3.1.2) Discrete systems: two-level system

In many systems, energy variations do not stem (solely) from motion in space, but instead due to changes in discrete observables. An important example is that of localized electrons on a lattice, in the presence of a magnetic field. Taking into account the g-ratio of the electrons ($g \simeq -2$), their energy is:

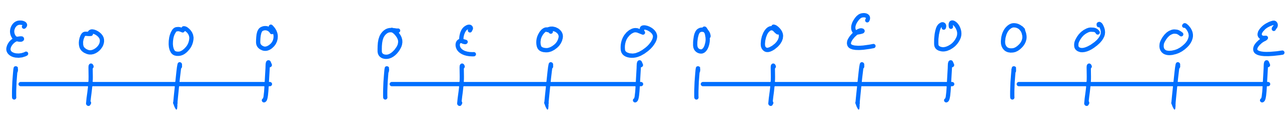
$$E = -\mu h \sum_{i=1}^{N} \sigma_i - J \sum_{i \sim j} \sigma_i \sigma_j$$

where μ is the magnetic moment of the electrons, J the exchange energy, and $\sigma = \pm 1$ is (minus) their normalized spins.

Two-level systems: A simpler version of this problem amounts to neglecting interactions and consider N atoms in a lattice that can each be in two possible energy levels, $\varepsilon_i = 0$ or ε.

Then $H = \sum_{i=1}^{N} \varepsilon_i = n\varepsilon$; $n \in [\![0, N]\!]$.

We note that the following configurations can be distinguished



thanks to the position of the atoms so that the number of configurations with energy $E = n\varepsilon$ is

$$\Omega(E = n\varepsilon) = \binom{N}{n} = \frac{N!}{n!\,(N-n)!}$$

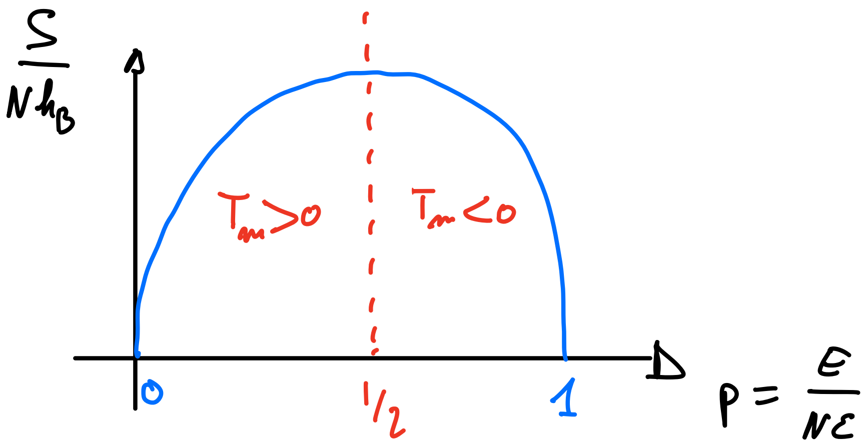
Entropy: $S_n = k_B \ln \Omega = k_B N \ln \frac{N}{e} - k_B n \ln \frac{n}{e} - k_B (N-n) \ln \frac{N-n}{e}$

Let us write $n = pN$, one finds

$$S_m = k_B N \left\{ \cancel{\ln N} - \cancel{1} - p\left[\ln p + \cancel{\ln N} - \cancel{1}\right] - (1-p)\left[\ln(1-p) + \cancel{\ln N} - \cancel{1}\right] \right\}$$

$$\boxed{S_m = -N k_B \left[p \ln p + (1-p)\ln(1-p)\right] \quad \text{with} \quad p = \frac{E}{N\varepsilon}}$$

$\left[\binom{N}{pN} \approx e^{-N k_B \left[p \ln p + (1-p)\ln(1-p)\right]} \right.$ is a useful formula$\left.\right]$



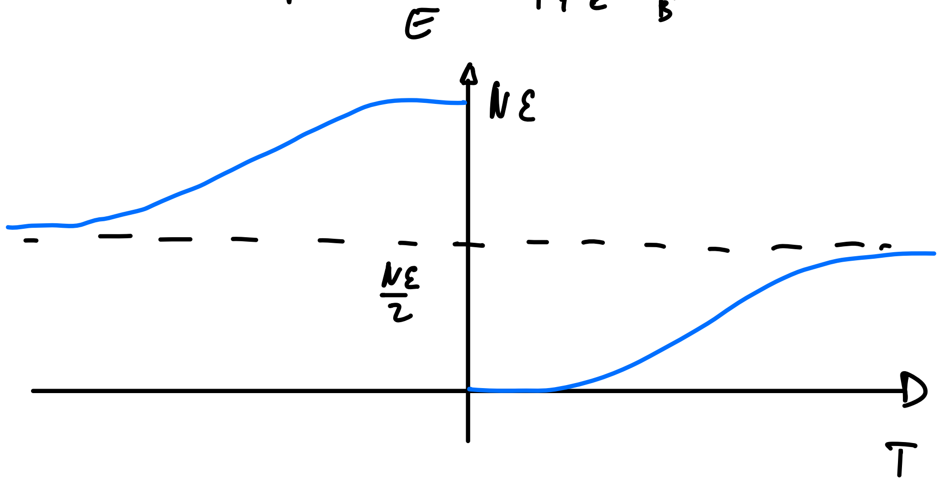
$\frac{S}{N} \to 0$ as $p \to 0$ or 1 since there is only 1 configuration with $E = 0, N\varepsilon$.

Temperature: S_m is not always increasing with $E \Rightarrow T_m$ can be negative.

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial p} \cdot \frac{\partial p}{\partial E} = \frac{k_B}{\varepsilon} \ln \frac{1-p}{p} < 0 \quad \text{if } p > \frac{1}{2}$$

Inverting this relation leads to $e^{\varepsilon/k_BT} = \frac{1-p}{p} \Rightarrow p = \frac{1}{1+e^{\varepsilon/k_BT}}$

& $\boxed{E = \frac{N\varepsilon}{1+e^{\varepsilon/k_BT}}}$



Heat capacity:

$$C_V = \frac{dE}{dT} = N k_B \frac{\varepsilon^2}{(k_BT)^2} \frac{e^{\varepsilon/k_BT}}{(1+e^{\varepsilon/k_BT})^2} \underset{T\to 0}{\sim} \frac{N k_B \varepsilon^2}{(k_BT)^2} e^{-\frac{\varepsilon}{k_BT}}$$

The exponential vanishing of C_V as $T\to 0$ is standard of gapped systems.

3.1.4) Large systems and thermodynamics

3.1.4.1) Macrostate

As in chapter 2, the microscopic configurations of a system, referred to as microstates φ_m, often contain too much information. One may thus introduce coarse grained descriptions of the system by grouping microstates together into macrostates φ_M.

Example: N spins, $\varphi_m = (S_1, \ldots, S_N)$

A macrostate φ_M can be defined using the magnetization per spin

$$m = \frac{1}{N}\sum_{i=1}^{N} S_i \quad ; \quad \varphi_M(m_0) = \{\varphi_m \text{ such that } m(\varphi_m) = m_0\}$$

There are 2^N microstates and $N+1$ macrostates since $Nm \in [\![-N, N]\!]$.

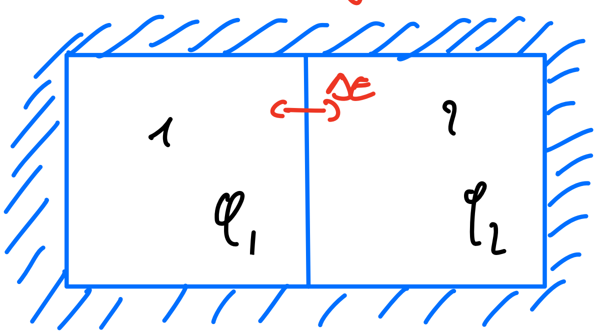
$\Rightarrow$ Strong dimensional reduction, hence the micro vs macro denomination.

Probability: $P(\varphi_M) = \sum_{\varphi_m \in \varphi_M} P(\varphi_m)$ is the probability of the macrostate.

Because there are many φ_m in one φ_M, $P(\varphi_M)$ is often simpler than $P(\varphi_m)$.

This is a case where more is simpler. Let us consider an important example: equilibration.

3.1.4.2) Subsystems & equilibration



Isolated system S divided into S_1 & S_2, with N_1, N_2, V_1, V_2 fixed but E_1 & E_2 fluctuating.

$$\varphi = \varphi_1 \otimes \varphi_2$$

Microcanonical measure $P_E(\varphi) = P(\varphi_1, \varphi_2) = \frac{1}{\Omega(E)} \delta(E(\varphi) - E)$

$$= \frac{1}{\Omega} \delta(E_1 + E_2 - E)$$

$\Omega_1(E_1)$: # of configurations φ_1 of S_1 with energy E_1.

$\Omega_2(E_2)$: ———— φ_2 of S_2 ———— E_2.

Q: In the large system limit, what are the typical values of E_1 & E_2?

S, S_1 & S_2 assume very large such that $E_{int} << E, E_1, E_2 \Rightarrow E_2 = E - E_1$.

$$\Rightarrow \Omega(E) = \sum_{E_1} \Omega_1(E_1)\, \Omega_2(E_2 = E - E_1)$$

Macrostate defined by E_1: $\{ (q_1, q_2)$ such that $E(q_1) = E_1 \}$

$$P(E_1) = \sum_{q_1, q_2 \mid E_1 + E_2 = E} \frac{1}{\Omega(E_1 + E_2)} = \frac{\Omega_1(E_1)\, \Omega_2(E_2)}{\Omega(E)}$$

Let's show that $P(E_1)$ is peaked at a given value E_1^*.

In large systems, E_1 varies continuously

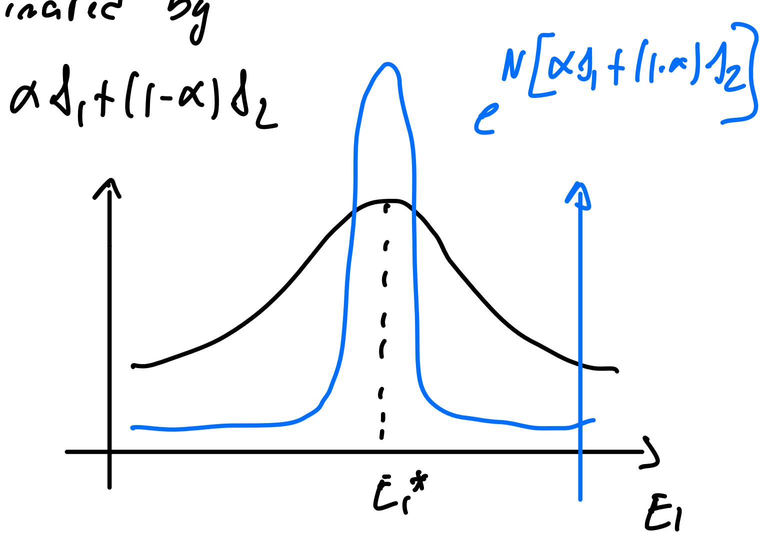
$$\Omega(E) = \int dE_1\, \Omega_1(E_1)\, \Omega_2(E - E_1) = \int dE_1\, e^{\frac{S_1(E_1)}{k_B} + \frac{S_2(E_2)}{k_B}}$$

$$\left.\begin{array}{l} S_1 \propto N_1 \equiv \alpha N \\ S_2 \propto N_2 \equiv (1-\alpha) N \end{array}\right\} \Omega(E) = \int dE_1\, e^{N \underbrace{\left[\frac{S_1(E_1)}{N k_B} + \frac{S_2(E - E_1)}{N k_B} \right]}_{\sim O(1),\ N \to \infty}}$$

$s_i = \frac{S_i}{N_i}$ the entropy per particle

When $N \to \infty$, the integral is dominated by

$$E_1^* = \underset{E_1}{\mathrm{argmax}} \left[\underbrace{\alpha\, s_1(E_1)}_{\text{increases with } E_1} + \underbrace{(1-\alpha)\, s_2(E - E_1)}_{\text{decreases with } E_1} \right]$$



Saddle point approximation

Consider $I = \int_a^b dx\, e^{N\phi(x)}$, with $\phi(x)$ a real function with a maximum at $x_0 \in (a,b)$

$$I = \int_a^b dx\; e^{N\left[\phi(x_0) + (x-x_0)\underbrace{\phi'(x_0)}_{=0} + \frac{1}{2}(x-x_0)^2\underbrace{\phi''(x_0)}_{<0} + \dots\right]}$$

$$\simeq e^{N\phi(x_0)} \int_a^b dx\; e^{-\frac{N}{2}(x-x_0)^2|\phi''(x_0)| + \sum_{k\geq 3} N\frac{(x-x_0)^k}{k!}\phi^{(k)}(x_0)}$$

$u = \sqrt{N}(x-x_0)$; $x = x_0 + \frac{u}{\sqrt{N}}$

$$I = \frac{e^{N\phi(x_0)}}{\sqrt{N}} \int_{\sqrt{N}(a-x_0)\to-\infty}^{\sqrt{N}(b-x_0)\to+\infty} du\; e^{-\frac{u^2}{2}|\phi''(x_0)| + \underbrace{\sum_{k\geq 3}\frac{N}{N^{k/2}}\frac{u^k}{k!}\phi^{(k)}(x_0)}_{\xrightarrow[N\to\infty]{} 0}}$$

$$\boxed{I \underset{N\to\infty}{\sim} \sqrt{\frac{2\pi}{N|\phi''(x_0)|}}\; e^{N\phi(x_0)}}$$

Back to $\Omega(E)$

Introducing the logarithmic equivalence to get rid of prefactors:

$a \approx b \iff \ln a \sim \ln b$, we rewrite $\Omega(E)$ as

$$\Omega(E) \approx e^{\frac{N}{k_B}\left[\alpha_1 s_1(E_1^*) + (1-\alpha) s_2(E_1^*)\right]} = e^{\frac{1}{k_B}\left[S_1(E_1^*) + S_2(E-E_1^*)\right]}$$

where $E_1^* = \arg\max[\;\underline{\qquad\qquad}\;] = \arg\max[S_1(E_1) + S_2(E-E_1)]$

$$\Leftrightarrow \quad S_1'(E_1^*) - S_2'(E-E_1^*) = 0$$

$$\Leftrightarrow \quad \left.\frac{\partial S_1}{\partial E_1}\right|_{E_1^*} = \left.\frac{\partial S_2}{\partial E_2}\right|_{E_2^* = E-E_1^*} \Leftrightarrow \boxed{T_m^1(E_1^*) = T_m^2(E_2^*)}$$

Back to $P(E_1)$

$$P(E_1) = \frac{1}{\Omega(E)} e^{\frac{1}{k_B}\left[S_1(E_1)+S_2(E-E_1)\right]} \simeq e^{\frac{1}{k_B}\left[\underbrace{S_1(E_1)+S_2(E-E_1) - S_1(E_1^*) - S_2(E-E_1^*)}_{<0 \text{ if } E_1 \neq E_1^*}\right]}$$

If $E_1 - E_1^* \sim \underset{\mathcal{O}(N)}{\overset{\shortparallel}{\mathcal{O}(E_1^*)}}$ & $E_1 \neq E_1^*$, the exponent is negative & $\mathcal{O}(N)$

$$\Rightarrow P(E_1 \neq E_1^*, E_1 - E_1^* \sim \mathcal{O}(N)) \propto e^{-N\,\mathcal{O}(1)} \xrightarrow[N\to\infty]{} 0$$

In the large N limit, $E_1 \simeq E_1^*$ is the only observed value

$\Rightarrow$ the systems adopt energies E_1^* & E_2^* such that $T_m^1 = T_m^2$

$\Rightarrow$ <u>This is the zeroth law of thermodynamics</u>

Additivity of entropy

$$S(E) = k_B \ln \Omega(E) \simeq k_B \ln \Omega_1(E_1^*) + k_B \ln \Omega_2(E_2^*) = S_1(E_1^*) + S_2(E_2^*)$$