* I will collect today's exercise (1 per group)
* Office hours: next week by appointment only (away Mon–Tues)
* Subsequently: M 12:15 – 1:30 + by appointment
* Quinn's OH moved to Varian 4th floor

Today: Entropy

(1) Simulation of Ehrenfest's urns

(2) Entropy — definition, intuitions from model system of paramagnet.

⟶ 2nd Law of Thermodynamics

Names:

EXERCISE 2A: ENTROPY AS MISSING INFORMATION

New concepts:

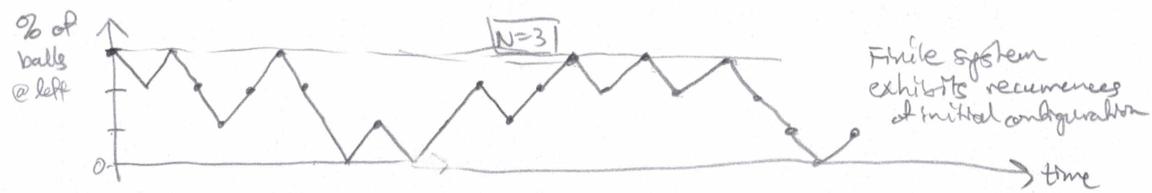
- **Entropy** as missing information
- The **fundamental assumption** of statistical mechanics
- The **First Law** and **Second Law of Thermodynamics**
- **Ensembles**; the **microcanonical ensemble**.

Reference: Kittel & Kroemer, Ch. 2

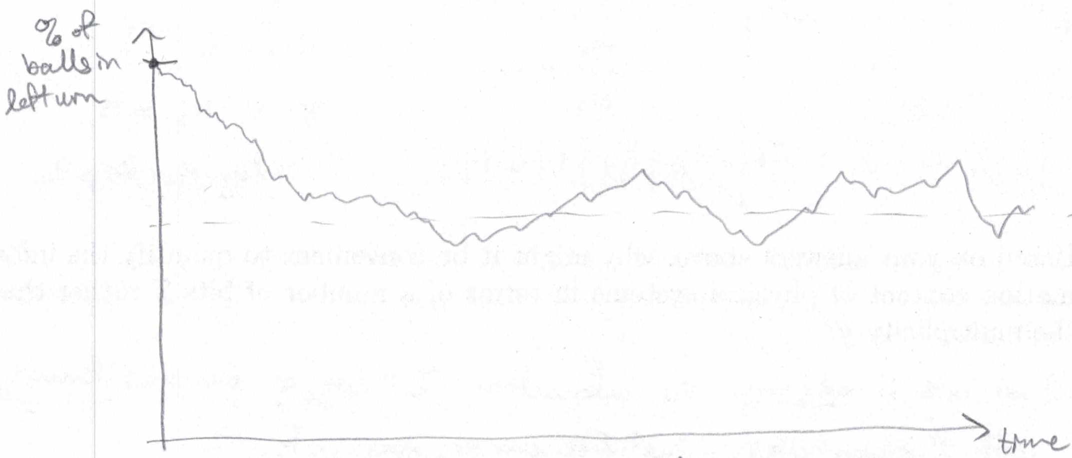
1. *Ehrenfest's Urns.* Watch the simulation of Ehrenfest's urns with $N = 3$ balls.

   a. Explain in words the microscopic laws governing the time evolution of the system.

   At each time step, a random ball is switched from one urn to the other.



   b. The plot labeled "percentage of balls" indicates the **macrostate** of the system. How will this plot look if we initialize the system with $N = 50$ balls in the left urn and allow it to evolve for a few hundred time steps? Sketch your prediction.



   At this rate, it will take about a million years to return to original configuration. (Estimate for $N=100$ balls on homework...)
   Recurrence time ≳ Age of universe?

   c. Are the dynamics of Ehrenfest's urns reversible, i.e., would the simulation look the same if we ran it backwards? Why or why not?

   * Although the microscopic rule is reversible, in the thermodynamic limit we seem to see an "arrow of time"... the system tends towards the macrostate that is most probable b/c ∃ many microstates with same % of balls.
   * The apparent "arrow of time" is because our initial condition was a very improbable one, to which the system will never return for $N \gg 1$. [Which law of thermodynamics?]

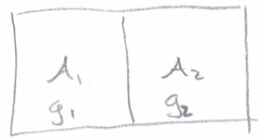
Counting Microstates in a Composite System

2. Consider, quite generically, two physical systems $\mathcal{A}_1, \mathcal{A}_2$ with respectively g_1 and g_2 possible microstates.
If you are unsure about a. or b., you may start with part c..

   a. How many microstates are available to the composite system $\mathcal{A} = \mathcal{A}_1 + \mathcal{A}_2$?

   $g = g_1 g_2$

   (For each configuration of A_1, need to count all g_2 configurations of A_2)

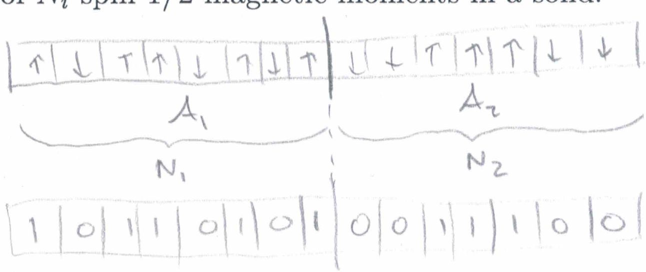


   b. What is the number of bits $\mathcal{I}$ required to specify the state of the composite system?

   $\mathcal{I} \equiv \log_2 g = \log_2 g_1 + \log_2 g_2$

   c. Explicitly check your answers to a.-b. for the case where each system $\mathcal{A}_i$ consists of N_i spin-1/2 magnetic moments in a solid.

spin = bit
↑,↓ 1,0



   $g_i = 2^{N_i}$

   $g_{tot} = 2^{N_1 + N_2}$

   $\mathcal{I} = N_1 + N_2$ bits

   $= \log_2 g_1 + \log_2 g_2$

   d. Based on your answers above, why might it be convenient to quantify the information content of physical systems in terms of a number of bits $\mathcal{I}$ rather than the multiplicity g?

   # of bits is additive, so information $\mathcal{I} = \log_2 g$ increases linearly with # of particles, just like energy, mass, etc.

Up to a multiplicative constant, $\mathcal{I}$ is equivalent to the **entropy**, variously defined as $\sigma = \ln g$ or $S = k \ln g$. We further examine its physical significance below.

$\mathcal{I}$ more convenient to work with natural log

3. *Entropy of a paramagnet.* Let us return to the paramagnet of N spins of magnetic moment μ in a magnetic field B, described by a Hamiltonian

$$H = -\varepsilon \sum_{i=1}^{N} \sigma_i^z, \tag{1}$$

where $\varepsilon = \mu B$ and $\sigma_i^z = \pm 1$ describes the state of the i^{th} spin. Suppose that we know the total energy E of the system.

a. Write down the **multiplicity** $g(E)$ of states with energy E. *Assume the thermodynamic limit (large N) and simplify the math by using the Gaussian approximation to the binomial distribution.*

Reminder:

Last time, we derived the probability distribution for spin excess $X = N_\uparrow - N_\downarrow$ when all microstates are equally probable ($p = \frac{1}{2}$):

$$P_N(X) = \frac{1}{\sqrt{2\pi N}} e^{-X^2/(2N)} = \frac{g_N(X)}{2^N} \Rightarrow g_N(X) = \frac{2^N}{\sqrt{2\pi N}} e^{-X^2/(2N)}$$

We have $E = -\varepsilon(N_\uparrow - N_\downarrow) = -\varepsilon X$, so

$$\boxed{g(E) = \frac{2^N}{\sqrt{2\pi N}} e^{-E^2/(2N\varepsilon^2)}}$$

* the large-N limit allowed us to make Gaussian approx (central limit thm).
* the approximation is valid around the peak, but not necessarily very in the wings near $X = \pm N$ ($E = \pm \varepsilon N$), where $P(X)$ is exponentially small.

b. Given our knowledge of the total energy (which specifies a macrostate of the system), how much additional information $\sigma(E)$ would be required to specify the microstate?

# of microstates w/ same energy

$$\sigma(E) = \ln g(E) = N\ln 2 - \tfrac{1}{2}\ln(2\pi N) - \frac{E^2}{2N\varepsilon^2}$$

Note: suppose $N = 10^{23}$. Then $\ln(2\pi N) = 23\ln(\underbrace{2\pi \times 10}_{4}) \approx 100 \lll 10^{23}$

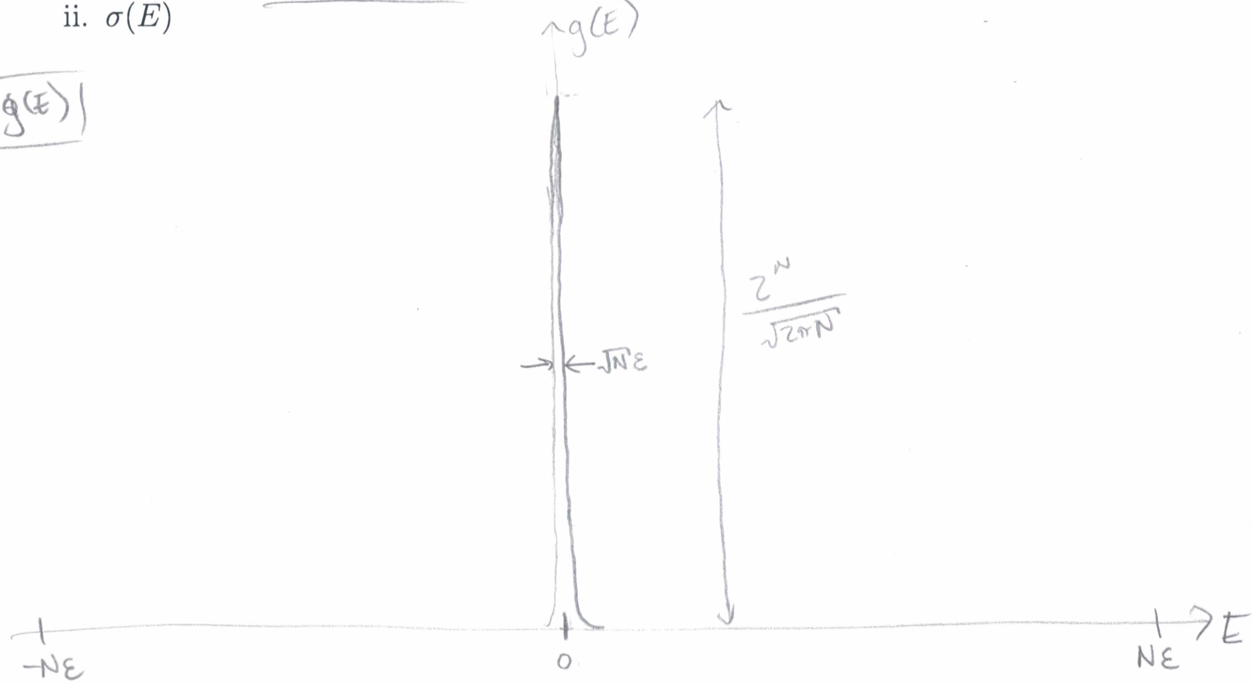
So to a very good approximation, $\sigma(E=0) = N\ln 2$

c. Sketch the following over the full domain $-N\mu B \leq E \leq N\mu B$, using your physical intuition in the regime where the Gaussian approximation breaks down:

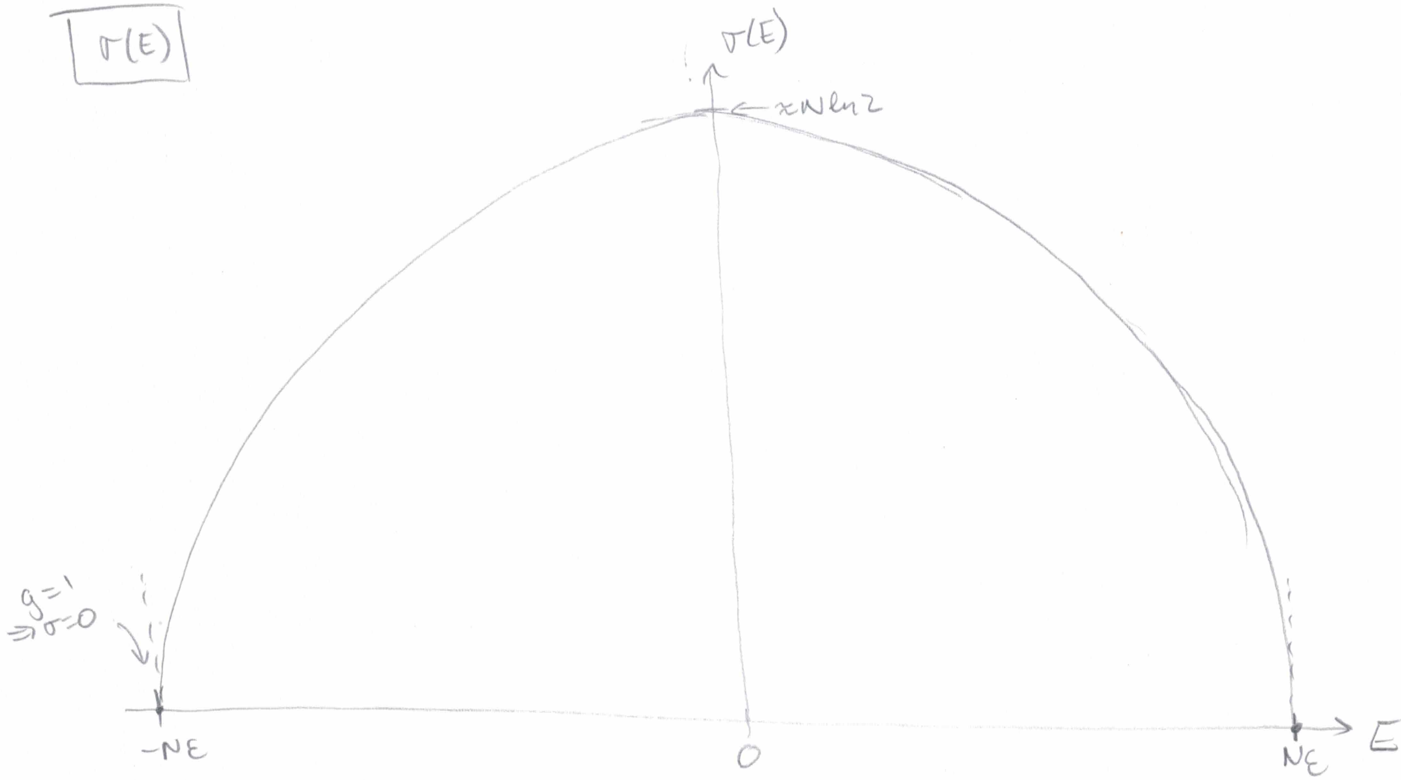
i. $g(E)$ Annotate sketches

ii. $\sigma(E)$

$\boxed{g(E)}$



$\boxed{\sigma(E)}$

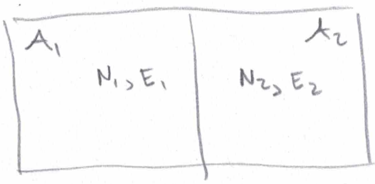


Names:

4. *Equilibration.* Suppose that we bring together two systems $\mathcal{A}_1, \mathcal{A}_2$ of N_1 and N_2 spins and allow energy to flow between them. The systems eventually equilibrate while conserving the total energy E.

   a. In **equilibrium**, what is the most probable value $\hat{E}_1$ of the energy of the subsystem of N_1 spins? Apply the following principles:

   - Conservation of energy, also known as the **First Law of Thermodynamics**.
   - The **fundamental assumption of thermodynamics**: all microstates consistent with our knowledge of the macroscopic properties of the system (e.g., total energy, particle number) are equally probable.



Cons. of Energy: $E_2 = E - E_1$

Fund. assumption $\Rightarrow$ most probable macrostate is the one with highest multiplicity g ...

... equivalently highest entropy $\sigma = \ln g$

$$g = g_1(E_1)\, g_2(E-E_1)$$

$$\ln g = \sigma_1(E_1) + \sigma_2(E-E_1) \quad \Leftarrow \text{Maximize}$$

$$\sigma = N_1 \ln 2 - \tfrac{1}{2}\ln(2\pi N_1) - \frac{E_1^2}{2N_1\varepsilon^2} + N_2 \ln 2 - \tfrac{1}{2}\ln(2\pi N_2) - \frac{(E-E_1)^2}{2N_2\varepsilon^2}$$

$$0 \overset{!}{=} \frac{d\sigma}{dE_1} = -\frac{E_1}{N_1\varepsilon^2} + \frac{(E-E_1)}{N_2\varepsilon^2}$$

$$\Rightarrow \quad E_1 \underbrace{\left(\frac{1}{N_1} + \frac{1}{N_2}\right)}_{= \frac{N_1+N_2}{N_1 N_2}} = \frac{E}{N_2} \quad \Rightarrow \quad E_1(N_1+N_2) = E N_1$$

$$\boxed{\hat{E}_1 = \frac{E N_1}{N_1+N_2}}$$

Makes sense: expect energy $\propto$ particle # in subsystem ✓

The intuitive result is the one that maximizes entropy of composite system: highest # of microstates.

b. For an **ensemble** of many identically prepared systems of N spins with the same total energy E, determine the rms fluctuations ΔE_1 in the energy of a subsystem of N_1 spins.
The ensemble of many replicas of a system with the same total energy E and particle number N is called the **microcanonical ensemble**.

i. ~~Find the Gaussian approximation to~~ Write down the multiplicity $g(E_1, E_2 = E - E_1)$ of states of the composite system with energy E_1 in $\mathcal{A}_1$. We will only care about the width of the distribution, so don't worry about the overall prefactor.

$$g = e^{\sigma} = A \times e^{-\frac{E_1^2}{2N_1\varepsilon^2} - \frac{(E-E_1)^2}{2N_2\varepsilon^2}}$$

ii. Show that your result from i. can be expressed in the form $g \propto e^{-\alpha(E_1 - \hat{E}_1)^2}$. Equivalently, show that

$$\ln g = -\alpha(E_1 - \hat{E}_1)^2 + \text{const.} \tag{2}$$

What is the value of α?

$$\ln g = \text{const} - \frac{E_1^2}{2N_1\varepsilon^2} - \frac{(E-E_1)^2}{2N_2\varepsilon^2}$$

$$= \text{const} - E_1^2 \underbrace{\left(\frac{1}{2N_1\varepsilon^2} + \frac{1}{2N_2\varepsilon^2}\right)}_{= \frac{1}{2\varepsilon^2}\cdot\frac{N_1+N_2}{N_1N_2}} + \frac{EE_1}{N_2\varepsilon^2}$$

$$= \text{const} - \frac{N_1+N_2}{2\varepsilon^2 N_1 N_2}\left(E_1^2 - \frac{2N_1}{N_1+N_2}\cdot EE_1\right)$$

$$= -\frac{N_1+N_2}{2\varepsilon^2 N_1 N_2}\left(E_1 - \frac{N_1 E}{N_1+N_2}\right)^2 + \text{const} = -\alpha(E_1 - \hat{E}_1)^2 + \text{const},$$

$$\text{Where } \alpha = \frac{N_1+N_2}{2\varepsilon^2 N_1 N_2} = \frac{1}{2(\Delta E^2)}$$

Gaussian $\propto e^{-x^2/(2\sigma^2)}$

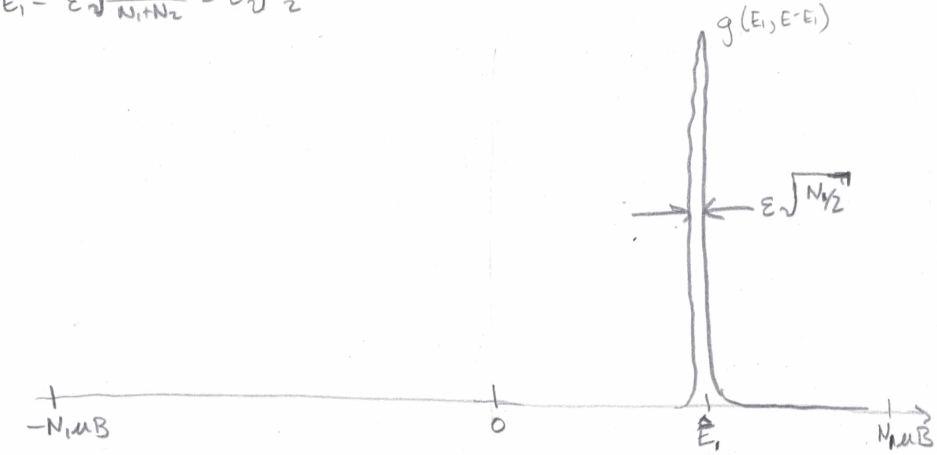
iii. Determine ΔE_1 from α.

$$(\Delta E_1)^2 = \frac{\varepsilon^2 N_1 N_2}{N_1+N_2} \Rightarrow \Delta E_1 = \varepsilon\sqrt{\frac{N_1 N_2}{N_1+N_2}}$$

c. Sketch the multiplicity function $g(E_1, E-E_1)$ illustrating the likelihood of finding the subsystem $\mathcal{A}_1$ to have energy E_1 for $N_1 = N_2$ and $E = (N_1 + N_2)\mu B/2.$ $= N_1\mu B$

$\hat{E}_1 = \frac{1}{2}E = \frac{N_1\mu B}{2}$

$\Delta E_1 = \varepsilon\sqrt{\frac{N_1 N_2}{N_1+N_2}} = \varepsilon\sqrt{\frac{N_1}{2}}$

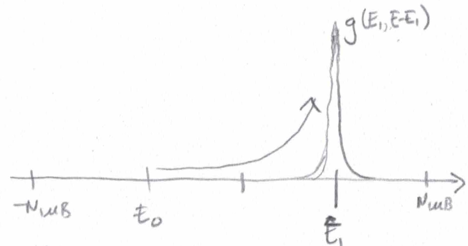


d. Does your ability to predict the fraction of the total energy in each subsystem improve or worsen in the thermodynamic limit?

Ability to predict the fraction improves: fluctuations $\frac{\Delta E_1}{E} = \sqrt{\frac{1}{2N_1}} \longrightarrow 0$ as $N_1 \to \infty$

So the "most probable" configuration becomes increasingly certain.

e. Suppose that, prior to letting the two systems exchange energy, the energy of system $\mathcal{A}_1$ was known to be E_0 (and hence the energy of $\mathcal{A}_2$ was $E - E_0$). When the systems are allowed to equilibrate, does the amount of information σ missing from a full description of $\mathcal{A} = \mathcal{A}_1 + \mathcal{A}_2$ increase, decrease, or remain the same? Explain.



The system tends toward the configuration $\hat{E}_1$ with the most microstates, so the entropy will increase. Or, in the very special case where $E_0 = \hat{E}_1$ already, the entropy will stay the same (but will never decrease).

Your result in Ex. 3.e. is a manifestation of the **Second Law of Thermodynamics**: when a constraint internal to a closed system is removed, the entropy tends to .... increase (or stay the same).