

PROBABILITY SPACES IN CLASSICAL MECHANICS

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1 Gibbs' Ensembles as Probability Spaces

- An “ensemble” consists of a large (possibly infinite) number of virtual copies of a system, considered all at once, each of which represents a possible state that the real system might be in.
- This notion was introduced by Gibbs introduced in his book *Elementary Principles in Statistical Mechanics* published in 1902, a year before his death.
- In the language of modern probability theory, **an ensemble is nothing but a probability space** $(\Omega, \mathcal{F}, \mathbb{P})$.
- The sample space Ω represents the set of **possible microscopic states of a physical system** and \mathbb{P} providing their **probability distribution**; \mathcal{F} is a suitable family of sets of micro-states (its choice is mainly dictated by mathematical considerations).
- The precise mathematical expression for Ω depends on the type of mechanics under consideration (quantum or classical). In each case the measure \mathbb{P} is a **probability distribution over microstates**.
- In quantum mechanics, the microstates are **vectors in the Hilbert space** of the system while in classical mechanics are **points in the phase space** of the system.

2 Classical mechanics

- Classical system with r degrees of freedom is described by r *generalized coordinates* $q = (q_1, \dots, q_r)$ and r *generalized momenta* $p = (p_1, \dots, p_r)$.
- Phase space $\Gamma = \{x = (q, p)\}$.

- $H(x) = H(q, p)$ the **Hamiltonian** of the system. Dynamics given by Hamilton's equations

$$\frac{dX}{dt} = v^H(X), \quad (1)$$

$$v^H(x) = v^H(q, p) = \left(\frac{\partial H(q, p)}{\partial p}, -\frac{\partial H(q, p)}{\partial q} \right). \quad (2)$$

- The solution map of Hamilton's equations $T_t : \Gamma \rightarrow \Gamma$, $t \in \mathbb{R}$, $X_t = T_t(X_0)$, is a flow on Γ , called the **Hamiltonian flow**.

Flow A **flow** on a space Ω is a continuous family of transformations $T_t : \Omega \rightarrow \Omega$ parametrized by $t \in \mathbb{R}$ (the time) obeying the rules:

- T_0 is the identity function on Γ ;
- $T_s \circ T_t = T_{t+s}$,
- $T_s^{-1} = T_{-s}$, whenever T_s^{-1} is well-defined.

For an Hamiltonian flow T_s^{-1} is well defined and in addition to the aforesaid properties we have

$$\frac{\partial T_t(x)}{\partial t} = v^H(T_t(x)). \quad (3)$$

Liouville s Theorem The volume element in phase space, $dx = \prod_{k=1}^r dq_k dp_k$ does not depend of the choice of coordinates and is thus invariant under canonical transformations. In particular, the volume

$$|A| = \int_A dx$$

is invariant under the canonical transformations realizing the time evolution of the system.

Proof *The Hamiltonian flows are incompressible since*

$$\operatorname{div} v^H = \frac{\partial}{\partial q} \frac{\partial H(q, p)}{\partial p} - \frac{\partial}{\partial p} \frac{\partial H(q, p)}{\partial q} = 0.$$

Then the conservation of the phase-space volume follows from the application of Gauss' theorem since the surface integral of v^H is the rate of change of the volume within the surface. \square

3 Micro-canonical Measure

- Given a microstate X at some time t_0 , the micro-state at any other time $t \in \mathbb{R}$, X_t is (as long as the system stays isolated) on the **energy surface** Γ_E , specified by $H(x) = E$.
- It is useful (especially when dealing with macroscopic systems) to think of Γ_E as an **energy shell** of thickness $\Delta E \ll E$, i.e.,

$$\Gamma_{E,\Delta E} = \{x \in \Gamma : E \leq H(x) \leq E + \Delta E\}. \quad (4)$$

- If the particles are confined in a box $\Lambda \subset \mathbb{R}^3$ of finite volume, then $|\Gamma_{E,\Delta E}|$ is finite (if the particles were not confined the volume would be infinite). Then one can define the probability measure

$$\mathbb{P}_{E,\Delta E} \{A\} = \frac{|A \cap \Gamma_{E,\Delta E}|}{|\Gamma_{E,\Delta E}|}, \quad A \in \mathcal{B}(\Gamma), \quad (5)$$

with $\mathcal{B}(\Gamma)$ the Borel algebra Γ , which is called the **microcanonical measure**. It is simply the Lebesgue measure restricted to the shell of constant energy and normalized to the volume of the shell.

★ Eventually, one may pass to the limit $\Delta E \rightarrow 0$ of both sides of eq. (5) and obtain in this way the probability measure \mathbb{P}_E on the surface Γ_E .

★ When no confusion will arise, we shall denote $\Gamma_{E,\Delta E}$ also by Γ_E , assuming, whenever needed, that a certain tolerance ΔE has been specified from the outset.

Microcanonical measure for $\Delta E \rightarrow 0$

$$\mathbb{P}_E \{dx\} = \frac{\delta(E - H(x)) dx}{\int \delta(E - H(x)) dx} \quad (6)$$

Notes:

- If the system has r degrees of freedoms, sometimes $dx \rightarrow dx/h^r$, with h a unitit of action (to be identified with Planck's constant) .
- The quantity

$$\Omega(E) = \int \delta(E - H(x)) dx \quad (7)$$

is called **microcanonical partition function** or **density of states**. It is the area of the surface Γ_E , i.e,

$$\Omega(E) = |\Gamma_E|$$

- For $\Delta E \ll E$, the quantity $\Omega(E)\Delta E$ is the volume of energy shell of thickness ΔE , i.e.,

$$\Omega(E)\Delta E = |\Gamma_{E,\Delta E}|.$$

- The volume of the phase space inside the surface Γ_E is

$$\Gamma(E) = \int^E \Omega(E) dE = |\Gamma_{\leq E}| \quad (8)$$

Clearly,

$$\Omega(E) = \frac{d}{dE} \Gamma(E).$$

- To compute the average of $Y = Y(x)$:

$$\mathbb{E}\{Y\} = \frac{1}{\Omega(E)} \int_{\Gamma} Y(x) \delta(E - H(x)) dx \quad (9)$$

$$= \frac{1}{\Omega(E)} \frac{d}{dE} \int_{\Gamma \leq E} Y(x) dx \quad (10)$$

$$= \frac{1}{\Omega(E)} \frac{d}{dE} \int_{H(x) \leq E} Y(x) dx \quad (11)$$

4 Measure preserving dynamical systems

- Definition for continuous time: $(\Omega, \mathcal{F}, \mathbb{P}, T_t)$, where $(\Omega, \mathcal{F}, \mathbb{P})$ is a probability space and T_t a flow on Ω such that

$$\mathbb{P}\{T_t^{-1}(A)\} = \mathbb{P}\{A\}, \quad (12)$$

for all $A \in \mathcal{B}(\Gamma)$ and $t \in \mathbb{R}$.

- Definition for discrete time: instead of T_t a map $T : \Omega \rightarrow \Omega$ satisfying the condition

$$\mathbb{P}(T^{-1}(A)) = \mathbb{P}(A), \quad \forall A \in \mathcal{F}. \quad (13)$$

- Two measure-preserving dynamical systems $(\Omega, \mathcal{F}, \mathbb{P}, T)$ and $(\Omega', \mathcal{F}', \mathbb{P}', T')$ are **isomorphic** if there a mapping $\phi : \Omega \rightarrow \Omega'$ that preserve the structure. This means that $(\Omega, \mathcal{F}, \mathbb{P})$ and $(\Omega', \mathcal{F}', \mathbb{P}')$ are isomorphic as measure spaces and that $\phi \circ T = T' \circ \phi$.

Poincaré's recurrence theorem can be stated for a general measure preserving dynamical system $(\Omega, \mathcal{F}, \mathbb{P}, T_t)$.

Proposition 1 (Poincaré recurrence theorem)

Let A be a subset of Ω such that $\mathbb{P}\{A\} > 0$. Then for almost every $\omega \in \Omega$ (i.e., except for a set of omega's of \mathbb{P} -measure 0) there exist arbitrarily large t such that $T_t(\omega) \in A$.

Proof First of all, rather than to consider continuous time let us discretize it and consider $T = T_\tau$, where τ is a fixed unit of time. A point $\omega \in A$ eventually returns to A if there is $k \geq 1$ for which $T^k(\omega) \in A$. Let B the set of all those points of A which will never return in A . Note that if $\omega \in B$, then $T^n(\omega) \notin B$ for each $n \geq 1$. Thus $B \cap T^{-n}(B) = \emptyset$ for $n \geq 1$ and hence $T^{-k}(B) \cap T^{-(n+k)}(B) = \emptyset$ for each $n \geq 1$ and each $k > 0$. Then the sets $B, T^{-1}(B), T^{-2}(B), \dots$ are pairwise disjoint and each has measure $\mathbb{P}\{B\}$. Since $\mathbb{P}\{\Omega\} = 1$, by additivity of the measure of disjoint sets, $\mathbb{P}\{B\}$ must be zero. \square

5 Newtonian systems

- N point masses m_1, \dots, m_N moving in physical space interacting through a pair potential with Hamiltonian

$$H = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2} \sum_{i \neq j} V_{ij}(\mathbf{q}_i - \mathbf{q}_j) \quad (14)$$

(If there there an external field with potential energy ϕ_i , the Hamiltonian contain the additional term $\sum_{i=1}^N \phi_i(\mathbf{q}_i)$.)

- The phase space Γ is the Cartesian product of the the **one-particle** phase spaces Γ_{1p} ,

$$\Gamma = \underbrace{\Gamma_{1p} \times \cdots \times \Gamma_{1p}}_{N \text{ times}} = \Gamma_{1p}^N. \quad (15)$$

where

$$\Gamma_{1p} = \mathcal{Q}_{1p} \times \mathcal{P}_{1p}, \quad (16)$$

with \mathcal{Q}_{1p} and \mathcal{P}_{1p} the one-particle configuration space and configuration space, respectively.

- Hamilton's equations become Newton's equations

$$m_i \frac{d^2 \mathbf{Q}_i}{dt^2} = -\nabla_i \sum_{j \neq i} V_{ij}(\mathbf{Q}_i - \mathbf{Q}_j), \quad i = 1, \dots, N \quad (17)$$

6 Identical particles

- If the particles are identical, they have the same mass m and interact trough the same pair potential V .
- Thus their motion is governed by the Hamiltonian

$$H = \frac{1}{2m} \sum_{i=1}^N \mathbf{p}_i^2 + \frac{1}{2} \sum_{i \neq j} V(\mathbf{q}_i - \mathbf{q}_j), \quad (18)$$

a function on Γ which is symmetric under permutations of the particles.

- Since the particles are identical, no physical distinction can be made between points in Γ_{1p}^N that differ only in the ordering of the particle phase points.
- Thus, two points in Γ_{1p}^N

$$\begin{cases} x = (x_1, \dots, x_N), & x_i \in \Gamma_{1p}, \\ x' = \pi(x) = (x_{\pi^{-1}(1)}, \dots, x_{\pi^{-1}(N)}) \end{cases} \quad (19)$$

where π is a permutation of the particles indices, both describe the same state of the system.

- Therefore the true phase space of the N -particle system is not the the Cartesian product Γ_{1p}^N , but the space obtained by identifying points in Γ_{1p}^N representing the same state. We shall denote such a space by ${}^N\Gamma_{1p}$ and we shall call it the **natural** phase space of N identical particles.

${}^N\Gamma_{1p}$ can be characterized mathematically in two equivalent ways:

- (i) Subtract from Γ_{1p}^N all the coincidence points and form the space

$$\Gamma_{1p \neq}^N = \{(x_1, \dots, x_N) \in \Gamma_{1p}^N : x_i \neq x_j, \forall i \neq j\}. \quad (20)$$

Then identify all points that differ by a permutation; in other words, "divide" the space by the action of the permutation group S_N , obtaining in this way the space

Γ_{1p}^N/S_N . This is the natural phase space ${}^N\Gamma_{1p}$. Note that the first step of the construction guarantees that the phase points represent exactly N particles (if the coincidence points were not removed, there would be phase points with a number of particles less than N).

- (ii) A point x in ${}^N\Gamma_{1p}$ can be considered as a set of N points in the one-particle phase space Γ_{1p} , i.e.,

$${}^N\Gamma_{1p} \ni x = \{x_1, \dots, x_N\} \quad x_i \in \Gamma_{1p}, \quad x_i \neq x_j \text{ if } i \neq j. \quad (21)$$

It can be shown that ${}^N\Gamma_{1p}$ is a smooth manifold.

Misconceptions about identical particles The fact that the phase space of N identical particles is ${}^N\Gamma_{1p}$ and not Γ_{1p}^N has usually been overlooked and is rarely mentioned in textbooks of classical mechanics and statistical mechanics. The textbooks tend to underline that the proper description of identical particles can be achieved only within the framework of quantum mechanics. The standard argument is something like this:

*Particles are identical if they cannot be distinguished by means of **measurements**. So, if particles have the same mass, charge, etc., they could be distinguished only by their location in space, as it is the case in classical mechanics. However, in quantum mechanics, particles do not have trajectories. Therefore they cannot be distinguished if they have the same mass, charge, etc.. Thus the notion of identical particles is purely a quantum one without any classical equivalent.*

The conclusion is faulty and the argument is **wrong**.

- The notion of identical was already recognized by Gibbs. In order to correctly calculate the entropy change in a process of mixing two identical fluids or gases (at the same temperature, etc.), Gibbs postulated that states differing only by permutations of identical particles should not be counted as distinct.
- Which is what we said above and repeat:

for non identical particles, the proper mathematical description of the state is in terms of the vector $x = (x_1, \dots, x_N)$; the vector is an ordered sequence of numbers, and so it keeps track of the labels of the particles; if the particles are identical, it is the set $x = \{x_1, \dots, x_N\}$ the right mathematical representation, since a set of objects does not involve any order of the objects themselves.

Another reason for overlooking the classical description of identical particles in terms of ${}^N\Gamma_{1p}$ could be the following.

- The dynamics of a classical system involves only **local** properties in phase space.
- That is the time evolution of a classical N -particle system is a continuous curve in ${}^N\Gamma_{1p}$.
- The one curve in ${}^N\Gamma_{1p}$ corresponds to $N!$ curves in Γ_{1p}^N . These curves do not intersect and are locally identical. Then one can just pick up one of them to describe the dynamics.
- In other words, the dynamics does not mix the $N!$ factorial copies of ${}^N\Gamma_{1p}$ whose union is just the space Γ_{1p}^N .

- So, the description of identical particles by means of the “wrong” space Γ_{1p}^N **is only redundant** (as the description of the electromagnetic field in terms of the vector potential), **but has not dynamical implications** (this redundancy manifests itself only when we count the states, as in the case considered by Gibbs).

Quantum Mechanics

- ★ **The situation in quantum mechanics is different, as the global properties of ${}^N\mathcal{Q}_{1p}$, the configuration space of N identical particles, then become essential, since the the wave function of the system $\psi(q)$ “sees” the global properties of configuration space.**

7 Confined systems

Usually, the particles are confined in a box (vessel) $\Lambda \subset \mathbb{R}^3$ of finite volume $V = |\Lambda|$. In this case, Newton’s equations eq. (17) for $Q_i \in \Lambda$ must be supplemented by conditions on the boundary $\partial\Lambda$. The simplest one is a **reflecting boundary condition**. As the name says, when a particle reaches a reflecting boundary it is reflected back into the box. In molecular dynamics, in order to mimic a liquid or solid without increasing the number of particles to be simulated, one uses **periodic boundary conditions**: a particle, going through a boundaries returns to the box from the opposite side.

8 Systems with a variable number of particles

- A central problem in statistical mechanics is the study of the properties of the subsystems of a large system.
- If the particles are identical, a natural way to specify a subsystem is by considering the particles in a certain region $\Delta \subset \Lambda$.
- A subsystem so defined will be called a **local-subsystem** associated with Δ .

Since in the course of time the number of particles in Δ may change, the microscopic state of the subsystem is specified by the number n of particles in Δ and by their state $x = (x_1, \dots, x_n)$.

Thus the phase space of the local subsystem associated with Δ is

$$\Gamma_{\Delta} = \bigcup_n^N \Gamma_{1p \Delta} \quad (22)$$

where $\Gamma_{1p \Delta}$ is the one-particle phase space restricted to Δ and N is the number of particles in Λ . If we wish to let unspecified the number of particles in Λ , we may set $N = \infty$ in eq. (22).