

Hylleraas School 2025

Molecular dynamics – 1

Macroscopic world - - thermodynamics



Macroscopic variables : Temperature, pressure, volume...

Energetics: heat exchange, free energy, entropy

Macroscopic properties: hardness, fragility, diffusion, viscosity, surface tension, elasticity...

Microscopic world - (quantum?) mechanics



Microscopic variables : number of particles, positions, linear momenta, eigenfunctions ...

Energetics: eigenvectors of the Schr. equation

Microscopic properties: h-bonding, polarization, correlation...

Mechanically reversible vs. thermodynamically irreversible phenomena



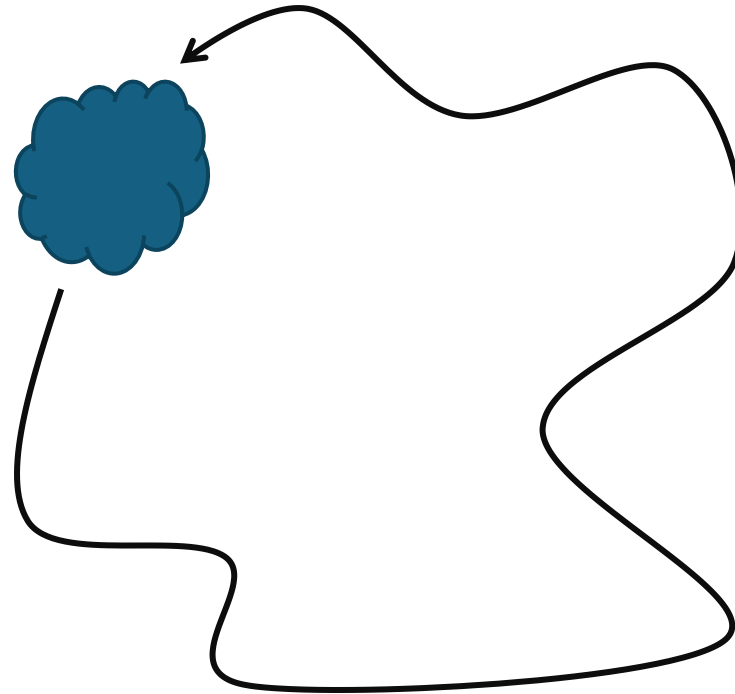
Mechanically reversible vs. thermodynamically irreversible phenomena



Henri Poincaré (1854-1912)

Theorem of recurrence

Close, isolated system --> after a certain time, it must recover its original state



???



DRINK IT FAST!!!!

Some elements of statistical mechanics

- Macroscopic observables O are associated to microscopic operators $O(\mathbf{r}, \mathbf{p})$, which depend on the **microscopic variables** of the system. The value experimentally measured is the **expectation value** of O , obtained on the thermodynamic ensemble of microscopic states populating the sample:

$$\langle \mathcal{O} \rangle = \iint o(\mathbf{r}, \mathbf{p}) \mathcal{P}(\mathbf{r}, \mathbf{p}) d\Gamma$$

The probability for each microstate, $\mathcal{P}(\mathbf{r}, \mathbf{p})$, depends on the thermodynamic conditions applied

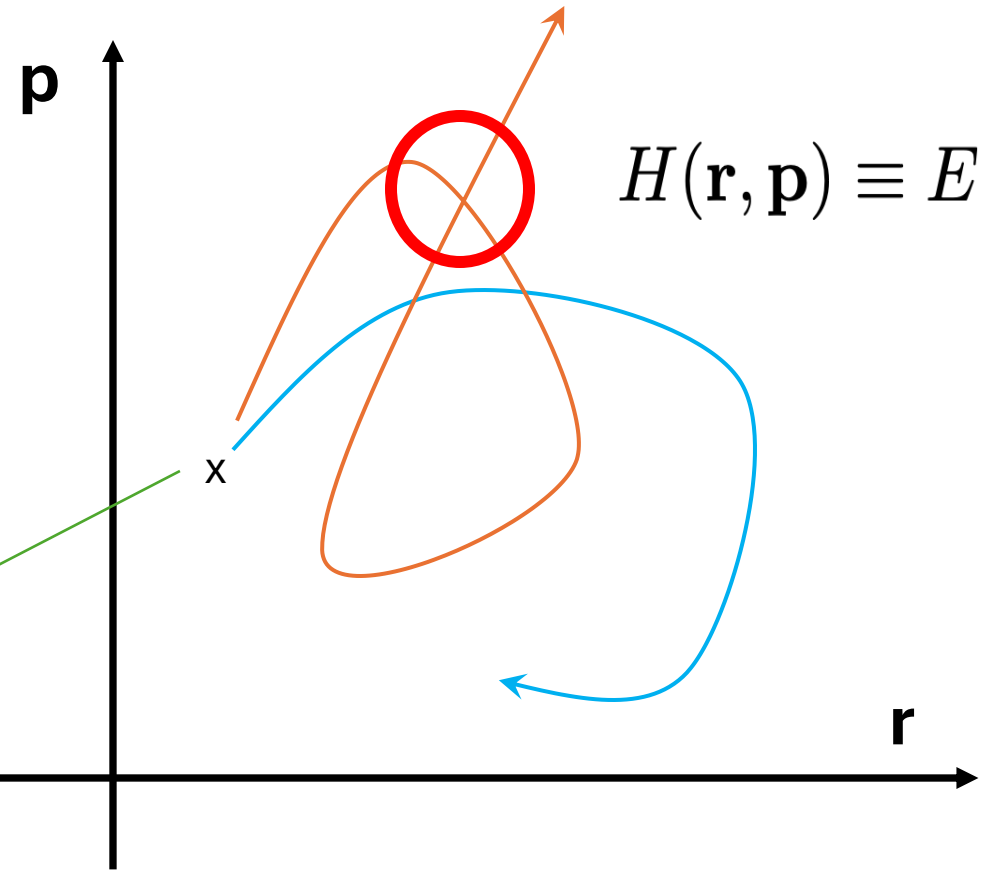
Dynamical systems: phase space

$$H = H(\mathbf{r}, \mathbf{p})$$

$$\mathbf{r} = \mathbf{r}(t)$$

$$\mathbf{p} = \mathbf{p}(t)$$

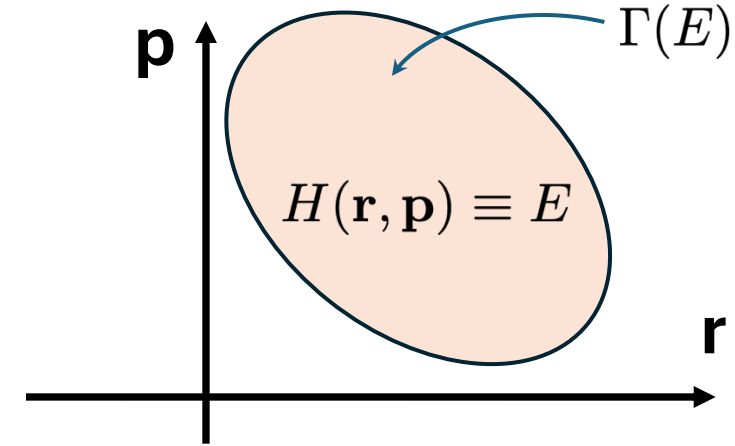
$$m \frac{\partial^2}{\partial t^2} \mathbf{r}(t) = -\nabla V(\mathbf{r}(t))$$



Microscopic state of a system at time t_0

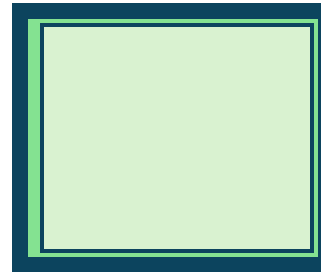
Statistical mechanics: ensembles

$$\langle \mathcal{O} \rangle = \iint o(\mathbf{r}, \mathbf{p}) \mathcal{P}(\mathbf{r}, \mathbf{p}) d\Gamma$$



- To estimate any observable of interest, we must solve this complicated $6N$ -dimensional integral, for which, knowledge of the probability distribution function is required. **P depends on the thermodynamic boundaries!**

Close, isolated system (NVE)
(*microcanonical ensemble*)



- The total energy of the system is well defined
- All the microscopic states must have the same energy
- There is no *a priori* hypothesis favouring one state over the other

$\Gamma(E)$ = number of microscopic states accessible at energy E

$S(E)$ = entropy of the system, defined as molecular disorder
(3rd principle of thermodynamics)

$$\Rightarrow \mathcal{P}(\mathbf{r}, \mathbf{p}) = \frac{1}{\Gamma(E)}$$

$$S(E) = k \ln \Gamma(E)$$

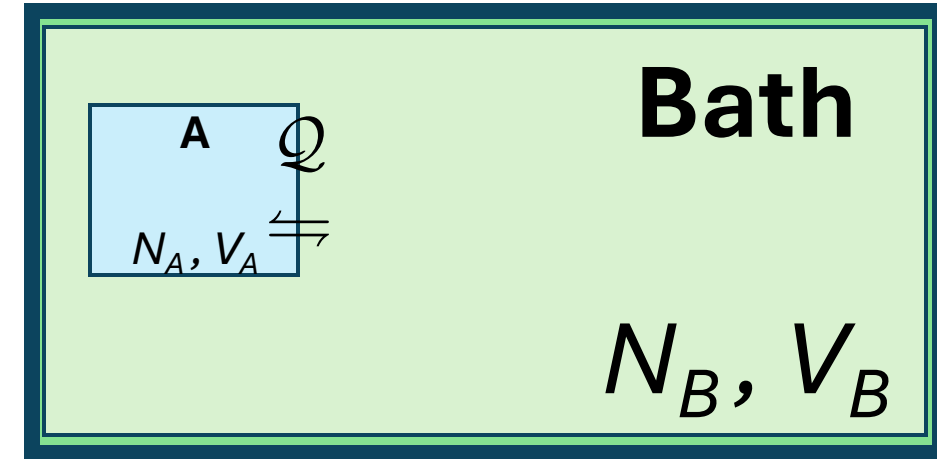
Condition of equilibrium $\rightarrow S(E)$ is maximal

Statistical mechanics: ensembles

Close system at equilibrium with external bath (NVT)

(canonical ensemble)

- The total energy of the system fluctuates
- Microscopic states can have different energy
- The principle of maximal entropy is valid for the universe only (system + bath), not for the system alone



$$\Rightarrow \mathcal{P}(\mathbf{r}, \mathbf{p}) \propto e^{-E(\mathbf{r}, \mathbf{p})/kT} \quad Q = \iint e^{-E(\mathbf{r}, \mathbf{p})/kT} d\Gamma \quad : \text{normalization function for the probability,} \\ \textbf{Canonical partition function}$$

Physical meaning of Q:

- Weighed counting of the accessible microscopic states
 - Direct connection to thermodynamic potentials:
- $$\begin{cases} A = -kT \ln Q \\ U = \langle E \rangle = -\frac{d}{d\beta} \ln Q \end{cases} \quad \beta = \frac{1}{kT}$$

The **HELMHOLTZ** free energy, (A, or sometimes F), is the reference thermodynamic potential (**...not G!!!!**)

Equipartition of the energy

Example of expectation value of an observable in the Canonical (NVT) ensemble

- Kinetic energy of a free gas: $H = \sum_{i=1}^N \frac{p_i^2}{2m}$

$$\begin{aligned}\langle H \rangle &= \frac{\iiint \sum_{i=1}^N \frac{p_i^2}{2m} e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}} d^{3N}p}{\iiint e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}} d^{3N}p} = \sum_{i=1}^N \sum_{\alpha=x,y,z} \frac{\int \frac{p_{i\alpha}^2}{2m} e^{-\beta \frac{p_{i\alpha}^2}{2m}} dp_{i\alpha}}{\int e^{-\beta \frac{p_{i\alpha}^2}{2m}} dp_{i\alpha}} \\ &= 3N \frac{\int \frac{p_x^2}{2m} e^{-\beta \frac{p_x^2}{2m}} dp_x}{\int e^{-\beta \frac{p_x^2}{2m}} dp_x}\end{aligned}$$

$$\int_{-\infty}^{\infty} \frac{x^2}{2m} e^{-\beta \frac{x^2}{2m}} dx = \frac{1}{2\beta} \sqrt{\frac{2m}{\beta}} 2\Gamma\left(\frac{3}{2}\right) = \frac{kT}{2} \sqrt{\frac{2\pi m}{\beta}}$$

$$\int_{-\infty}^{\infty} e^{-\beta \frac{x^2}{2m}} dx = \sqrt{\frac{2\pi m}{\beta}} \quad U \equiv \langle H \rangle = 3N \frac{\frac{kT}{2} \sqrt{\frac{2\pi m}{\beta}}}{\sqrt{\frac{2\pi m}{\beta}}} = \frac{3}{2} N kT$$

Remarkable result:

At thermodynamic equilibrium, the average energy stored into each degree of freedom with a quadratic expression of the energy, is exactly $\frac{1}{2} kT$; regardless of its nature.

<<Principle of equipartition of the energy>>

Quadratic terms appear everywhere!! Exactly, for kinetic energy, harmonic oscillator... approximately, for all small deformations around their equilibrium value.

So far so good... or not?

- Determining the thermodynamics of a systems means determining its partition function... which is not possible by direct calculus!

$$Q = \iint e^{-E(\mathbf{r}, \mathbf{p})/kT} d\Gamma$$

6N-dimensional integral;

**For interacting systems,
not factorizable**

The H-theorem of Boltzmann, or: the most important theorem for a chemist you have most likely never heard of...

- Heuristically, we know that $\mathcal{P}(\mathbf{r}, \mathbf{p})$ exists, because we experience that thermodynamic system, eventually, reach equilibrium.
- That dynamical systems composed by many particles reach equilibrium, was, in fact, demonstrated by Boltzmann through his celebrated H-theorem.

A fiercely disputed theorem

- The H-theorem considers the time-dependent statistical distribution of the momenta in a gas composed of particles that move according to classical EoM, and shows that, after a time, **it necessarily reaches a state of equilibrium (time-independent probability distribution of its microscopic states), regardless of its starting conditions.**
- The theorem requires the hypothesis of what Boltzmann labelled ***“molecular chaos”***

Molecular chaos

- The H-theorem is true under the assumption that, in a gas, the momentum vectors of two colliding particles are random, so that:

$$\langle \mathbf{p}_i \cdot \mathbf{p}_j \rangle = 0$$

- The H-theorem of Boltzmann offered the microscopic of understanding, without additional needs, of experimental facts known by everybody... But its apparent “assault” on determinism made it not acceptable to many.

Molecular chaos – a definition

Fast-forward to XXI century: we are all familiar with chaos in dynamical systems..



Butterfly effect!



Intrinsic instability of in dynamic trajectory

<https://www.youtube.com/embed/0vkV5AduqOw?feature=oembed>

Ljapunov instability

<https://www.youtube.com/watch?feature=oembed&v=uSZnv2bxgNw>

https://www.youtube.com/watch?feature=oembed&v=7Ae_-sL2kFw

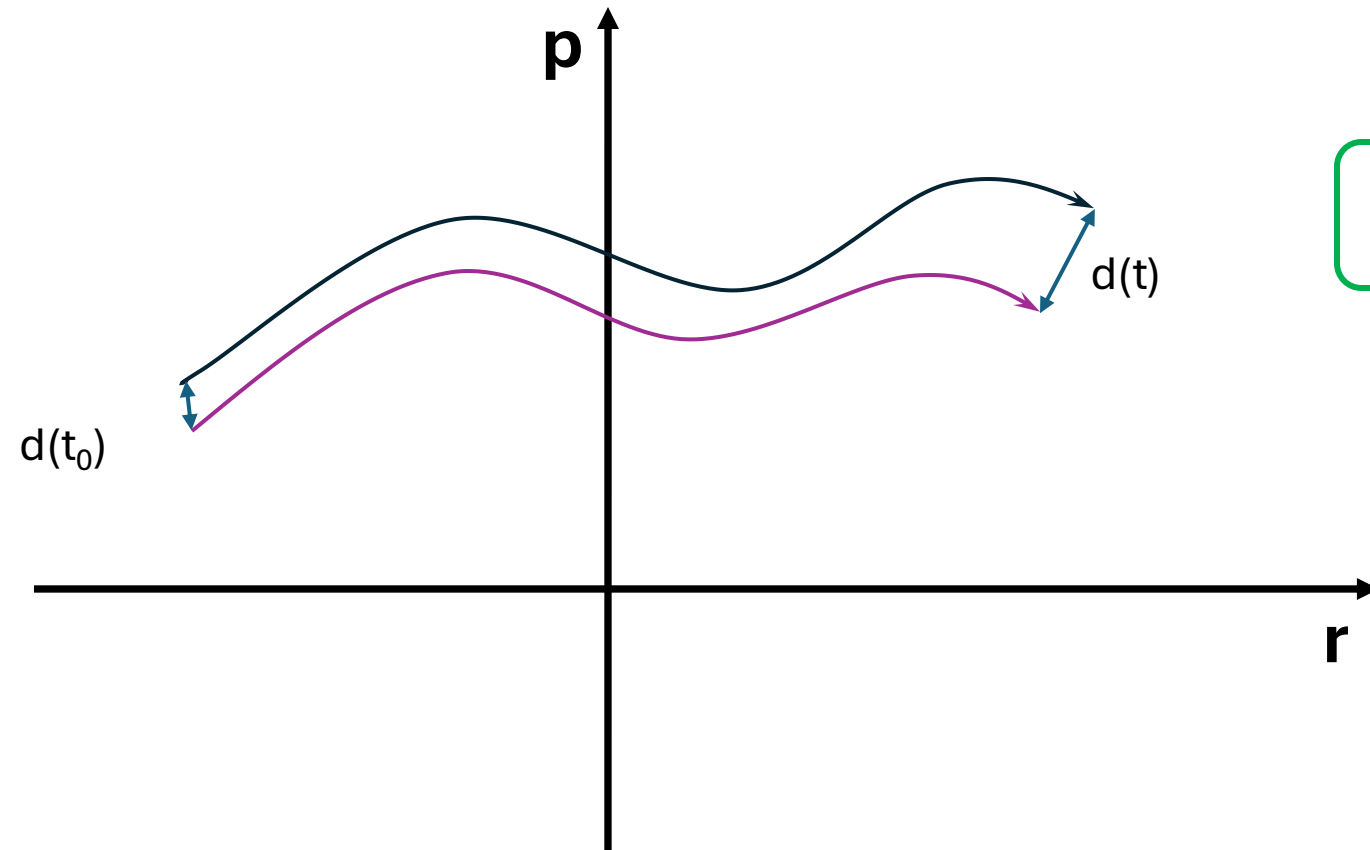
Discussion time!

How would you determine if a dynamical system shows chaotic behaviour?

<https://www.youtube.com/watch?feature=oembed&v=pjnFsk5b8XM>

Discussion time!

How would you determine if a dynamical system shows chaotic behaviour?

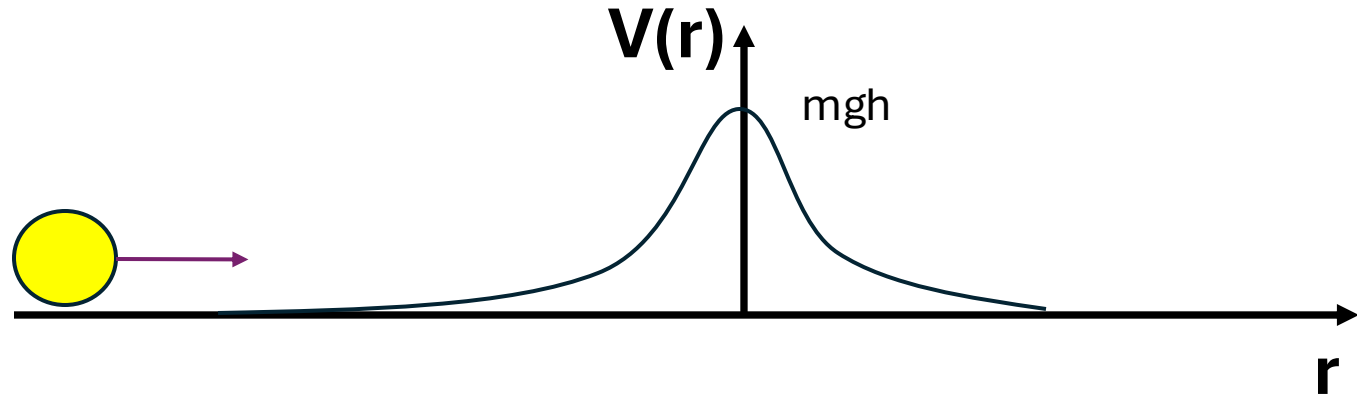


$$\forall t; \text{ if } d(t_0) < \epsilon \Rightarrow d(t_0) < \Delta$$

Non-chaotic

Example: a “mostly non-chaotic” system

$$K = \frac{p^2}{2m} \quad p^* = \sqrt{2m^2gh}$$

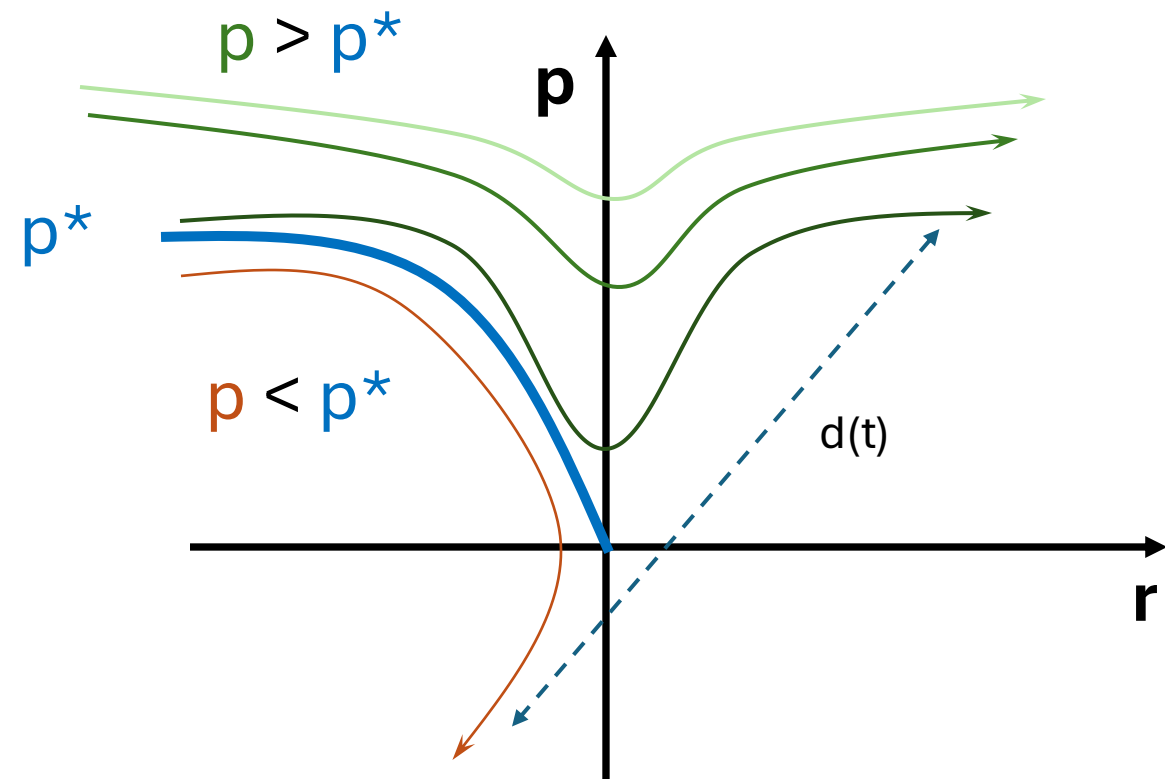


$$p = p^* + \varepsilon/2$$

$$p = p^* - \varepsilon/2$$

$$p - p^* < \varepsilon \rightarrow d(t) > \Delta$$

Around p^* , regardless of the likelihood of the initial conditions, trajectories will produce drastically different outcomes



A closer look at disorder

<https://www.youtube.com/watch?feature=oembed&v=QyJYkqEsuRE>

Statistical ensemble of conformations

<https://www.youtube.com/watch?v=RIcrnYp4DkM>

Over time, the system explores the full ensemble of conformations with the appropriate probability

Ergodic hypothesis:

(Fundamental theorem for MD!)

“Time averages computed over sufficiently long physical trajectories converge to statistical ensemble averages”

$$\langle \mathcal{O} \rangle = \iint o(\mathbf{r}, \mathbf{p}) \mathcal{P}(\mathbf{r}, \mathbf{p}) d\Gamma$$

$$= \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau \mathcal{O}(t) dt$$

So, what is molecular dynamics?????

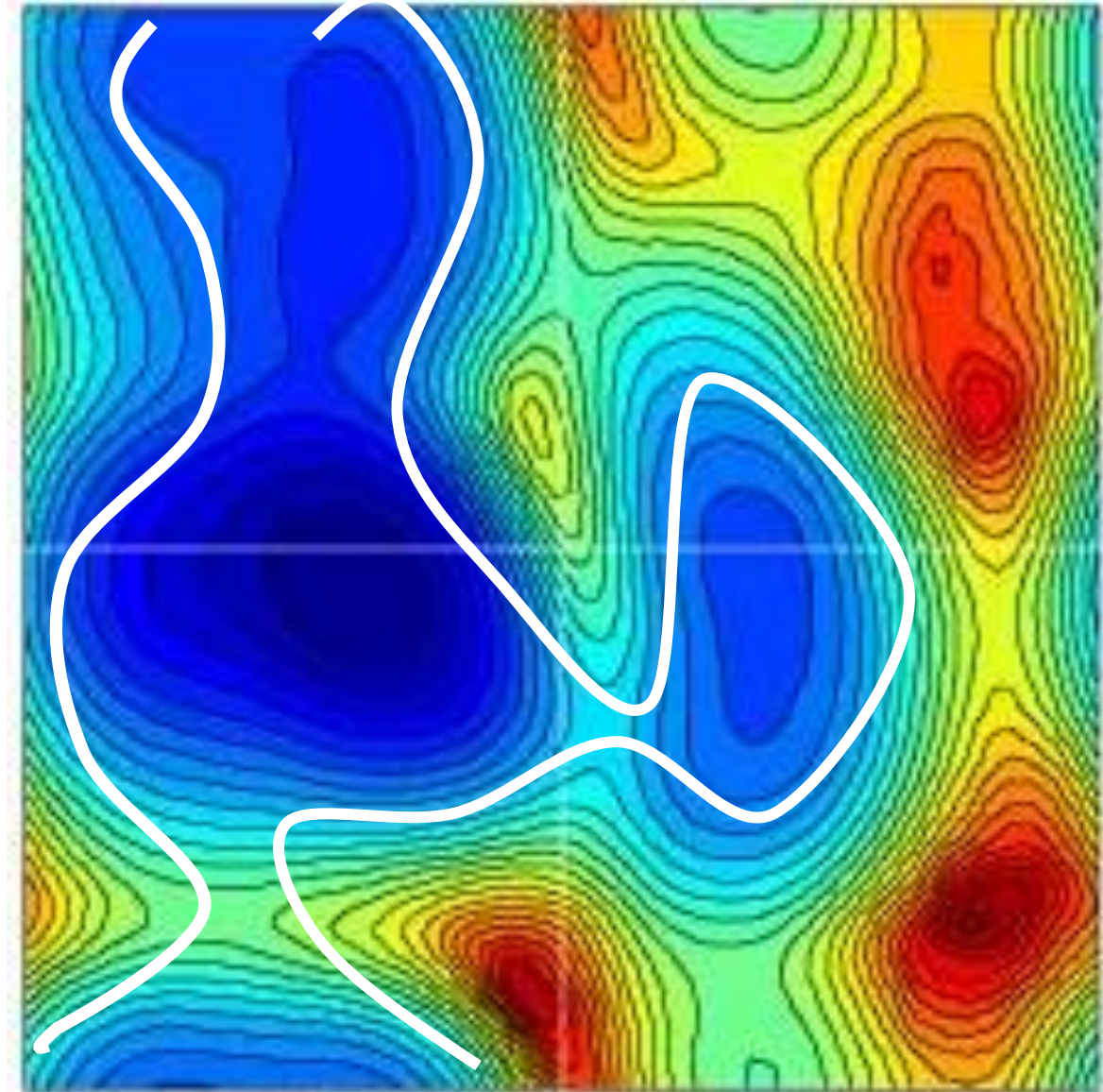
- **Statistical sampling approach!!**

- Aimed at solving efficiently statistical mechanics integrals
- Treatment of atoms and molecules as a dynamical system → Study of the time-evolution by numerical integration of the equations of motion
- Link to macroscopic ensemble properties (ergodic theorem) → thermodynamics

$$\langle \mathcal{O} \rangle = \frac{1}{Q} \int \cdots \int \mathcal{O}(\{\mathbf{r}, \mathbf{p}\}) e^{-\frac{E(\{\mathbf{r}, \mathbf{p}\})}{kT}} d\Gamma = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau \mathcal{O}(t) dt$$

- Straightforward implementation of non-equilibrium phenomena
- ***Only apply the boundary conditions of interest***, the thermodynamic ensemble *builds up automatically*
- Realistic description of microscopic events → kinetics

Importance sampling



What about quantum mechanics??????

Isn't all this classical mechanics conundrum incorrect, in a molecular world?

OF COURSE IT IS!

(...if you care about realistic description of the detailed motion of things)

...so, are we modelling what???

- In fact, we mainly do MD to **sample statistical ensembles**; to a lesser extent, to have a realistic representation of molecular motion.
- Statistically, we care about expectation values of variables.

Discussion time!

What's the behaviour (in time) of the expectation values of position and momentum, over a quantum mechanical state?

We profit from the Ehrenfest theorem:

$$\frac{d}{dt} \langle \hat{A} \rangle = \left\langle \frac{d\hat{A}}{dt} \right\rangle + \frac{1}{i\hbar} \langle [\hat{A}, \hat{H}] \rangle$$

$$\frac{d}{dt} \langle \hat{x} \rangle = 0 + \frac{1}{i\hbar} \langle [\hat{x}, \hat{H}] \rangle = \frac{1}{i\hbar} \left\langle \frac{1}{2m} [\hat{x}, \hat{p}^2] \right\rangle = \frac{1}{2mi\hbar} \langle \hat{p}[\hat{x}, \hat{p}] + [\hat{x}, \hat{p}]\hat{p} \rangle = \frac{\langle \hat{p} \rangle}{m}$$

“classical” definition of velocity

$$\frac{d}{dt} \langle \hat{p} \rangle = 0 + \frac{1}{i\hbar} \langle [\hat{p}, \hat{H}] \rangle = \frac{1}{i\hbar} \langle [\hat{p}, \hat{V}] \rangle = - \left\langle \psi \left| \frac{d}{dx} \hat{V} - \hat{V} \frac{d}{dx} \right| \psi \right\rangle = - \left\langle \frac{d\hat{V}}{dx} \right\rangle$$

“classical” Newton’s law

High-temperature regime for statistical ensembles

Discussion time!

What's the Canonical partition function of a quantum mechanical harmonic oscillator?

What's its high-temperature limit??

... and what's its relationship with a classical harmonic oscillator???

Reminder:

$$Q = \iiint e^{-E(\mathbf{r}, \mathbf{p})/kT} d\Gamma$$

- The classical partition function is:

$$Q = \iint e^{-\beta \left(\frac{p^2}{2m} + \frac{kx^2}{2} \right)} dp dx / h$$

- Quantum mechanically, we sum over all the existing microscopic states (which are the eigenstates of the total Hamiltonian operator).

$$Q = \sum_{n=0}^{\infty} e^{-\beta E_n} \quad \hat{H} |\varphi\rangle_n = \hbar\omega \left(n + \frac{1}{2} \right) |\varphi\rangle_n; \quad n \in \mathbb{N}$$

Classical Mechanics

$$\begin{aligned} Q &= \iint e^{-\beta \left(\frac{p^2}{2m} + \frac{kx^2}{2} \right)} dp dx / h \\ &= \frac{1}{h} \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} p^2} dp \int_{-\infty}^{\infty} e^{-\frac{\beta k}{2} x^2} dx \\ &= \frac{1}{h} \sqrt{2m\pi kT} \sqrt{\frac{2\pi kT}{k}} \\ &= \frac{kT}{\hbar\omega} \end{aligned}$$

Quantum Mechanics

$$Q = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega \left(\frac{1}{2} + n \right)} = e^{-\frac{\beta \hbar \omega}{2}} \sum_{n=0}^{\infty} e^{-\beta \hbar \omega n}$$

$$\sum_{n=0}^{\infty} e^{-\beta \hbar \omega n} = \sum_{n=0}^{\infty} \rho^n; \quad \rho = e^{-\beta \hbar \omega} < 1$$

$$= \frac{e^{-\frac{\beta \hbar \omega}{2}}}{1 - e^{-\beta \hbar \omega}} = \frac{1}{2 \sinh \left(\frac{\beta \hbar \omega}{2} \right)}$$

for $x \ll 1$ $\sinh x \sim x$

$$\Rightarrow Q \sim \frac{kT}{\hbar\omega}$$

Outlook

- Statistical ensembles describe thermodynamics from a microscopic perspective
- Thermodynamic equilibrium is a consequence of the chaotic behaviour of particles
- Thermodynamics properties of molecular systems can be deduced by studying their motion