3.1) The microcanonical ensemble

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3.1.1) Continuous systems

$\Omega(E,\delta E) \Leftrightarrow$ volume such that $E \leq E(q) \leq E+\delta E$

$\mathcal{V}(E) \Leftrightarrow$ volume such that $E(q) \leq E$

$\Omega(E,\delta E) \simeq \omega(E)\,\delta E$ with $\omega(E) = \dfrac{d\mathcal{V}(E)}{dE}$

Fixing units in phase space:

$\tilde{\Omega}(E) = \dfrac{\Omega(E)}{h^{3N}}$ & $p(q) = \dfrac{1}{\tilde{\Omega}(E)}$ if $E(q) \in [E, E+\delta E]$

together with $\displaystyle\int \prod_{i=1}^{N} \left(\frac{d^3\vec{q}_i\, d^3\vec{p}_i}{h^3} \right)$ for the phase space measure so that

$$\langle O(q) \rangle = \int \prod_{i=1}^{N} \frac{d^3\vec{q}_i\, d^3\vec{p}_i}{h^3}\; O(q)\, P(q)$$

$$= \int_{E \leq E(q) \leq E+\delta E} \prod_{i=1}^{N} d^3\vec{q}_i\, d^3\vec{p}_i\; O(q)\, \frac{1}{\Omega(E)}$$

$\Rightarrow$ optional at the level of classical stat mech.

3.1.2) The ideal gas

Distinguishable particles $S_m \simeq N k_B \ln\left[V\left(\frac{4\pi m E e}{3N h^2}\right)^{\frac{3}{2}}\right]$

For undistinguishable particles, $\Omega(E) \to \frac{\Omega(E)}{N!}$ and

$$\boxed{S_m(E) \simeq N k_B \ln\left[\frac{eV}{N}\left(\frac{4\pi e m E}{3N}\right)^{3/2}\right]} \Rightarrow \text{extensive}$$

$s_m = \frac{S_m}{N}$ is a function of $\frac{V}{N}$ & $\frac{E}{N}$, that are intensive quantities.

Comment: In quantum mechanics, particles are waves and cannot be distinguished if they are of the same nature and they should then be treated as indistinguishable

Thermodynamic quantities

From S, we can compute $\frac{1}{T_m} = \frac{\partial S_m}{\partial E} = \frac{3}{2} N k_B \frac{1}{E} \Rightarrow \boxed{E = \frac{3}{2} N k_B T_m}$

$$\boxed{C_V = \frac{\partial E}{\partial T_m} = \frac{3}{2} N k_B} \Rightarrow C_V \text{ constant, independent of } T.$$

3.1.3) Discrete systems: the two-level system

In many systems, the variations of energy are not (solely or at all) due to 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, their energy is then
$E = -\mu h \sum_{i=1}^{N} \sigma_i - J \sum_{i \vee j} \sigma_i \sigma_j$ where μ is the magnetic moment of the electrons, J the exchange energy, and $\sigma_j = \pm 1$ (minus) their normalized spins.

Two level systems: The simplest system corresponds to N atoms in a lattice that can be in two energy levels, 0 & ε.
Then $H = \sum_{i=1}^{N} \varepsilon_i = n\varepsilon = pN\varepsilon$; $n \in \{0, \dots, N\}$. p is the fraction of sites with NRG ε.
Since the atoms have fixed positions, they are distinguishable

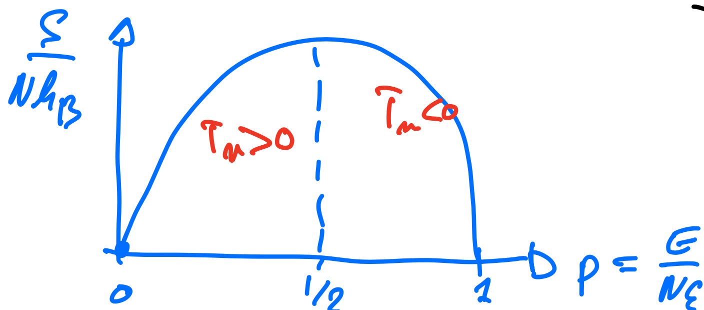
and $\Omega(E = pN\varepsilon) = \binom{N}{pN} = \dfrac{N!}{pN!\,(N-pN)!}$ (number of ways to choose pN atoms among N.)

Entropy: (Stirling $\ln N! \simeq N \ln \frac{N}{e} = N\ln N - N$)

$S_m = k_B \ln \Omega(E) = k_B N[\ln N - 1] - k_B pN[\ln pN - 1] - k_B(N-pN)[\ln(N-pN) - 1]$

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

with $p = \dfrac{E}{N\varepsilon}$



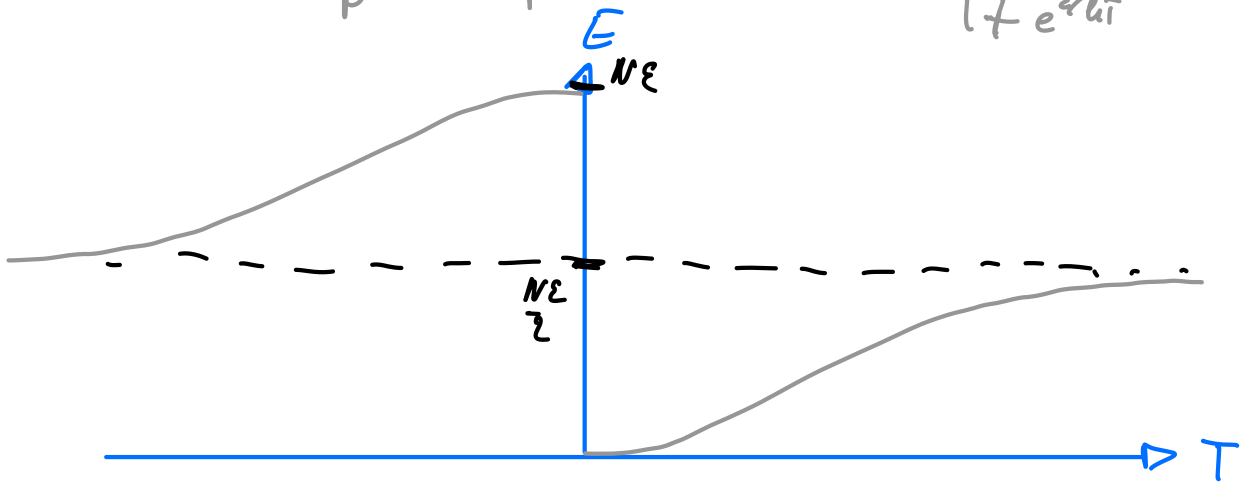
$\frac{S}{N} \to 0$ as $p \to 0$ or $p \to 1$ since there is only 1 configuration corresponding to $E = 0$ or $E = N$

Temperature S_m not always increasing with $E \Rightarrow T_m$ can be negative!

$$\frac{1}{T_m} = \frac{\partial S_m}{\partial E} = \frac{\partial S_m}{\partial p} \cdot \frac{\partial p}{\partial E} = \frac{k_B}{\varepsilon} \ln\left(\frac{1-p}{p}\right) < 0 \text{ if } p > \frac{1}{2}$$

Inverting this relation, $E = N\varepsilon p$

$$e^{\varepsilon/kT} = \frac{1-p}{p} \Rightarrow \frac{1}{p} = e^{\varepsilon/kT}+1 \Rightarrow p = \frac{1}{1+e^{\varepsilon/kT}} \Rightarrow E = \frac{N\varepsilon}{1+e^{\varepsilon/kT}}$$



Heat capacity

$$C_V = \frac{dE}{dT} = -\frac{N\varepsilon}{(1+e^{\varepsilon/kT})^2}\left(-\frac{\varepsilon}{kT^2}e^{\varepsilon/kT}\right)$$

$$C_V = N k_B \frac{\varepsilon^2}{(k_BT)^2}\frac{e^{\varepsilon/kT}}{(1+e^{\varepsilon/kT})^2}$$

$$T \to 0 \quad C_V \sim \frac{N k_B \varepsilon^2}{(k_BT)^2} e^{-\frac{\varepsilon}{kT}} \to 0$$

We observe an exponential decay of the heat capacity which is standard of gap systems.

3.1.4) Large systems and thermodynamics

3.1.4.1) Macrostates

As for the kinetic theory of gases, the microscopic configurations of the system, referred to as microstates q_n, often contain too much information on the system. One may then introduced coarse grained description of the system by grouping microstates together into macrostates φ_M.

<u>example</u>: In a spin system, a microstate φ_m is defined by the values $(S_1, \ldots, S_N) \Rightarrow \{\varphi_m\} = \{(S_1, \ldots, S_N)\}$

A macrostate $\varphi_M(m)$ can be defined by the system "magnetisation"

$$m = \frac{1}{N}\sum_{i=1}^{N} S_i \quad (\text{setting } \mu = 1)$$

$$\varphi_M(m) = \{ \varphi_m, \text{ such that } \frac{1}{N}\sum_i S_i = m \}$$

There are 2^N microstates φ_m and $N+1$ macrostates φ_M since $Nm \in \{-N, -N+2, -N+4, \ldots, N-2, N\} \Rightarrow$ strong dimensional reduction $\Rightarrow$ hence the micro vs macro denomination.

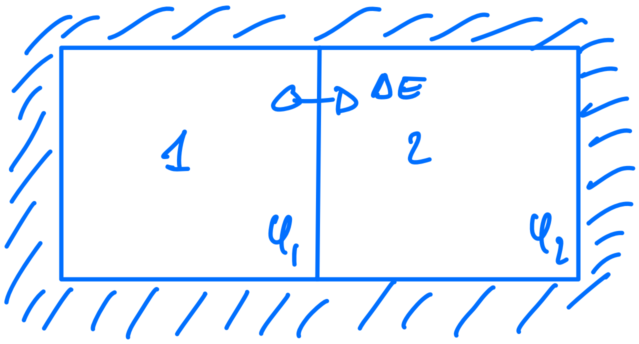
<u>probability</u> $\sum_{\varphi_m} P_m(\varphi_m) = \sum_{\varphi_M} P_M(\varphi_M) = 1$, where

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

Because there are many φ_m in $\sum_{\varphi_m \in \varphi_M}$, we can often simplify $P(\varphi_M)$ to extract information on the macrostates.

$\Rightarrow$ More is simpler. Let us look at an important example: equilibration

3.1.4.2) Sub systems and equilibration



Let us divide an isolated system S into two subsystems S_1 & S_2.

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

$E \simeq E_1 + E_2 \Rightarrow$ neglect interaction energy

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

$\Omega_1(E_1)$ = number of configurations φ_1 of S_1 with energy E_1.

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

Q: What are the typical values of E_1 & E_2?

We assume that S, S_1 & S_2 are very large such that

$E \simeq E_1 + E_2$ (interaction energy $E_{int} \ll E$) $\Rightarrow E_2 = E - E_1$

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

To characterize $P(E_1)$, we define the corresponding macrostate:

Macrostate: $\{(\varphi_1, \varphi_2)$ such that $E(\varphi_1) = E_1\}$

$$\underbrace{P(E_1, E_2 = E - E_1)}_{\equiv P(E_1)} = \sum_{\varphi_1, \varphi_2 | E_1 + E_2 = E} \frac{1}{\Omega(E_1 + E_2)} = \frac{\Omega_1(E_1) \times \Omega_2(E_2)}{\Omega(E)}$$

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

In large system, we replace

$$\Omega(E) = \sum_{E_1} \Omega_1(E_1)\, \Omega_2(E - E_1) \quad \& \quad \sum_{E_1} P(E_1) \frac{dE_1}{dE_1} = 1 \qquad \frac{P(E_1)}{dE_1} \simeq \tilde{P}(E_1)$$

by their continuous approximation $\qquad \simeq \int dE_1\, \tilde{P}(E_1)$

$$\Omega(E) = \int dE_1 \, \underbrace{\Omega_1(E_1)}_{\exp[S_1(E_1)/k_B]} \, \Omega_2(E-E_1) \quad \& \quad \int \tilde{P}(E_1)\, dE_1 = 1$$

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$\Rightarrow \tilde{P}(E_1)$ probability density.

We define the entropy density $s = \dfrac{S}{N} \underset{N\to\infty}{\sim} \mathcal{O}(1)$

$$\Omega(E) = \int dE_1 \, e^{\frac{S_1(E_1)}{k_B} + \frac{S_2(E-E_1)}{k_B}} = \int dE_1 \, e^{\frac{N}{k_B}\left(s_1(E_1) + s_2(E-E_1)\right)}$$

When $N\to\infty$ this integral is strongly dominated by the maximum of $s_1(E_1) + s_2(E-E_1)$

$s_1(E_1)$: increases with E_1

$s_2(E-E_1)$: decreases with E_1

$\Rightarrow$

Saddle point approximation

How can we approximate $I = \int_a^b dx \, \underbrace{e^{N\phi(x)}}_{\varphi_N(x)}$ as $N\to\infty$, when $\phi(x)$ is a real function with a maximum at $x = x_0 \in (a,b)$ and $\phi(x) \underset{N\to\infty}{\sim} \mathcal{O}(1)$?

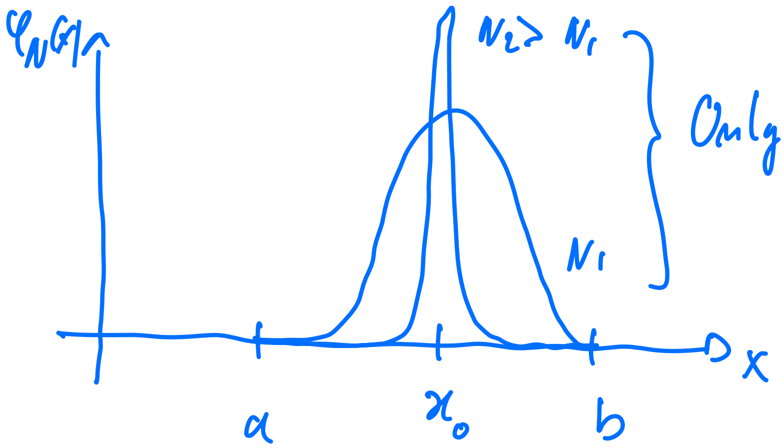
$$I = \int_a^b dx \, e^{N\left[\phi(x_0) + (x-x_0)\underbrace{\phi'(x_0)}_{=0} + \frac{1}{2}(x-x_0)^2 \underbrace{\phi''(x_0)}_{<0} + \dots\right]}$$

$\frac{1}{3!}(x-x_0)^3 + \frac{1}{4!}(x-x_0)^4$

$$\sim e^{N\phi_0(x)} \int_a^b dx \, e^{-\frac{N}{2}(x-x_0)^2 |\phi''(x_0)|} \underbrace{+ \dots}$$

$$\left(1 + (\dots) + \frac{(\dots)^2}{2} + \right)$$

$$\sum \frac{(\dots)^k}{\dots}$$



Only the vicinity of x_0 matters

$$\int_a^b dx \Rightarrow \int_{-\infty}^{+\infty} dx$$

$$\Rightarrow I \sim e^{N\phi_0(x)} \sqrt{\frac{2\pi}{N\,|\phi''(x_0)|}}$$

Comment: You can expand the terms neglected in [...] to show that they are subdominant.

Back to $\Omega(E)$

$$\Omega(E) \underset{N\to\infty}{\approx} e^{\frac{N}{k_B}\left[s_1(E_1^*) + s_2(E-E_1^*)\right]}$$

where $a \underset{N\to\infty}{\approx} b \Leftrightarrow \ln a \underset{N\to\infty}{\sim} \ln b$

$\Rightarrow$ get rid of prefactors.

where E_1^* such that $\phi(E_1) = s_1(E_1) + s_2(E - E_1)$

$[\phi'(E_1) = 0] \times N$

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

Equality of temperatures and the 0^{th} law

$$\Leftrightarrow \left.\frac{\partial S_1}{\partial E_1}\right|_{E_1^*} = \left.\frac{\partial S_2}{\partial E_2}\right|_{E_2^* = E - E_1^*} \Leftrightarrow T_{m,1} = T_{m,2}$$

We have equality of the microcanonical temperatures of

S_1 and S_2, which is sometimes called the 0^{th} law of thermodynamics.

Additivity of the entropy:

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

Thermodynamic stability

E_1^* maximizes $S_1(E_1) + S_2(E - E_1) \Rightarrow \dfrac{\partial S_1}{\partial E_1} - \dfrac{\partial S_2}{\partial E_2} = 0$ (extremum)

$$\& \quad \underbrace{\frac{\partial^2 S_1}{\partial E_1^2} + \frac{\partial^2 S_2}{\partial E_2^2}}_{\Rightarrow \frac{1}{C_V^1} + \frac{1}{C_V^2} > 0} < 0 \quad \text{(maximum)}$$

$$\frac{\partial S}{\partial E} = \frac{1}{T} \Rightarrow \frac{\partial^2 S}{\partial E^2} = -\frac{1}{T^2}\frac{\partial T}{\partial E} = -\frac{1}{C_V T^2}$$

The thermodynamic stability of a system requires a positive heat capacity.

Fluctuations of E_1:

$$P(E_1) = \frac{1}{\Omega(E)} e^{\frac{N}{k_B}[s_1(E_1) - s_2(E - E_1)]} \simeq e^{\frac{N}{k_B}\left[s_1(E_1) - s_1(E_1^*) + s_2(E - E_1) - s_2(E - E_1^*)\right]}$$

$$\xrightarrow[N \to \infty]{} 0 \quad \text{if } E_1 \neq E_1^* \Rightarrow \text{strongly peaked distribution}$$

Expanding close to $E_1 \simeq E_1^*$ leads to

$$\Rightarrow P(E_1) \sim \exp\left[-\frac{(E_1 - E_1^*)^2}{2 k T^2 \frac{C_V^1 C_V^2}{C_V^1 + C_V^2}}\right] \qquad (*)$$

Proof:

$$P(E_1) \simeq e^{\frac{N}{k_B}\left[s_1(E_1) - s_1(E_1^*) + s_2(E-E_1) - s_2(E-E_1^*)\right]}$$

$$\simeq \exp\left\{\frac{N}{k_B}\left[\frac{\partial s_1}{\partial E_1}(E_1-E_1^*) + \frac{1}{2}\frac{\partial^2 s_1}{\partial E_1^2}(E_1-E_1^*)^2 - \frac{\partial s_2}{\partial E_2}(E_1-E_1^*) + \frac{1}{2}\frac{\partial^2 s_2}{\partial E_1^2}(E_1-E_1^*)^2\right]\right\}$$

$$\simeq \exp\left[\frac{1}{k}\left(\frac{1}{T_1}(E_1-E_1^*) - \frac{(E_1-E_1^*)^2}{2C_V^1 T^2} - \frac{1}{T_2}(E_1-E_1^*) - \frac{(E_1-E_1^*)^2}{2C_V^2 T^2}\right)\right]$$

where we used

$$s_2(E-E_1) = s_2(E-E_1^*) + (E_1-E_1^*)\left(-s_2'(E-E_1^*)\right) + \frac{1}{2}(E_1-E_1^*)^2 s_2''(E-E_1^*)$$

Since $C_V = \frac{\partial E}{\partial T}$ and $E \propto N$, then $C_V \sim N$

$$(*) \Rightarrow \langle (E_1-E_1^*)^2 \rangle \sim C_V \sim N \Rightarrow E_1 - E_1^* \sim \sqrt{N} \ll E_1, E_1^*$$

The relative fluctuations of E_1 vanish as $N \to \infty$. $\frac{E_1-E_1^*}{\sqrt{(E_1-E_1^*)^2}} \sim 0$ $N\to\infty$

Again, we need $C_V^i > 0$ for $P(E_1)$ to be normalizable.

Comment: Another way to see that C_V is extensive is through:

$$\frac{\partial S}{\partial T} = \frac{\partial S}{\partial E}\cdot\frac{\partial E}{\partial T} = \frac{C_V}{T} \Rightarrow C_V \propto N.$$ This also allows calculating S as

$$S(T) - S(0) = \int_0^T dT\, \frac{C_V}{T}$$

Third law: At low temperatures, quantum fluctuations become important and classical statistical mechanics is not valid any-more. At $T=0$, the system is in the ground state so that $S = k_B \ln g$, where g is the degeneracy of the ground state. If $g = 1$, $S(0) = 0$. Typically, quantum fluctuations make g subextensive so that $S(0) \ll N$ &

$$S(T) \simeq \int_0^T \frac{C_V}{T}$$

Second law of thermodynamics

Take two systems with initial energy E_1 & E_2. Let them evolve in contact with each other and they will relax to E_1^* & E_2^* such that

$$S_{final} = S_1(E_1^*) + S_2(E_2^*) \geq S_{initial} = S_1(E_1) + S_2(E_2)$$

$\Rightarrow$ the entropy of the isolated system $S = S_1 \oplus S_2$ has increased

$\Rightarrow$ this is the second law of thermodynamics. Note that it relies on $N \to \infty$.