Statistical Mechanics and Thermodynamics

Résumé

Short Summary

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Chaos

Hamilton mechanics: trajectories cannot intersect in phase space. Hence a chaotic dynamics requires at least 3 degrees of freedom. Stationarity means time-independence (fixed points).

Fixed points of first-order differential equations:

$$\frac{\mathrm{d}}{\mathrm{d}t} y(t) = f(y) \quad \Rightarrow \quad f(y^*) = 0.$$

Stability of a fixed point of such a differential equation:

$$f'(y^*) > 0 \Leftrightarrow \text{unstable}, \qquad f'(y^*) < 0 \Leftrightarrow \text{stable}$$

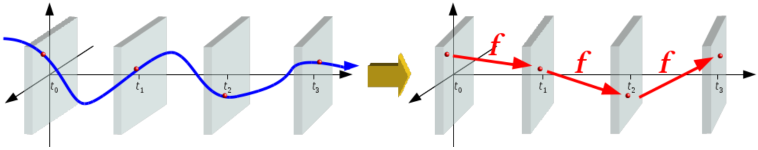
There are several types of solutions:

- **Stationary** solutions (fixed points)
- **Periodic** solutions (system returns to initial state)
- **Chaotic** solutions (system never returns to the initial state)

One goes from periodic to chaotic behavior by **period doubling**.

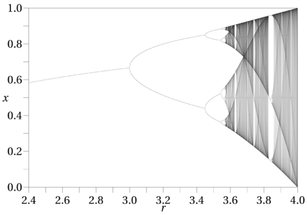
Iterative maps

Poincaré sections motivate the study of **iterative maps**:



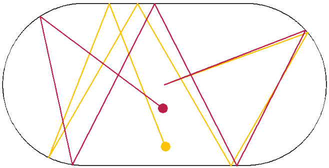
Iterative map:	$x_{n+1} = g(x_n)$
Ordinary fixed point:	$x^* = g(x^*)$
Stability condition:	$\lvert g'(x^*) \rvert < 1$

Bifucations: When a fixed point $x^* = g(x^*)$ becomes unstable, it may split up into two new branches (period doubling) given by $x^* = g(g(x^*))$, $x^* = g(g(g(x^*)))$,... .

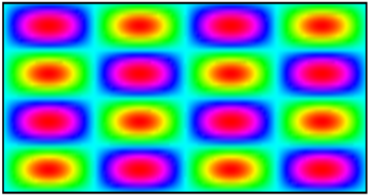


Classical and quantum billiards

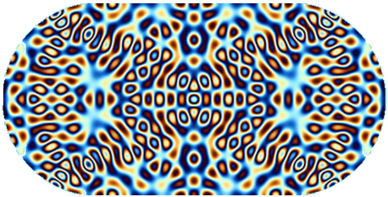
Stadium billiard: The round edges of a stadium billiard magnify small changes in the initial condition, leading to a chaotic behavior.



Quantum-mechanical wave functions:



non-chaotic



chaotic

Most complex systems in Nature are chaotic!

Time reversal symmetry

In **classical mechanics**, the Hamilton equations

$$\frac{\mathrm{d}}{\mathrm{d}t} q = \frac{\partial H}{\partial p}, \qquad \frac{\mathrm{d}}{\mathrm{d}t} p = -\frac{\partial H}{\partial q}$$

is invariant under $p \to -p, t \to -t$, meaning that it can run backward in time. It has a **time-reversal symmetry**.

In **quantum mechanics**, the Schrödinger equation

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} |\psi(t)\rangle = \mathbf{H} |\psi(t)\rangle \quad \Rightarrow \quad |\psi(t)\rangle = e^{-\frac{i}{\hbar}\mathbf{H}t} |\psi(0)\rangle$$

is invariant under $\mathbf{H} \to -\mathbf{H}, t \to -t$, hence it can also run backward in time. Thus it is also symmetric under time-reversal.

Randomness is by definition *not* invariant under time reversal. The quantum-mechanical measurement process is in fact random and cannot be reversed.

Probability

- **Objective (frequentist) interpretation:** Probability is a property of a system, given by the relative frequency in the limit of infinitely many stochastically independent experiments.
- **Subjective interpretation:** Probability reflects a subjective believe of a likelihood. Different persons may describe the same situation with different probabilities.

Definitions:

- The **outcome** or result of an experiment, and likewise the microstate of a physical system, is denoted by $\omega \in \Omega$.
- The **sample space** Ω is the set of all possible outcomes.
- An **event** $A, B, C, \ldots$ is defined as a subset of Ω
- The **event space** Σ is the set of all events, the power set of Ω.

Axiomatic definition of probability

Kolmogorov Axioms:

A function $P : \Sigma \to \mathbb{R}$ is called a **probability measure**, if

K1: *P is a probability-valued, i.e.* $\forall A \in \Sigma : P(A) \in [0, 1]$

K2: *The certain event Ω occurs with prob.* $P(\Omega) = 1$.

K3: *P is additive on non-overlapping events, that is, for a set of events $\{A_1, A_2, \ldots\}$ which cannot happen simultaneously ($A_i \cap A_j = \emptyset$) we have*

$$P[\bigcup_i A_i] = \sum_i P(A_i)\,.$$

The triple (Ω, Σ, P), i.e., the sample space Ω together with its own power set Σ and a probability measure P, which obeys the three axioms of Kolmogorov listed above, is called **probability space**.

Conditional probabilities

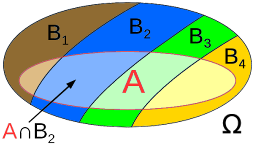
$P(A|B)$ is the probability of A under the condition that B is true.
It is defined by

$$P(A|B) \;=\; \frac{P(A\cap B)}{P(B)}$$

The vertical dash "$|$" is read as *"conditioned on"* of *"given that"*.

Law of total probability:
($\{B_j\}$ = segmentation of Ω):

$$P(A) = \sum_j P(A|B_j)\, P(B_j)$$



Bayes theorem:
Important in economics, relates $P(A|B)$ and $P(B|A)$:

$$P(A|B) = \frac{P(A)}{P(B)}\, P(B|A)$$

Statistical independence

Two events A, B are called **statistically independent** if mutual conditioning does not have any effect, i.e.

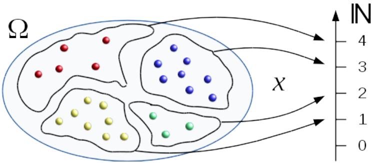
$$P(A|B) = P(A)\,, \quad P(B|A) = P(B).$$

This implies that two events are statistically independent if and only if the intersection event **factorizes**:

$$\boxed{P(A \cap B) = P(A)P(B)}$$

Functions on state spaces

Random variables:
A random variable X maps the elements of the sample space onto numbers $(\mathbb{N}, \mathbb{Z}, \mathbb{C}, \mathbb{R})$, z.B.:



$$X : \Omega \mapsto \mathbb{R} : \omega \mapsto x$$

This map induces a **probability distribution** of X, namely, the probability $P(x) = P_X(x)$ that X gives the result x is defined by

$$P_X(x) = \sum_{\omega \in X(\Omega)} P_\omega .$$

Average:
The arithmetic average of X tends to the **expectation value**:

$$\langle x \rangle = \mathbb{E}(X) := \sum_{x \in X(\Omega)} x P(x)$$

Moments

Each discrete probability distribution is characterized by certain (non-central) **moments**:

$$\boxed{m_n \;=\; \mathbb{E}(X^n) \;=\; \langle x^n \rangle.} \qquad (n = 0, 1, 2, \ldots)$$

Important statistical quantities are:

- $m_0 = 1$ Normalization
- m_1 Expectation value
- $\sigma^2 = m_2 - m_1^2$ Variance

Because of the subtraction of m_1^2 in the variance, some people like to define the so-called **central moments**:

$$\mu_n \;:=\; \mathbb{E}\Big((X - \mathbb{E}(X))^n\Big) \;=\; \langle (x - \langle x \rangle)^n \rangle\,.$$

Then the variance is simply given by $\sigma^2 = \mu_2$.

Chapter 2: Information Entropy

Information Entropy

What is information?

- Information reduces the ignorance about an object.
- Information is measured in the unit of *bit*.
- The information of an object is the minimal number of *bits* that is needed to fully characterize its state or condition.

Entropy and Information are synonymous.

The main properties of information

- **Contextuality**: Information depends on the context of the description.
- **Additivity**: The information of uncorrelated systems is the sum of the information of its parts.
- **Relativity**: Information describes the relation between object and observer. Previous knowledge reduces the information.

Information without previous knowledge

Without previous knowledge, the entropy (information) of an object is given by

$$\boxed{H = \log_2 |\Omega|}$$

- H is the number of bits needed to identify an object of Ω.
- Information can be non-integer if $|\Omega|$ is not a power of 2.

- The **context** is defined by the choice of Ω.
- The **additivity** is ensured by the logarithm:

$$|\Omega| = |\Omega_1| \cdot |\Omega_2| \quad \Rightarrow \quad H = H_1 + H_2.$$

- The aspect of **relativity** enters by specifying that the observer has no previous knowledge.

Definition of Information in various disciplines

The definition of entropy/information differs in various fields:

Information technology:	$H = \log_2 \lvert\Omega\rvert$
Mathematics:	$H = \ln \lvert\Omega\rvert$
Physics:	$S = k_B \ln \lvert\Omega\rvert$

The most obscure definition is used in Physics, where we use the letter S and assign the unit $[Joule/Kelvin]$ by multiplying the logarithm with the Boltzmann constant

$$k_B \simeq 1.38065 \cdot 10^{-23} \text{ J/K}\,.$$

This is a historical accident.

- **All these definitions differ only by a prefactor.**
- **In this course we will mainly use the second definition.**

Information with previous knowledge

- Previous knowledge is encoded in a **probability distribution** P_ω.
- Here each configuration $\omega \in \Omega$ carries an **individual entropy**:

$$\text{Individual entropy:} \quad \boxed{H_\omega = -\log_2 P_\omega}$$

- This allows us to compute the **average entropy**:

$$\text{Average entropy:} \quad \boxed{H \;=\; \langle H \rangle \;=\; -\sum_{\omega\in\Omega} P_\omega \log_2 P_\omega}$$

This is the Shannon-Gibbs-Boltzmann entropy/information.

- From now on we will use the **natural logarithm** instead of $\log_2$.

Properties of the Shannon entropy

- By Jensens inequality we can prove that the mean entropy is bounded from above by

$$H \leq \ln |\Omega|$$