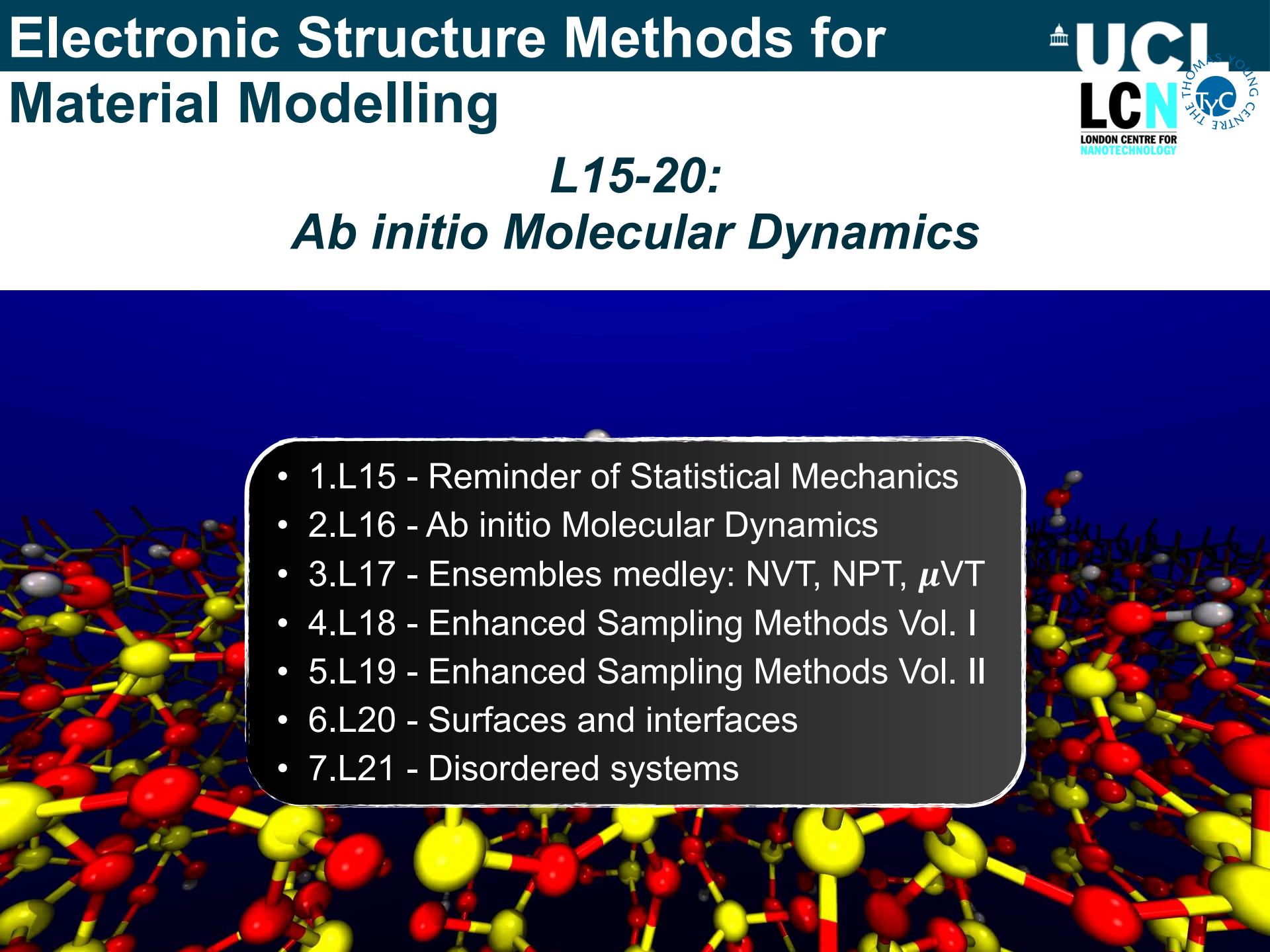


# Electronic Structure Methods for Material Modelling

## *L15-20: Ab initio Molecular Dynamics*

- 
- A detailed 3D molecular dynamics simulation of a material, likely a metal-oxide interface. The structure features a network of atoms represented by spheres: large yellow spheres for metal atoms, smaller red spheres for oxygen atoms, and small grey spheres for hydrogen atoms. The atoms are connected by sticks representing chemical bonds. The background is a solid dark blue.
- 1.L15 - Reminder of Statistical Mechanics
  - 2.L16 - Ab initio Molecular Dynamics
  - 3.L17 - Ensembles medley: NVT, NPT,  $\mu$ VT
  - 4.L18 - Enhanced Sampling Methods Vol. I
  - 5.L19 - Enhanced Sampling Methods Vol. II
  - 6.L20 - Surfaces and interfaces
  - 7.L21 - Disordered systems

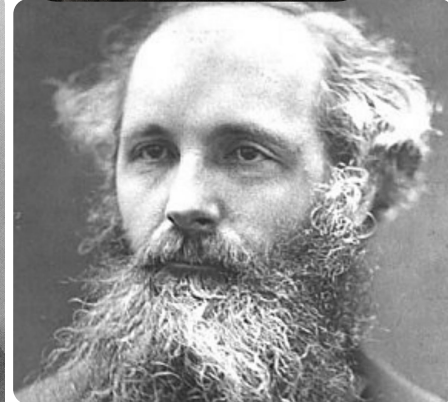
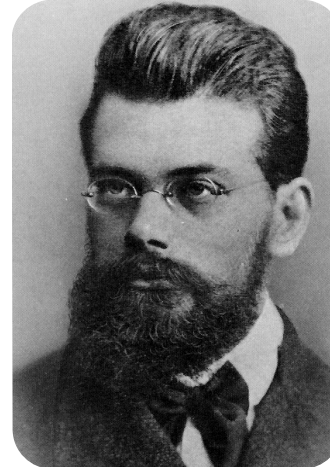
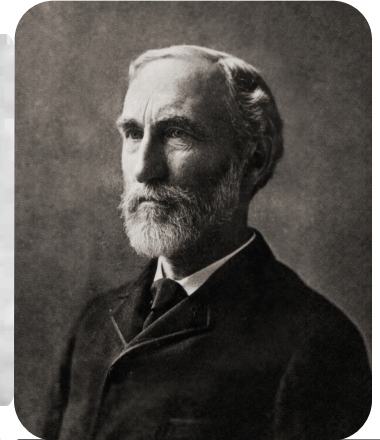
- Contact: [g.sosso@ucl.ac.uk](mailto:g.sosso@ucl.ac.uk)
- Lecture slides (including The Hidden Math and What's Next): on Moodle
- Digging a little deeper...
  - M. Tuckermann, *Statistical Mechanics: Theory and Molecular Simulation* (L15,L17)
  - D. Frenkel. & B. Smith, *Understanding Molecular simulations* (L15,L17-19)
  - M.P. Allen, D.J. Tildesley, *Computer Simulations of Liquids* (L15,L21)
  - R. Martin (no, not THAT guy) *Electronic structure: Basic Theory and Practical Methods* (L16)
  - T. Kühne, *Ab initio Molecular Dynamics* (<http://arxiv.org/abs/1201.5945v2>) (L16)
  - C. Chipot & A. Pohorille, *Free Energy Calculations: Theory and Applications in Chemistry and Biology* (L18-19)
  - H. Lüth, *Solid Surfaces, Interfaces and Thin Films* (L20)
  - K. Binder, *Glassy Materials and Disordered Solids: An Introduction to Their Statistical Mechanics* (L21)
  - R. Zallen, *The Physics of Amorphous Solids* (L21)

## *Electronic Structure Methods for Materials Modelling*

# (Extremely compact) reminder of Statistical Mechanics

- Learning Outcomes
  - The concept of *phase space*
  - The origin and the role of the *partition function*
  - How do we switch *from classical to quantum statistical mechanics*

- Why MD?
- Classical statistical mechanics
  - Phase space
  - Classical mechanics
  - Liouville equation
  - The microcanonical ensemble
- Introducing MD
  - Ergodic principle
  - Integrating the equations of motion
  - Initial conditions
- The quantum case
  - Quantum statistical mechanics
  - The Born-Oppenheimer approximation
- Next: how do we deal with the electrons?

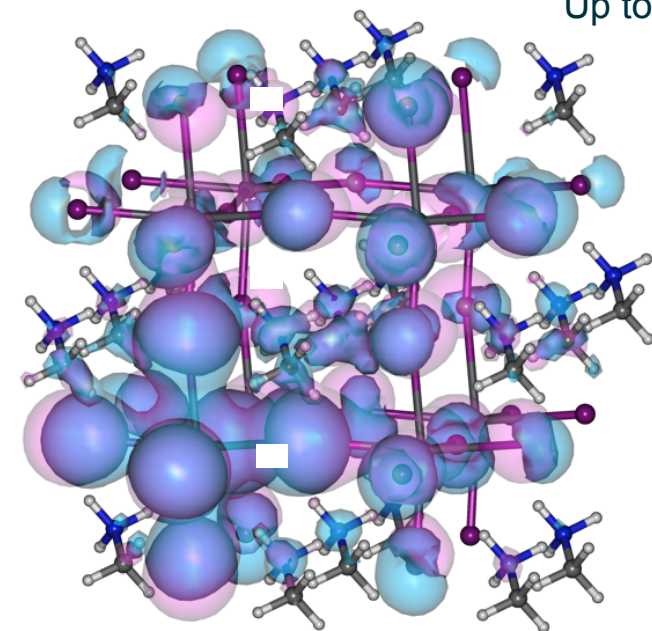




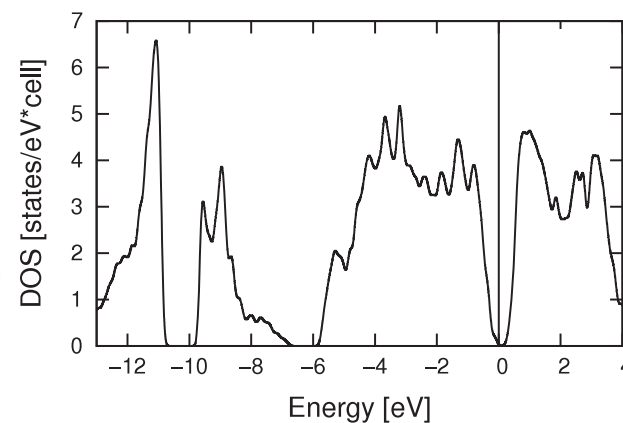
# Why (ab initio) Molecular Dynamics?

## Computer experiments

Up to now in this course: static properties at 0 K



e.g. the electronic density of state of an ideal crystalline structure at 0 K



(ab initio) molecular dynamics allows the investigation of:

- Dynamical properties
- Properties evaluated at e.g. finite temperature
- Characterization of liquid phases
- Non equilibrium problems, e.g. thermal transport
- Chemical reactions, phase transitions

Disclaimer: some of these can be studied by (quantum) Monte Carlo simulations

We want to obtain **macroscopic properties** of the system of interest at certain conditions (maybe not accessible experimentally), providing at the same time **microscopic insight**

# Connecting Macro and Micro

## *The concept of ensemble*

No electronic structure method is (will ever be?) able to deal with the macroscopic ( $10^{23}$  particles) world



got  $6.02214 \times 10^{23}$ ?

The workaround (Boltzmann ~1800, Gibbs ~1900):  
***The macroscopic properties of a macroscopic system  
are not that sensitive to its exact microscopic ( $10^1$ - $10^6$  particles) details***



### **The concept of ensemble**

- A collection of microscopic systems described by the same set of **microscopic interactions** and sharing a common set of **macroscopic properties**
- Each of these microscopic systems evolves in time according to certain microscopic laws of motion from a different initial condition, such as at any time each system has a unique microscopic state.

## Ensamble averages


(Under certain conditions) we are allowed to estimate a macroscopic property  $\mathcal{P}$  of the actual system by performing an average of the microscopic property  $p$  over all the microscopic systems of the ensemble



Ensemble average,  $\langle p \rangle$

If your favourite electronic structure method can deal with these microscopic systems, you have decomposed your unfeasible macroscopic problem into an intrinsically parallel problem made of a set of  $Z$  microscopic systems

Thus, in classical ensemble theory:

$$\mathcal{P} = \frac{1}{Z} \sum_{\lambda=1}^Z p(x_{\lambda, t=t^*}) \equiv \langle p \rangle$$


*Microscopic state of the system*

# Microscopic states

## *The concept of phase space*

The microscopic state of a system containing  $N$  particles at time  $t=t^*$  is given by  $6N$  numbers:

$$x_{\lambda, t=t^*} = \left( \underbrace{\mathbf{r}_{\lambda, t=t^*, 1}, \dots, \mathbf{r}_{\lambda, t=t^*, N}}_{\text{Positions}}, \underbrace{\mathbf{p}_{\lambda, t=t^*, 1}, \dots, \mathbf{p}_{\lambda, t=t^*, N}}_{\text{Momenta = mass } m \text{ times velocity } \mathbf{v}} \right)$$

These  $6N$  numbers define a **phase space vector**, which lives in a  $6N$ -dimensional space called **phase space**.

Remember: this is classical statistical mechanics!



The system evolves according to Newton's equations of motion

$$\mathbf{F}_i(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_i) = m_i \mathbf{a}_i = \frac{\partial \mathbf{p}_i}{\partial t}$$

If

- The forces acting on the system are conservative:  $\mathbf{F}_i(\mathbf{r}_1, \dots, \mathbf{r}_N) = -\nabla_i U(\mathbf{r}_1, \dots, \mathbf{r}_N)$

- We can define the kinetic energy of the system as:  $K(\dot{\mathbf{r}}_1, \dots, \dot{\mathbf{r}}_N) = \frac{1}{2} \sum_{i=1}^N m_i \dot{\mathbf{r}}_i^2$

Potential Energy

we can define a Lagrangian:

$$\mathcal{L}(\mathbf{r}_1, \dots, \mathbf{r}_N, \dot{\mathbf{r}}_1, \dots, \dot{\mathbf{r}}_N) = K(\dot{\mathbf{r}}_1, \dots, \dot{\mathbf{r}}_N) - U(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

which generates Newton's equation of motion via the Eulero-Lagrange equation:



\* The Hidden Math - on Moodle

$$\frac{d}{dt} \left( \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i} \right) - \frac{\partial \mathcal{L}}{\partial \mathbf{r}_i} = 0$$



The Hamiltonian formulation of classical mechanics is quite useful as well...  
How do we get it from the Lagrangian formulation?

Recall the Legendre transform:

$$\tilde{f}(s) = f(x(s)) - sx(s), \quad s = f'(x)$$

$$\tilde{f}(s_1, \dots, s_n) = f(x_1(s_1, \dots, s_n), \dots, x_n(s_1, \dots, s_n)) - \sum_{i=1}^n s_i x_i(s_1, \dots, s_n)$$

As

$$\mathbf{p}_i = \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i}$$

If you take the Legendre transform of the Lagrangian, you end up with the Hamiltonian of the system:

$$\mathcal{H}(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, \dots, \mathbf{r}_N)$$



# Liouville theorem

## How do we move in the phase space?

Think about this question: the Hamiltonian (or the Lagrangian...) of the system tells you about the motion of each individual member of the ensemble

**What about the time evolution of the ensemble as a whole?**

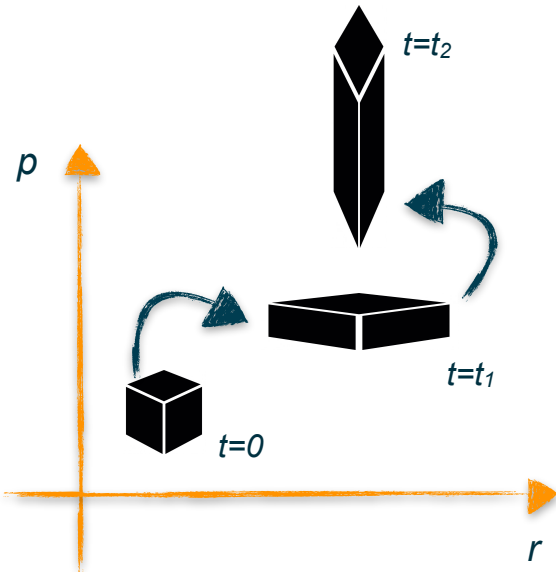
Well, if the system evolves in time according to Hamilton's equation...

Liouville theorem

$$dx_t = dx_0$$

The phase space volume is conserved in time

Imagine your ensemble at  $t=0$  as an (hyper)cube in the  $6N$  phase space



The time evolution of each system within the ensemble (Hamilton equations) will lead to a distortion of this hypercube in time

Liouville theorem says that *no matter the shape of the region of the phase space occupied by the ensemble, the volume of that region does not change*

Nor does the number of systems → **the density stays the same**



# Liouville theorem

## *Practical meaning?*

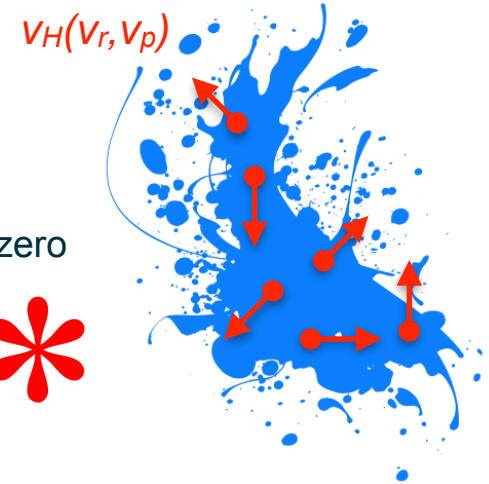
Note *the analogy with an incompressible fluid*

Given a velocity field  $v$

$$\nabla \cdot v = 0$$

And in fact, the divergence of an Hamiltonian field is zero

$$\nabla \cdot v_H(v_r^i, v_p^i) = 0$$



One of the most important consequences of Liouville theorem:

*(Equilibrium) ensemble averages can be evaluated at any point in time*

$$\mathcal{P} = \frac{1}{Z} \sum_{\lambda=1}^Z p(x_{\lambda, t=t^*}) \equiv \frac{1}{Z} \sum_{\lambda=1}^Z p(x_{\lambda, t=t^\dagger})$$

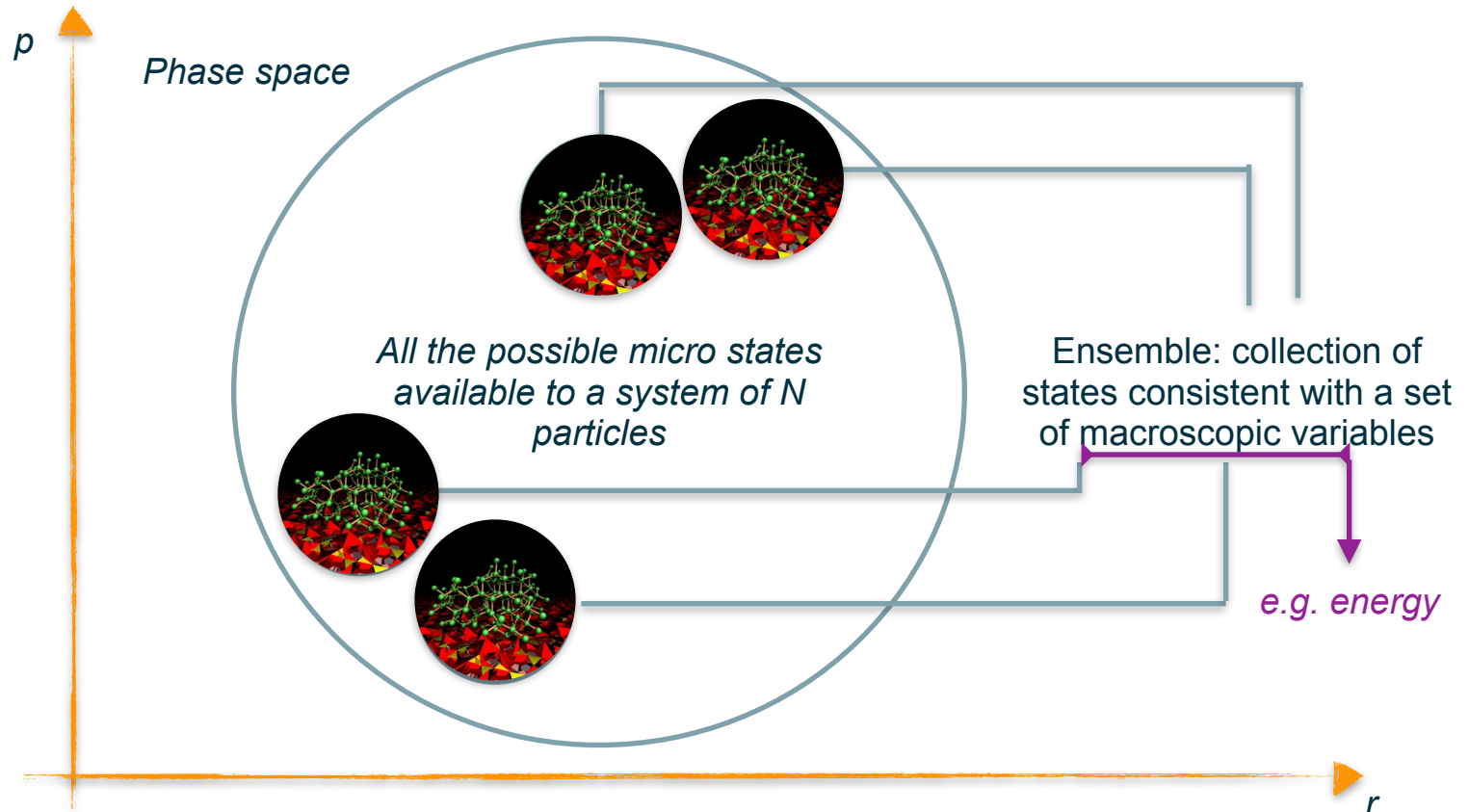
# Liouville equation

## *The ensemble distribution function*

How exactly the micro states of the ensemble are distributed within the phase space?

The ensemble distribution function

$$f(x, t)$$



# Liouville equation

## *Time evolution of the ensemble distribution*

Let's define a sort of phase space velocity

$$\dot{x} = \left( \frac{\partial \mathcal{H}}{\partial p_1}, \dots, \frac{\partial \mathcal{H}}{\partial p_{3N}}, -\frac{\partial \mathcal{H}}{\partial q_1}, \dots, -\frac{\partial \mathcal{H}}{\partial q_{3N}} \right)$$

The ensemble distribution function and the phase space velocity are connected by the ***Liouville equation***

$$\frac{\partial}{\partial t} f(x, t) = -\dot{x} \cdot \nabla f(x, t)$$

It tell us how the ensemble evolves in time - and more!



# Liouville equation

## *Equilibrium solutions*

Recall the connection between macro and micro

$$\mathcal{P} = \frac{1}{Z} \sum_{\lambda=1}^Z p(x_{\lambda, t=t^*}) \equiv \langle p \rangle \quad \text{or} \quad \mathcal{P} = \langle p(x) \rangle = \int f(x, t) \cdot p(x) \, dx$$

For an equilibrium ensemble average, though:

$$\frac{\partial}{\partial t} f(x, t) = 0$$

And the Liouville equation becomes:

$$\dot{x} \cdot \nabla f(x, t) = 0$$

At this stage, basically any function of the Hamiltonian is a solution of the equilibrium Liouville equation

$$f(x) \propto \mathcal{F}(\mathcal{H}(x))$$

# Liouville equation

## *The origin of the partition function*

We cannot say much about the specific form of the Liouville equilibrium equation without knowing some more about the ensemble

However, we do know that we have to normalize the solution, whatever that is

$$\int f(x, t) \, dx = 1$$

Thus

$$f(x) = \frac{1}{\mathcal{Z}} \mathcal{F}(\mathcal{H}(x))$$

where  **$\mathcal{Z}$  is the partition function**, defined as

$$\mathcal{Z} = \int \mathcal{F}(\mathcal{H}(x)) \, dx$$

# Ensemble averages

## *The central role of the partition function*

Thanks to the partition function, we can now compute any equilibrium observable as

$$\mathcal{P} = \langle p(x) \rangle = \frac{1}{\mathcal{Z}} \int p(x) \mathcal{F}(\mathcal{H}(x)) dx$$

Remember: this holds because of Liouville theorem

$$dx_t = dx_0$$

which implies that

$$f(x_t) dx_t = f(x_0) dx_0$$

# The microcanonical ensemble

## Focusing on the “right” energies

Now we have the tools we need!

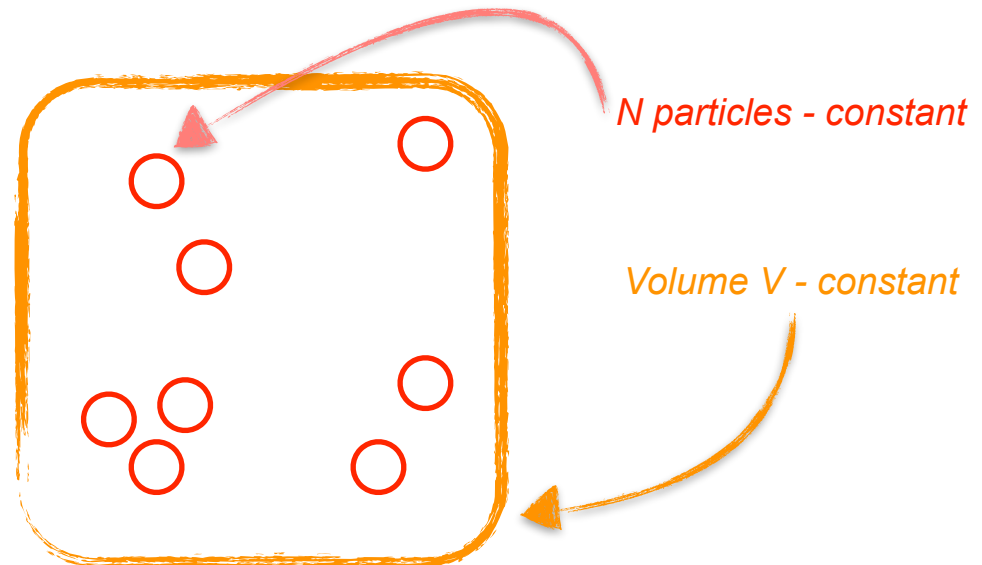
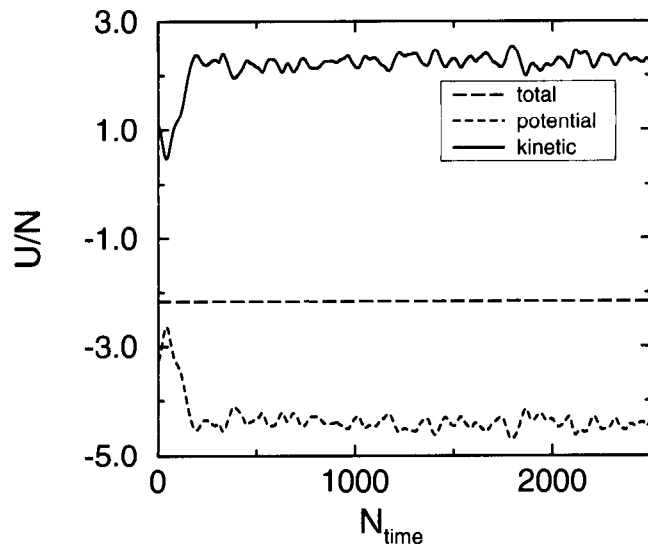
We can choose the ensemble we want, in order to mimic the experimental conditions we are interested in

Simplest option? **The microcanonical ensemble (NVE)**

Number of particles, volume of the system and its total energy are conserved.

Imagine an isolated box of volume  $V$  containing  $N$  particles, unable to exchange energy  $E$  with the external world

*Total Energy  $E$  - conserved*



# The microcanonical ensemble

## Focusing on the “right” energies

Let us solve the equilibrium Liouville equation

$$\dot{x} \cdot \nabla f(x, t) = 0$$

This time, on top of the generic solution

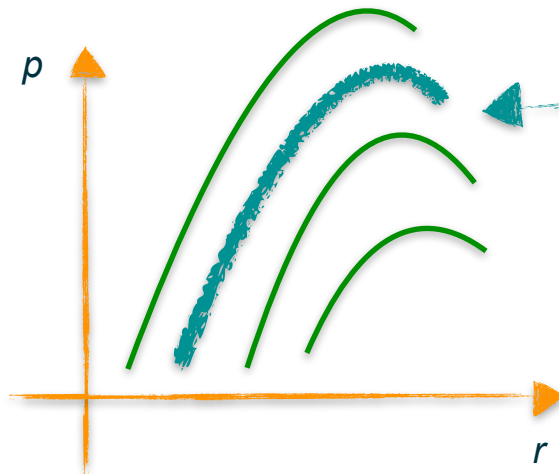
$$f(x) \propto \mathcal{F}(\mathcal{H}(x))$$

We know that  $F$  must be restricted to those states for which

$$\mathcal{H}(x) = E$$

The simplest option is the Dirac delta function, so that we can write the solution as

$$\mathcal{F}(\mathcal{H}(x)) = \delta(\mathcal{H}(x) - E)$$



$$f(x, t) \rightarrow E = H(x)$$

In the NVE ensemble, the phase distribution function lies entirely on the hyper surface defined by the Hamiltonian




# The microcanonical ensemble

## *NVE partition function*

Assumption of equal a prior probability:  
all the points of the space phase on that hyper surface **have the same probability**,  
(while any point outside has zero probability)

How much phase space is available to the system?  
That is, how extended is that hyper surface?  
Or again, what is the partition function of the NVE ensemble?



Recall:  $\mathcal{Z} = \int \mathcal{F}(\mathcal{H}(x)) dx$    $\mathcal{Z} = \Omega(NVE) = A \cdot \int \delta(\mathcal{H}(x) - E) dx$

$$A = \frac{E_0}{N! h^{3N}}$$

$E_0$  is irrelevant but makes the partition function dimensionless

$h^{3N}$  is the volume of an hypercube in the phase space

$N!$  is quantum mechanics!

Over counting of indistinguishable states/particles

# The microcanonical ensemble

## Entropy

Basically, *the partition function in the NVE is just the sum of the states with the right energy*.  
As such, this ensemble is dominated by entropy, as demonstrated by the famous Boltzmann formula (~1870, then Planck):

$$S(N, V, E) = k_B \ln \Omega(N, V, E)$$

Macroscopic entropy

Microscopic partition function

Boltzmann (well, actually Planck...) constant  
New value (2013, impossibly accurate measurement of the speed of sound in a monoatomic gas) could be  $1.38065156(98) \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$



Again, we are interested in macroscopic equilibrium properties, and we now we know how to compute:

$$\mathcal{P} = \langle p(x) \rangle = \frac{1}{\mathcal{Z}} \int p(x) \mathcal{F}(\mathcal{H}(x)) dx$$

In NVE

$$\langle p(x) \rangle = \frac{\int p(x) \delta(\mathcal{H}(x) - E) dx}{\int \delta(\mathcal{H}(x) - E) dx}$$

However, in MD we evolve the equation of motion of the system, so that we perform time averages, not ensemble averages! Are the two equivalent? Yes, if the ergodic principle holds (for a long enough simulation time, the time average does not depend on the initial conditions):

$$\langle p(x) \rangle = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t p(x_{\lambda, t=t^*}) dt$$

*Not every system is ergodic!*

### **Ergodic Hypothesis:**

A system, given an infinite amount of time, will cover the entire constant energy hypersurface

# MD in practice

## Solving Newton's equations

In classical MD, all we have to do is to integrate Newton's equations of motion:

$$\mathbf{F}_i(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_i) = m_i \mathbf{a}_i = \frac{\partial \mathbf{p}_i}{\partial t}$$

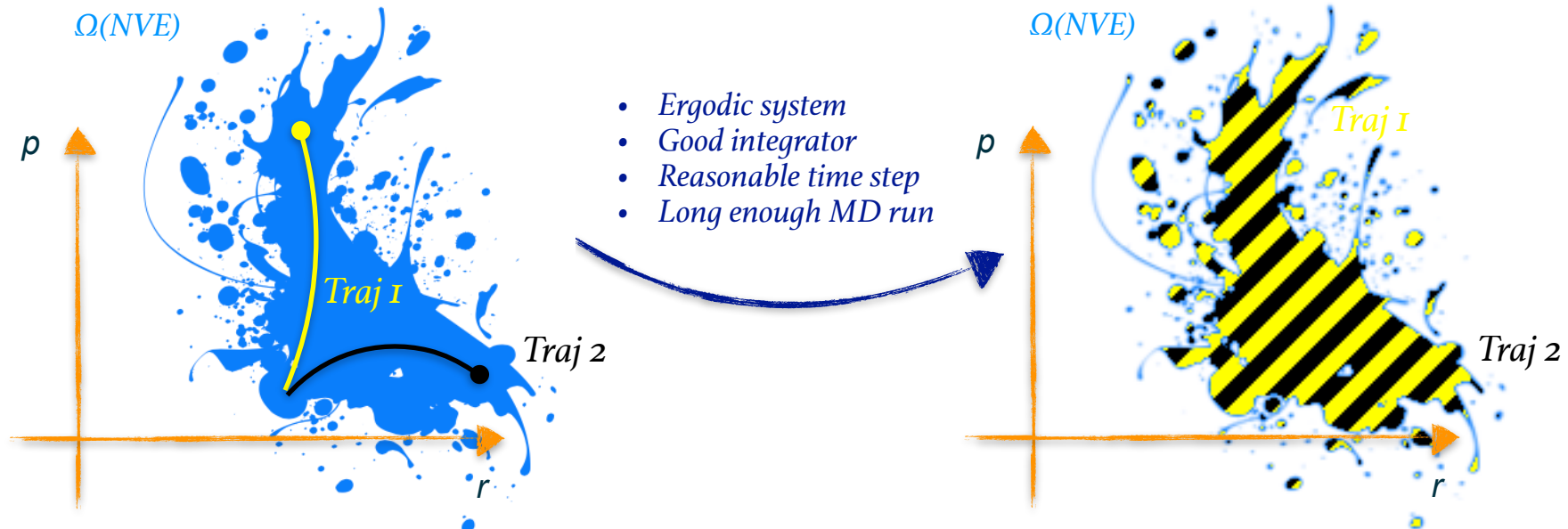
*In ab initio MD,  
this is just half of the story...*

We cannot generate the actual trajectory of the system  
We can, however, integrate numerically the equations of motion

Chaotic trajectories:

exponential divergence with respect to the initial conditions (positions and momenta)

Still, with a good integrator the discrete trajectory is close enough to the analytical one:  
divergent, yes, but still sampling the same NVE ensemble



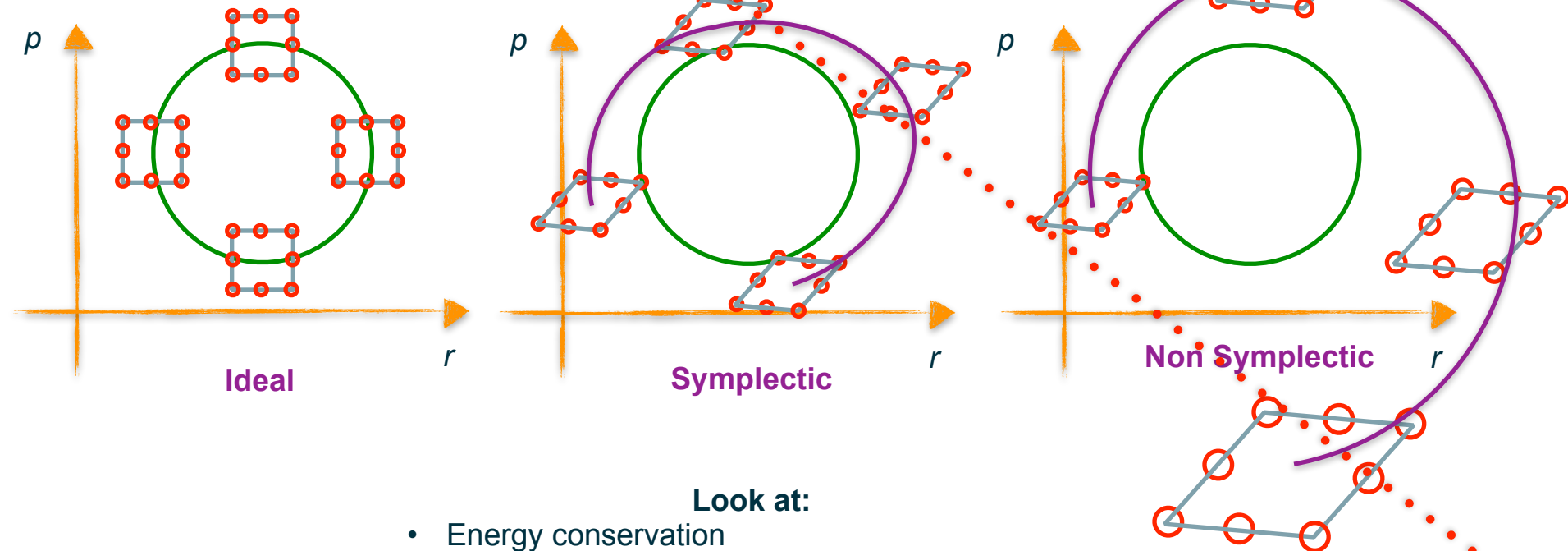
## Symplectic integrators

### Good integrators

- Time reversible, consistently with Newton's equations
- Long time energy conservation

Symplectic algorithms:  
they conserve the phase space measure  
That is: A symplectic integrator conserves the  
area/volume of the phase space  
delimited by an ensemble of systems.

*e.g. 8 harmonic oscillator in time...*



### Look at:

- Energy conservation
- Consistency with respect to Liouville theorem



## The Velocity Verlet algorithm

One option (widely used within many many flavours of MD and usually rather robust):  
The Velocity Verlet (VV) algorithm

The goal:

We know positions and velocities ( $r, v$ ) at time  $t$   
How do we get  $r$  &  $v$  at time  $t + \Delta t$ ?

We put together two Taylor expansions (2nd order):  
 $r(t + \Delta t)$  centered in  $t$   
+  
 $r(t)$  centered in  $t + \Delta t$

Generic Taylor expansion of a function  $f(x)$  centered in  $x_0$

$$f(x) = \sum_{n=0}^{\infty} \frac{1}{n!} \left. \frac{\partial^n f}{\partial x^n} \right|_{x=x_0} (x - x_0)^n$$

## VV derivation



Get the time evolution of the position via a first Taylor expansion (2nd order):

$$f(x) = \mathbf{r}_i(t + \Delta t) \quad \text{and} \quad x_0 = t$$



$$\mathbf{r}_i(t + \Delta t) \approx \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + \mathbf{F}_i(t)\frac{\Delta t^2}{2m_i} \quad \text{a.}$$

Get back in time via a second Taylor expansion (2nd order as well):

$$f(x) = \mathbf{r}_i(t) \quad \text{and} \quad x_0 = t + \Delta t$$



$$\mathbf{r}_i(t) \approx \mathbf{r}_i(t + \Delta t) - \mathbf{v}_i(t + \Delta t)\Delta t + \mathbf{F}_i(t + \Delta t)\frac{\Delta t^2}{2m_i} \quad \text{b.}$$

## VV derivation

Get the time evolution of the velocities by substituting a. in b.



$$\mathbf{v}_i(t + \Delta t) \approx \mathbf{v}_i(t) + [\mathbf{F}_i(t) + \mathbf{F}_i(t + \Delta t)] \frac{\Delta t}{2m_i}$$

The VV algorithm evolves positions and velocities simultaneously

$$\mathbf{r}_i(t + \Delta t) \approx \mathbf{r}_i(t) + \mathbf{v}_i(t) \Delta t + \mathbf{F}_i(t) \frac{\Delta t^2}{2m_i}$$

$$\mathbf{v}_i(t + \Delta t) \approx \mathbf{v}_i(t) + [\mathbf{F}_i(t) + \mathbf{F}_i(t + \Delta t)] \frac{\Delta t}{2m_i}$$

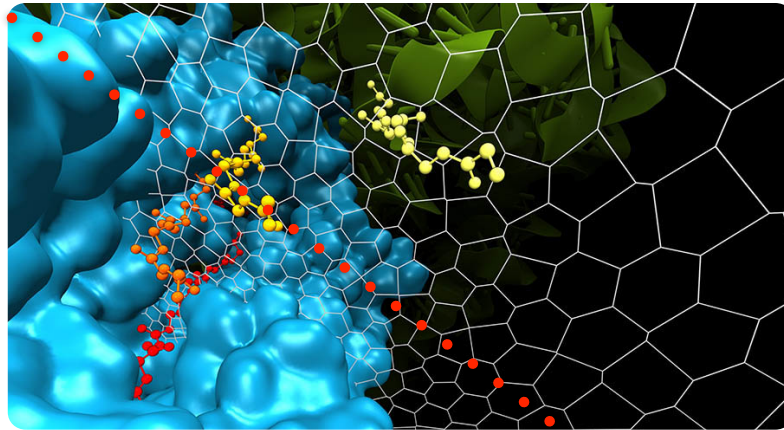
The crucial quantity:  $\Delta t$ , to be tested carefully. The choice is often a compromise between computational efficiency and good conservation of the conserved quantities (total energy and momenta for NVE)

Remember: equilibrium ensemble averages mean that the system has to be equilibrated!

- We need to specify coordinates and momenta (positions and velocities)

Positions at  $t=0$ :

Experimental data, physical intuition, random coordinates, periodic lattice at high temperature...



Velocities at  $t=0$  determine the initial temperature

Equipartition theorem (classical manybody system):  
 $1/2 k_B T$  for each quadratic term in the Hamiltonian

$$\mathcal{H}(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

Single particle

$$K_i = 3 \cdot \frac{1}{2} k_B T$$



$$T = \sum_{i=1}^N \frac{m_i v_i^2}{3N k_B}$$

Whole system

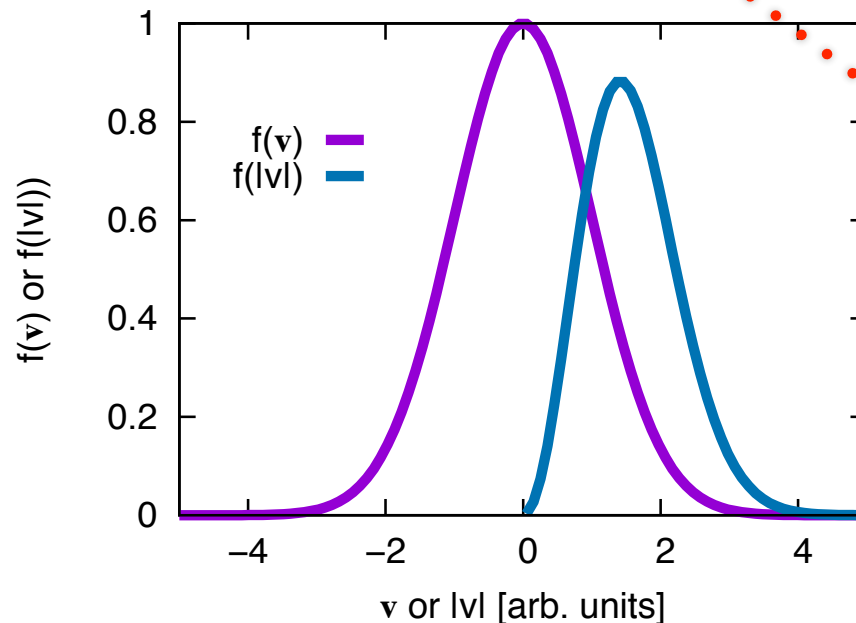


## Initial conditions

How do we pick up the initial momenta?

- Random numbers plus shifting such as the total momentum is zero and then rescaling to adjust the kinetic energy
- Draw them randomly from a Gaussian (Maxwell-Boltzmann velocity distribution)

$$f(\mathbf{v}) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp \left( -\frac{m|\mathbf{v}|^2}{2k_B T} \right)$$



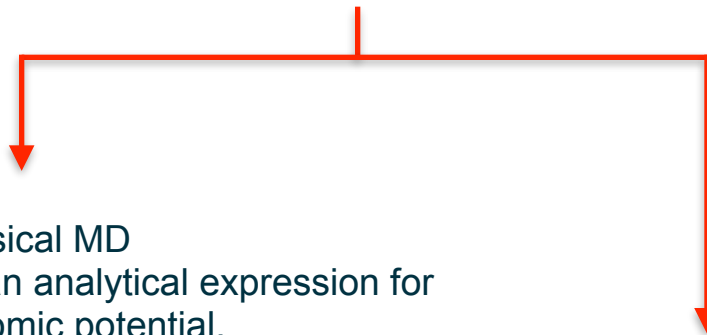
Note the difference between  $f(\mathbf{v})$  and  $f(|\mathbf{v}|)$

## Class vs *ab initio*

So far, so good.

But wait. How do we get the forces? We have to know the potential!

$$\mathbf{F}_i(\mathbf{r}_1, \dots, \mathbf{r}_N) = -\nabla_i U(\mathbf{r}_1, \dots, \mathbf{r}_N)$$



Classical MD

We write - somehow - an analytical expression for the interatomic potential.

ab initio MD

We get the forces by electronic structure calculations

Which one do I choose?

The subtle compromise between computational speed and physical accuracy

**BEWARE...**

- \* Only phenomena whose characteristic correlation length is much smaller than the simulation box can be simulated, unless a finite-size scaling is applicable
- \* Only processes whose typical relaxation time is significantly smaller than the simulation time can be studied

## *Quantum statistical mechanics?!*

We have derived most of the statistical mechanics we need for MD within classical mechanics



Electronic structure methods deal with quantum mechanics



Luckily

- For (almost...) every concept of classical statistical mechanics one can find the quantum equivalent
- Atomic nuclei are still treated as classical particles

Phase space vector  $\rightarrow$  Quantum state vector

$$x(\mathbf{r}, \mathbf{p}) \rightarrow |\psi\rangle$$

It's a (column) vector of  $N_s$  complex numbers,  
where  $N_s$  is the total number of states in which the system can be observed

Lives in Hilbert space, which counterpart is the dual space (where the bra lives)

(Classical) Phase space

Quantum phase space





Classical observables become operators (matrices...) that act on the quantum state vectors

$$\mathcal{P} \rightarrow \hat{\mathcal{P}}$$

We can “promote” the classical position and momentum operators to the correspondent quantum operators

$$x \rightarrow \hat{x} \quad \text{and} \quad p \rightarrow \hat{p}$$

So that the quantum Hamiltonian for a generic system reads:

$$\hat{\mathcal{H}}(\hat{x}, \hat{p}) = \frac{\hat{p}^2}{2m} + \hat{\mathcal{U}}(\hat{x})$$

## Quantum ensemble averages

As in classical mechanics, the (quantum) Hamiltonian of the system governs its time evolution  
Time dependent, non relativistic Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{\mathcal{H}} |\psi(t)\rangle$$

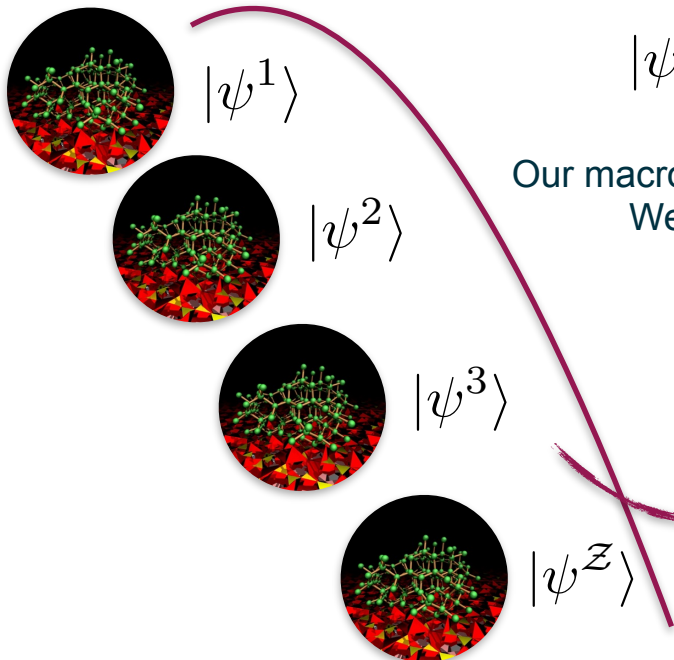
We now have - almost - all we need to deal with quantum ensembles:

Collections of  $Z$  quantum systems, each with a unique state vector corresponding to a unique microscopic state

$$|\psi^\lambda\rangle, \lambda = 1, \dots, Z$$

Our macroscopic property is now the expectation value of a certain operator  
We write this formulation as a - quantum - ensemble average:

$$\langle \hat{\mathcal{P}} \rangle = \frac{1}{Z} \sum_{\lambda=1}^Z \langle \psi^{(\lambda)} | \hat{\mathcal{P}} | \psi^{(\lambda)} \rangle$$





What about Liouville equation? Will it hold in here as well?  
And what do we use in place of the phase distribution function?

We build something similar.  
Let's start by expanding the state vector into a certain basis - sounds familiar?

$$|\psi^{(\lambda)}\rangle = \sum_k C_k^{(\lambda)} |\phi^{(\lambda)}\rangle$$

Substitute the expansion in to the average

$$\langle \hat{\mathcal{P}} \rangle = \sum_{k,l} \left( \frac{1}{\mathcal{Z}} C_l^{(\lambda)} C_k^{(\lambda)*} \right) \langle \phi_k | \hat{\mathcal{P}} | \phi_l \rangle$$

We can define the matrix elements

$$\rho_{lk} = \sum_{\lambda=1}^Z C_l^{(\lambda)} C_k^{(\lambda)*}$$

of the so called density matrix:

$$\hat{\rho} = \sum_{\lambda=1}^Z |\psi^{(\lambda)}\rangle \langle \psi^{(\lambda)}|$$



A central quantity in ab initio MD

A time dependent density matrix means time dependent state vectors:

$$\hat{\rho}(t) = \sum_{\lambda=1}^Z |\psi^{(\lambda)}(t)\rangle \langle \psi^{(\lambda)}(t)|$$

In the Schrödinger picture, observables are time independent. We evolve the state vectors in time as:

$$|\psi(t)\rangle = \hat{U}|\psi(0)\rangle \qquad |\psi(t)\rangle = e^{-\frac{i}{\hbar}\hat{\mathcal{H}}t}|\psi(0)\rangle$$

Now, if you take the time derivative, you end up with the Liouville-von Neumann equation:

$$\frac{\partial}{\partial t}\hat{\rho} = \frac{1}{i\hbar}[\hat{\mathcal{H}}, \hat{\rho}]$$



also known as the quantum Liouville equation

It tells you how the quantum system explores in time the quantum phase space - and more!

## *Equilibrium solutions of the quantum Liouville Eq.*



Exactly as we did in the classical case, we consider equilibrium ensembles. Thus:

$$\frac{\partial}{\partial t} \hat{\rho} = 0 \quad [\hat{\mathcal{H}}, \hat{\rho}] = 0$$

These two commute, so they share the same eigenvectors:  
The actual states of the system,  $|E_m\rangle$

$$\hat{\rho} = \sum_m |E_m\rangle \langle E_m|$$

**NVE**

Recall classical mechanics: all states with “the right” energy (imposed by the Hamiltonian) have the same probability



$$\hat{\rho}_{NVE} = \sum_m P_m |E_m\rangle \langle E_m|, \quad \text{with } P_m = \gamma \text{ if } E < E_m < E + \Delta E \text{ and } 0 \text{ otherwise}$$

Normalize  $P_m$  such as

$$\text{Tr}(\hat{\rho}) = \sum_m E_m = 1$$

And we end up with:

$$P_m = \frac{1}{\Omega_{NVE}} \quad \text{with} \quad \Omega_{NVE} = \sum_{E_m=E} 1 = \text{number of states } |E_m\rangle \quad \text{with} \quad E_m = E$$

The microcanonical quantum partition function is - again - just the sum of all the possible states  
(This time is already dimensionless!)

## *The Born-Oppenheimer approximation*

The starting point of ab initio MD:  
the (non-relativistic) time dependent Schrödinger equation for a system of nuclei and electrons

$$\mathcal{H}|\psi(\mathbf{r}_{el}, \mathbf{R}_{nu}, t)\rangle = i\hbar \frac{\partial}{\partial t} |\psi(\mathbf{r}_{el}, \mathbf{R}_{nu}, t)\rangle$$

### **Born-Oppenheimer approximation**

Due to the large separation of the nuclear and electronic masses,  
the electrons can be expected to be in instantaneous equilibrium with the much heavier nuclei,  
so that the electronic subsystem can be treated independently at constant  $\mathbf{R}_{nu}$



$$|\psi(\mathbf{r}_{el}, \mathbf{R}_{nu}, t)\rangle = \phi_{el}(\mathbf{r}_{el}, \{\mathbf{R}_{nu}^*\}) \cdot \chi_{nu}(\mathbf{R}_{nu}, t)$$

Is this always a fairly accurate assumption? What if it's not?

Most of the times, then, we treat quantum nuclei as classical particles,  
applying all the - classical - machinery we have seen so far! However: how do we deal with the electrons?



# End of Lesson

*End of lesson*