1.2.1) The microcanonical ensemble

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Take an isolated classical system characterized by positions & momenta: $\varphi = \{q_1, \ldots, q_N, p_1, \ldots, p_N\}$ and a time independent Hamiltonian $H(q_1, \ldots, q_N, p_1, \ldots, p_N)$.

Dynamics Trajectories $q_i(t), p_i(t)$ are solutions of

$$\frac{d}{dt} q_i(t) \equiv \dot{q}_i(t) = \frac{\partial H}{\partial p_i} \equiv \partial_{p_i} H \; ; \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

$H(q_1(t), \ldots, q_N(t), p_1(t), \ldots, p_N(t))$ is a constant of motion:

Chain rule:

$$\frac{d}{dt} H(\vec{q}(t), \vec{p}(t)) = \underbrace{\frac{\partial H}{\partial t}}_{=0} + \sum_i \frac{\partial H}{\partial q_i} \dot{q}_i + \frac{\partial H}{\partial p_i} \dot{p}_i = \sum_i \partial_{q_i} H \times \partial_{p_i} H + \partial_{p_i} H \left(-\partial_{q_i} H\right) = 0$$

The dynamics of the system takes place along the energy surface.

Microcanonical hypothesis: For a classical complex system, the energy surface is visited uniformly & ergodically $\Rightarrow$ all configurations with the same energy are visited with equal probability.

Discrete system: Consider a classical isolated system described by a set of configurations $\{\varphi\}$. Then if the system is at energy E

$$\boxed{P_E(\varphi) = \frac{1}{\Omega(E)} \, \delta_{H(\varphi), E}} \qquad (1)$$

where $\Omega(E)$ is the number of configurations of energy E.
$\delta_{a,b}$ is the KRONECKER delta, such that $\delta_{a,b} = 1$ if $a=b$ & $\delta_{a,b} = 0$ otherwise.

Continuous system: If $\{q\}$ is a continuous space, $P_E(q)$ is a probability density and $\Omega(E)$ is the area of the energy surface with energy E. (See recitations & Chapter 3).

Comment: $\Omega(E)$ is a normalization constant such that

$$\boxed{\sum_q P_E(q) = 1}$$

Microcanonical Entropy: The number of configurations vary with E, typically exponentially, so that a better way to measure $\Omega(E)$ is Boltzmann microcanonical entropy

$$S_m(E) = k_B \ln \Omega(E),$$

where $k_B = 1.380\,649\ 10^{-23}\ J.K^{-1}$

Microcanonical temperature: The variations of Ω & S vary with E, this is quantified by temperature

$$\boxed{\frac{1}{T_m} \equiv \frac{\partial S_m}{\partial E}}$$

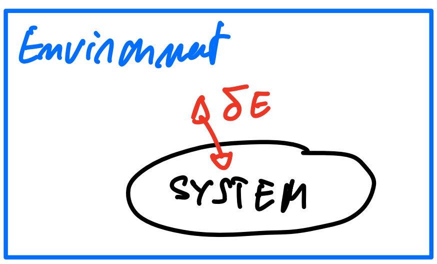
Comment:

Q1: Is Eq. (1) simple? Yes! As simple as it gets

Q2: Is Eq. (1) practical? No! Computing $\Omega(E)$ is often a combinatorics challenge.

Q3: Is Eq. (1) useful? Yes & No. We can engineer isolated systems (ultrahigh vacuum), but most systems are not isolated $\Rightarrow$ account for energy fluctuations & exchanges $\Rightarrow$ how?

1.2.2) The principle of minimal information



Let's say that instead of $E = E_0$, the environment imposes

$$\sum_q E(q) P(q) \equiv \langle E \rangle = E_0$$

Which $P(q)$ should we pick?

JAYNES (1957): the simplest so as not to bias our information.

$\Rightarrow$ Minimise information in $P(q)$ / Maximize the surprise.

Shannon information theory (1948): Take a distribution p that measures the result of sampling a random variable $n \in \{1, \dots, N\}$.

Q: How surprising is the fact of sampling a value n?

Surprise function $s(p(n))$

a) $s(1) = 0$; if $p(n) = 1 \Rightarrow$ no surprise

b) s decreases as $p(n)$ increases

c) The surprise of two independent event should add up:

$$s(p(n_1, n_2)) = s(p(n_1)) + s(p(n_2)) = s(p(n_1) \cdot p(n_2))$$

a+b+c $\Rightarrow$ $s(p(n)) = -k \ln(p)$ with $k > 0$ (Shannon)

Shannon entropy: The average surprise is called Shannon entropy:

$$S_S = -\sum_q p(q) \ln p(q)$$

Gibbs entropy (1906) Gibbs proposed that the thermodynamic entropy be given by $S_G = -k_B \sum_q p(q) \ln(q)$

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For the microcanonical ensemble

$$S_G(E) = -k_B \sum_{q} \frac{1}{\Omega(E)} \delta_{E(q),E} \ln\left(\frac{1}{\Omega(E)} \delta_{E(q),E}\right)$$

$$= -k_B \underbrace{\sum_{q|E(q)=E} \frac{1}{\Omega(E)}}_{1} \left(-\ln \Omega(E)\right) = k_B \ln \Omega(E)$$

$$S_G(E) = S_B(E)$$

$\Rightarrow$ Boltzmann, Gibbs & Shannon coincide in the microcanonical ensemble

1.2.3) The canonical ensemble

Constraints: $\sum_q p(q) = 1$ & $\sum_q E(q)\, p(q) = E_0$

$\Rightarrow$ Minimize the information in P / Maximize the surprise under these constraints.

$$\mathcal{L}(P) = -\sum_q p(q) \ln p(q) + \beta\left[E_0 - \sum_q p(q) E(q)\right] + \alpha\left[1 - \sum_q p(q)\right]$$

Extremize with respect to $p(q_i)$ and use the Lagrange multipliers to enforce the constraints

$$\frac{\partial \mathcal{L}}{\partial p(q_i)} = 0 = -\ln p(q_i) - 1 - \beta E(q_i) - \alpha \Rightarrow p(q_i) = e^{-1-\alpha-\beta E(q_i)}$$

Normalization fixes α: $\frac{1}{Z} = e^{-1-\alpha}$ and

$$\boxed{p(q_i) = \frac{1}{Z} e^{-\beta E(q_i)}} \qquad (2)$$

where $\boxed{Z = \sum_i e^{-\beta E(q_i)}}$ is called the partition function.

This is the celebrated CANONICAL DISTRIBUTION. From this derivation, we see that it is the least biased distribution constrained to $\langle E \rangle = E_0$. Also known as BOLTZMANN WEIGHT.

Q: How is β fixed?

$$\langle E \rangle = E_0 \Leftrightarrow E_0 = \frac{1}{Z} \sum_q E(q) e^{-\beta E(q)} = -\frac{1}{Z} \partial_\beta \sum_q e^{-\beta E(q)}$$

$$\Leftrightarrow \boxed{E_0 = -\partial_\beta \ln Z}$$

Comments: (I) this can be generalized to other constraints (see Pset 1)

(II) this is nice but our ignorance does not determine the laws of nature $\Rightarrow$ need more reasons

(III) Sam Edwards generalized this to granular media $\Rightarrow$ ok but not perfect.

If applied to active matter $\Rightarrow$ terribly wrong predictions.

$\Rightarrow$ Need better control $\Rightarrow$ next chapter