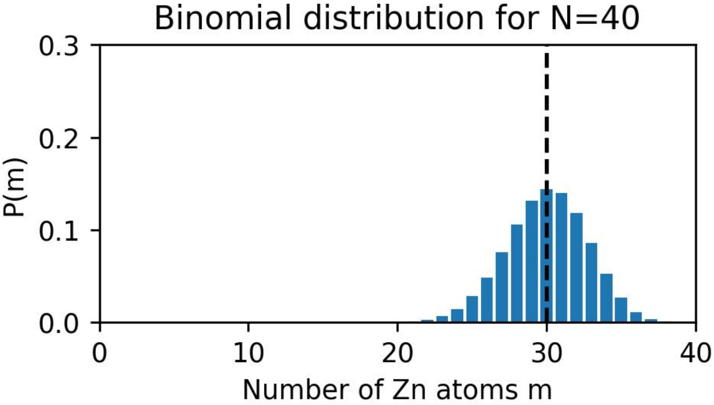
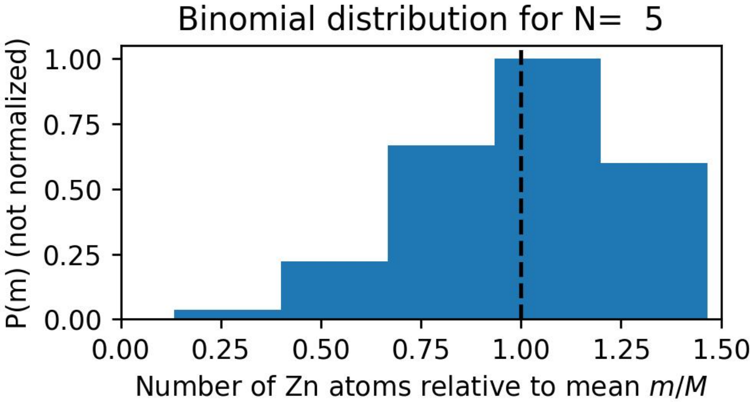


Same plots, but fix the x-axis so that the mean is always in the same spot.



Thus, in a certain sense, the probability measure at fixed p

$$P_{\mathrm{canonical}}(m) = \binom{N}{m} p^m (1-p)^{N-m} \tag{34}$$

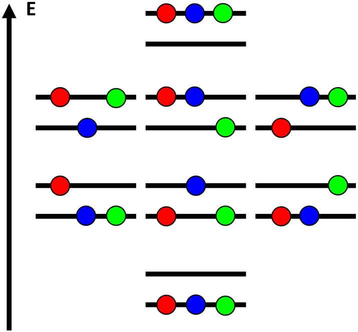
converges to the probability measure at fixed $m = M$

$$\tilde{P}_{\mathrm{micro}}(\frac{m}{N}) = \begin{cases} 1 & m/N = p \\ 0 & \mathrm{else} \end{cases} . \tag{35}$$

And hence the asymptotic equivalence as $N \to \infty$:

$$S_{\mathrm{Alice}} \sim S_{\mathrm{Bob}} \tag{36}$$

Microcanonical vs Canonical: 2-level system. Each particle can have energies 0 or ϵ (example for $N = 3$).



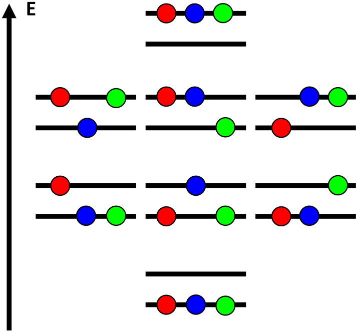
Alice (microcanonical):
Fix total energy E.

$$P(\nu) = \begin{cases} \frac{1}{\Omega} & \text{if} \quad E_\nu = E \\ 0 & \text{else} \end{cases} \tag{37}$$

For the energy:

$$P_{\text{micro}}(E') = \begin{cases} 1 & E' = E \\ 0 & \text{else} \end{cases} \tag{38}$$

Microcanonical vs Canonical: 2-level system. Each particle can have energies 0 or ϵ (example for $N = 3$).



Bob (canonical):
Fix temperature T.

$$P(\nu) = \frac{1}{Q} e^{-\beta E_\nu} \tag{39}$$

For the energy:

$$P_{\text{canonical}}(E) = \sum_{\nu : E_\nu = E} P(\nu)$$

$$= \sum_{\nu : E_\nu = E} \frac{e^{-\beta E_\nu}}{Q} = \Omega(N, E) \frac{e^{-\beta E}}{Q}.$$

In the canonical case, since $\log Q$ is extensive, the mean and variance scale as:

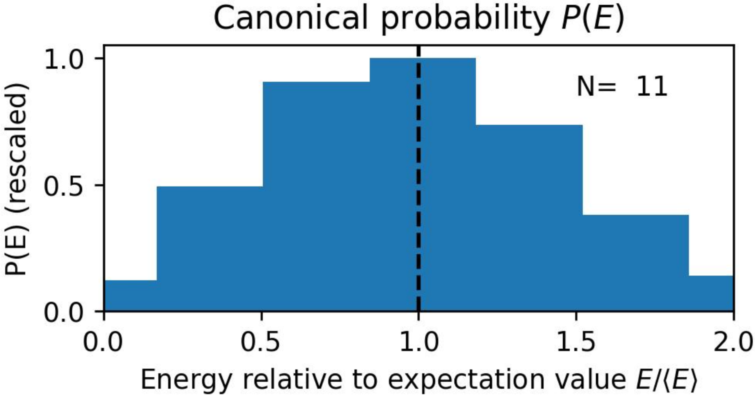
$$\langle E \rangle = -\frac{\partial \log Q}{\partial \beta} \propto N \tag{40}$$

$$\mathrm{Var}[E] = -\frac{\partial^2 \log Q}{\partial \beta^2} \propto N \tag{41}$$

and thus

$$\sigma(E) = \sqrt{\mathrm{Var}[E]} \propto \sqrt{N} \tag{42}$$

Convergence of the canonical $P(E)$ to the microcanonical one:



Where does this come from? Recall:

$$P_{\text{canonical}}(E) = \sum_{\nu : E_\nu = E} P(\nu) = \sum_{\nu : E_\nu = E} \frac{e^{-\beta E_\nu}}{Q} = \Omega(N, E) \frac{e^{-\beta E}}{Q}.$$

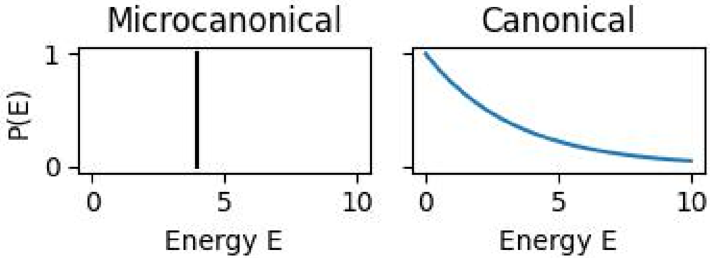
One example for possible behavior:

$$\Omega(N, E) \propto E^N \tag{43}$$

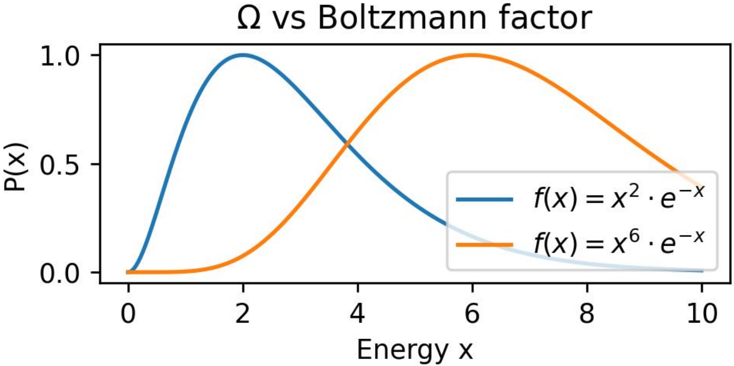
Then:

$$P(E) \propto \Omega e^{-\beta E} \propto E^N e^{-\beta E} \tag{44}$$

Example for $P(E) \propto \Omega e^{-\beta E} \propto E^N e^{-\beta E}$:



Example for $P(E) \propto \Omega e^{-\beta E} \propto E^N e^{-\beta E}$:



Where is the peak of the probability?

Where is the peak of the probability? Using

$$S = k_B \log \Omega \Leftrightarrow \Omega = e^{\frac{S}{k_B}}, \tag{45}$$

we get:

$$P_{\text{canonical}}(E) \propto \Omega(N, E)e^{-\beta E} = e^{\frac{S}{k_B}} e^{-\beta E} = e^{-\beta(E - TS)} \tag{46}$$

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$$S = k_B \log \Omega \Leftrightarrow \Omega = e^{\frac{S}{k_B}}, \tag{45}$$

we get:

$$P_{\text{canonical}}(E) \propto \Omega(N,E) e^{-\beta E} = e^{\frac{S}{k_B}} e^{-\beta E} = e^{-\beta(E-TS)} \tag{46}$$

The maximum of $P_{\text{canonical}}(E)$ is at the minimum of $E - TS$. Thus, the probability peaks where the **free energy is minimized**!

Three key concepts to understand StatMech:

1. Nature tries to minimize the (Helmholtz) free energy

$$A = E - TS \tag{47}$$

2. The Boltzmann (Planck) entropy formula

$$S = k_B \log \Omega \tag{48}$$

3. The canonical probability measure

$$P(\nu) \propto e^{-\frac{E_\nu}{k_B T}} \tag{49}$$