Chapter 3: Classical equilibrium statistical mechanics

Chapters 1 & 2 have provided us with qualitative and quantitative reasons to believe that equilibrium statistical mechanics is relevant to describe the late time statistics of isolated systems. In this chapter, we study the properties of the corresponding ensembles and show their equivalence in the large system size limit. This allows us to recover standard results of thermodynamics.

3.1) The microcanonical ensemble

For an isolated system at temperature E, all states with the same energy are assumed equiprobable in the steady state. Formally, if we denote by $\{q\}$ the configurations of the system,

probability:

$$p(q) = \frac{1}{\Omega(E)} \quad \text{if } E(q) = E$$
$$= 0 \quad \text{otherwise}$$

entropy: $S_m(E) = k_B \ln \Omega(E)$

Temperature: $$\frac{1}{T_m(E)} = \frac{\partial S_m(E)}{\partial E}$$

Heat capacity: To increase the temperature of the system by δT, we need to bring some energy δE. The **heat capacity** is defined as $\frac{\delta T}{\delta E} \underset{\delta T \to 0}{\sim} \frac{1}{C_V}$. Inverting $T(E)$ into $E(T)$, C_V is defined as

$$\boxed{C_V = \frac{\partial E}{\partial T}}$$

The subscript "V" refers to the fact that the volume V is kept constant as $E \to E + \delta E$ and $T \to T + \delta T$.

3.1.1) Continuous system

density of states

If we consider a system described by continuous variables, defining the "number" $\Omega(E)$ makes no sense. Instead, we want to characterize the "measure" of the energy surface defined by $E(q) = E$. If we consider any measure that is absolutely continuous with respect to the Lebesgue measure in the full space, the measure of this surface is zero...

A solution is to consider instead configurations of energy $E \leq E(\varphi) \leq E + \delta E$. Then the volume / measure of this set scale as $\Omega(E, \delta E) \simeq \omega(E)\,\delta E$.

$\omega(E)$ is called the density of states of the system.

The entropy is then given by $S = k_B \ln \Omega = k_B \ln \omega(E) + k_B \ln \delta E$

In the large-system-size limit, $k_B \ln \omega(E)$ diverges and the constant $k_B \ln \delta E$ can be neglected.

Phase space measure Consider a classical system, the probability measure of the system is

$$\underbrace{d\rho_E(\{\vec{q}_i, \vec{p}_i\})}_{\text{probability measure}} = \underbrace{\frac{1}{\Omega(E)} \mathbb{1}_{H(\{\vec{q}_i, \vec{p}_i\}) \in [E, E+\delta E]}}_{\text{probability density}} \underbrace{\prod_i d^3\vec{q}_i\, d^3\vec{p}_i}_{\text{phase space measure}}$$

If we change units, the phase space volume $\Omega(E)$ & the measure $d^3\vec{q}\,d^3\vec{p}$ change in the same way so that $d\rho$ does not depend on the unit (which is great!). But $S = k_B \ln \Omega$ does! To fix this, we write

$$d\rho_E = \frac{h^{3N}}{\Omega(E)} \mathbb{1}_{H(\{\vec{q}_i, \vec{p}_i\}) \in [E, E+\delta E]} \prod_i \frac{d^3\vec{q}_i\, d^3\vec{p}_i}{h^{3N}}$$

Why? (i) Because it does not matter $\Rightarrow d\rho_E$ is unchanged

(ii) $S = k_B \log \frac{\Omega(E)}{h^{3N}} = k_B \ln \tilde{\Omega}(E)$ does not depend on units :-)

(iii) Because it is consistent with the high temperature limit of quantum stat mech. The real available states are quantized and h is the right way to count states in phase space.
h^3 can be seen as the right unit of phase space volume.

3.1.2) The ideal gas

N particles in a box of volume $V = L^3$. In the dilute limit, their interactions suffice for the gas to equilibrate but they do not enter the phase space distribution and we approximate the energy as $H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$

Density of states

$$\tilde{\Omega}_{\delta E}(E) = \int_{E \leq H(\{\vec{q}_i, \vec{p}_i\}) \leq E+\delta E} \prod_{i=1}^{N} \frac{d^3\vec{q}_i \, d^3\vec{p}_i}{h^3} = \frac{\mathcal{V}(E+\delta E) - \mathcal{V}(E+\delta E)}{h^{3N}}$$

where $\mathcal{V}(E)$ is the phase space volume such that $H(\{\vec{q}_i, \vec{p}_i\}) \leq E$.

$$\Rightarrow \tilde{\Omega}_{\delta E}(E) \simeq \frac{\delta E}{h^{3N}} \frac{d\mathcal{V}(E)}{dE} \quad \Rightarrow \text{let's compute } \mathcal{V}(E).$$

$$\mathcal{V}(E) = L^{3N} \int_{\sum_i \vec{p}_i^{\,2} \leq 2mE} \prod_{i=1}^{N} d^3\vec{p}_i = L^{3N} \int_{\sum_{i=1}^{N} x_i^2 = 2mE} \prod_{i=1}^{3N} dx_i \quad ; \quad x_i = \sqrt{2mE}\, u_i$$

$$= L^{3N} (2mE)^{\frac{3N}{2}} \int_{\sum_i u_i^2 \leq 1} \prod_{i=1}^{3N} du_i$$

Going to spherical coordinates, we get

$$\mathcal{V}(E) = L^{3N}(2mE)^{\frac{3N}{2}}\, \Omega_{SO}(3N) \underbrace{\int_0^1 du\, u^{3N-1}}_{1/3N}$$

where $\Omega_{SO}(3N)$ is the total solid angle in $3N$ dimensions

Solid angle in d dimension

Let's find an integral we can do in cartesian & spherical coordinates.

$\Rightarrow$ Gaussian integral

$$I_d \equiv \Big(\underbrace{\int_{-\infty}^{+\infty} dx\, e^{-x^2}}_{\sqrt{\pi}}\Big)^d = \pi^{d/2}$$

$$= \int \prod_{i=1}^{d} dx_i\, e^{-\sum_{i=1}^{d} x_i^2} = \Omega_{SO}(d) \int_0^\infty dx\, x^{d-1} e^{-x^2}$$

$w = x^2$; $x = \sqrt{w}$ & $dx = \frac{dw}{2\sqrt{w}}$

$$I_d = \frac{1}{2}\Omega_{SO}(d) \int_0^\infty dw\, e^{-w} w^{\frac{d}{2}-1} = \frac{1}{2}\Omega_{SO}(d)\, \Gamma\left(\frac{d}{2}\right)$$

where $\Gamma(u) = \int_0^\infty dw\, w^{u-1} e^{-w}$ is the Gamma function such that $\Gamma(n) = (n-1)!$

$$\Rightarrow \Omega_{SO}(d) = \frac{2\pi^{d/2}}{\left(\frac{d}{2}-1\right)!}$$

Back to the density of states: $\mathcal{V}(E) = L^{3N}(2mE)^{\frac{3N}{2}} \dfrac{2\pi^{\frac{3N}{2}}}{3N\left(\frac{3N}{2}-1\right)!}$

$$\Rightarrow \hat{\Omega}(E) = \mathcal{V}'(E)\,\frac{\delta E}{h^{3N}}$$

$$\boxed{\hat{\Omega}(E) = \delta E \left(\frac{L}{h}\right)^{3N} m\,(2mE)^{\frac{3N}{2}-1} \frac{2\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}-1\right)!}}$$

Entropy: $S_m = k_B \ln \hat{\Omega}(E)$

$$\underset{N\to\infty}{=} 3Nk_B \ln\left(\frac{L}{h}\right) + \frac{3N}{2}k_B \ln(2mE\pi) - k_B \ln\left[\left(\frac{3N}{2}-1\right)!\right] + o(N)$$

a bunch of subdominant terms.

Stirling formula:

$$n! \sim \sqrt{2\pi n}\left(\frac{n}{e}\right)^n \Rightarrow \ln(n!) \simeq n \ln\left(\frac{n}{e}\right) + o(n) \qquad \left(a = o(n) \text{ if } \frac{a}{n} \underset{n\to\infty}{\to} 0\right)$$

$$\Rightarrow S_m = Nk_B\left[\ln\frac{V}{h^3} + \ln(2mE\pi)^{\frac{3}{2}} - \frac{3}{2}\ln\frac{3N}{2e}\right] + o(N)$$

$$\boxed{S_m \simeq Nk_B \ln\left[V\left(\frac{4mEe\pi}{3Nh^2}\right)^{\frac{3}{2}}\right]} \qquad (1)$$

Comments:

- $S_m \to +\infty$ as $N \to +\infty$ $\Rightarrow$ legitimate disregarding δE
- S_m increases with E, as expected. $\frac{1}{T} = \frac{\partial S}{\partial E} > 0$.
- S_m not extensive! $(E, V, N) \to (\lambda E, \lambda V, \lambda N)$

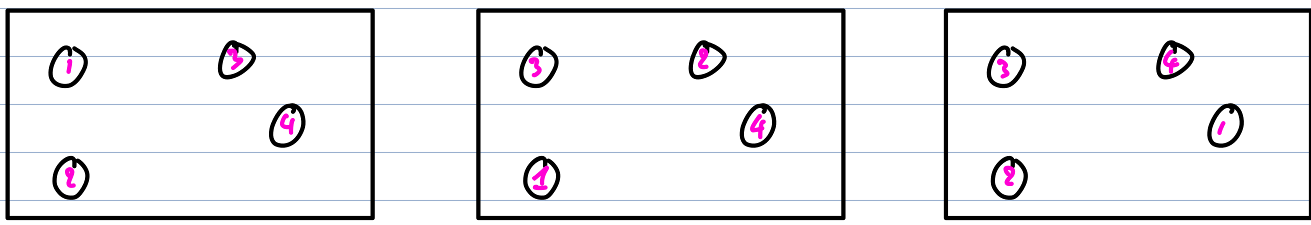
$$S_m \to \underbrace{\lambda N k_B \ln\left[V\left(\frac{4mEe\pi}{3Nh^2}\right)^{\frac{3}{2}}\right]}_{\lambda S_m} + \lambda N k_B \ln \lambda \neq \lambda S_m$$

This is because of the factor V instead of $\frac{V}{N}$ in (1).

Indistinguishability

The computation above is wrong for a real gas; we know since thermodynamics that the entropy of a gas is additive.
This was first discussed by Gibbs and is unfortunately called the Gibbs paradox in the context of the mixing of two identical gases.

This computation is ok if the particles are distinguishable, i.e. we can label them and track them.



These 3 configurations are different and the entropy should be superextensive since swapping particles create new configurations.

If the particles are undistinguishable, these 3 configurations are identical but we have counted them as different configurations in $\Omega(E)$.

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

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

$s_m = \frac{S_m}{N}$ 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 $\frac{1}{T_m} = \frac{\partial S_m}{\partial E} = \frac{3}{2} N k_B \frac{1}{E} \Rightarrow \boxed{E = \frac{3}{2} N k_B T_m}$

$$\boxed{C_V = \frac{\partial E}{\partial T_m} = \frac{3}{2} N k_B}$$

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 accont the g ratio of the electrons, their energy is then $E = -\mu h \sum_{i=1}^{N} \sigma_i - J \sum_{ij} \sigma_i \sigma_j$ 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 $H = \sum_{i=1}^{N} \varepsilon_i = n\varepsilon$; $n \in \{0, -, N\}$

Since the atoms have fixed positions, they are distinguishable

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

Entropy: $S = k_B \ln \Omega(E) = k_B\left[N \ln \frac{N}{e} - \frac{E}{\varepsilon} \ln \frac{E}{e\varepsilon} - \left(N - \frac{E}{\varepsilon}\right) \ln\left(N - \frac{E}{\varepsilon}\right)\right]$