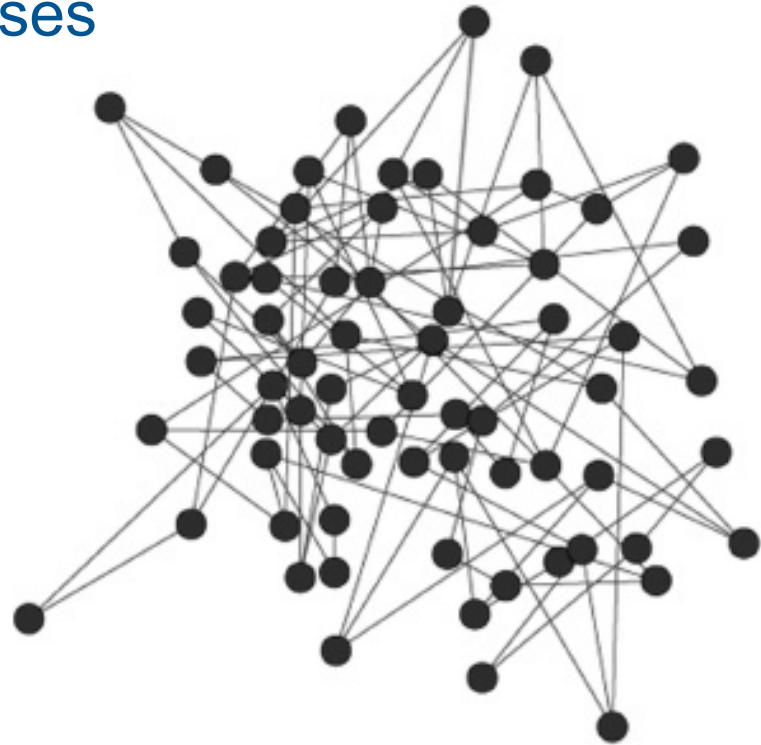


Electronic Structure Methods for Materials Modelling

An impossibly short introduction to

Disordered Systems

- It's all about disorder
 - Gases, liquids, amorphous solids, glasses
- Disordered - condensed - phases
 - Structure (topology)
 - Electronic structure
- Transport coefficients
 - Green-Kubo relations
 - Linear response



- Next: *Ab-initio Random Structure Search* [Prof. C. Pickard]

It's all about disorder

And yet...

Most of the matter in the universe is in disordered states

- Gases
- Plasmas
- Liquids
- Amorphous solids and glasses

and yet...

If you open any electronic structure book, disordered systems get usually very little (if any) space

This is because is so much easier to devise, demonstrate, implement and verify theories and algorithms when dealing with ideal systems - like a perfect crystalline solid



When translational, long range order is lost,
the math gets tough and the level of approximation increases

“Disordered systems” mean too many topics even for a big book. In here:

- An introduction to the electronic structure of amorphous solids - and why it matters
- A brief discussion about transport coefficient via equilibrium (ab initio) MD

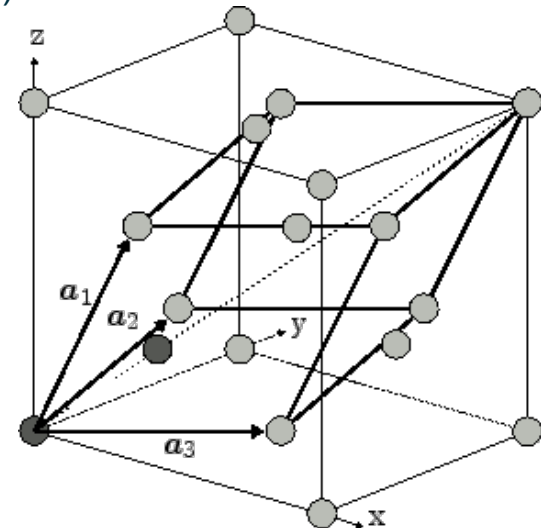
Structural disorder

Tessellation time

How do characterise the structure of a disordered system
(liquid, amorphous solid)?

For a crystalline system, the only things you need are:

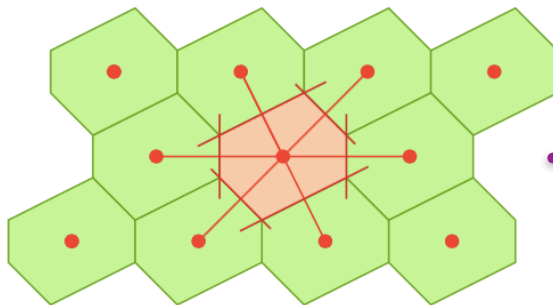
- The cell matrix
- The lattice positions within the cell



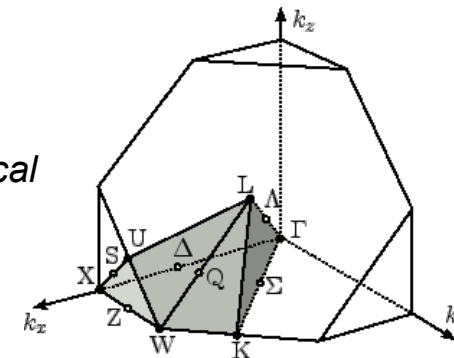
Alternatively, you can construct Wigner-Seitz cells:

- They are still primitive cells
- Contains every information you need with respect to the symmetry of the system
- If you switch to reciprocal space, the Wigner-Seitz cell becomes the first Brillouin zone

Real space



Reciprocal space



Structural disorder

Tessellation time

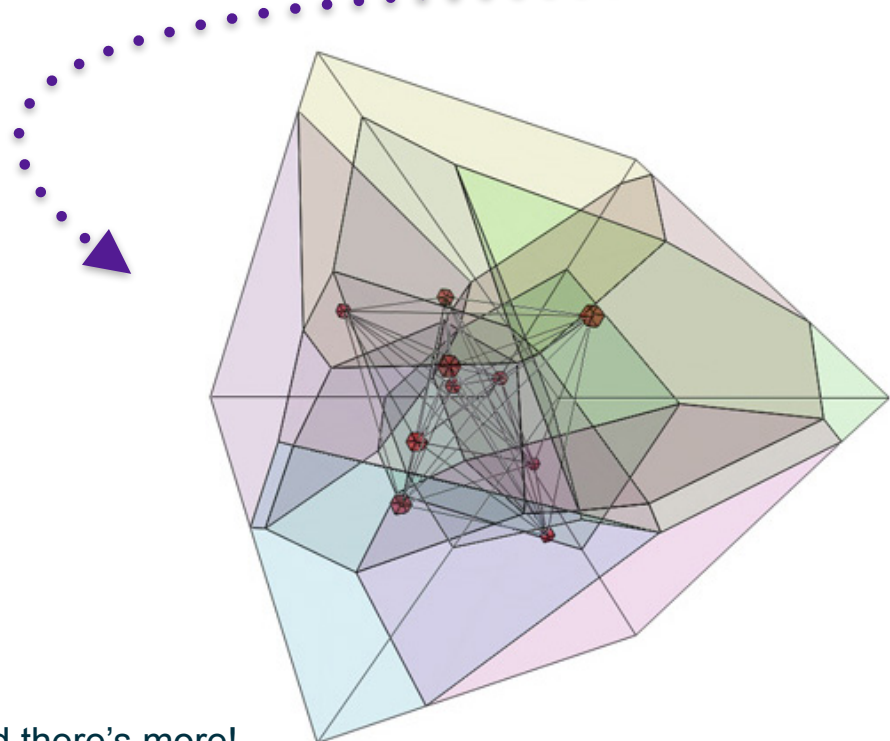
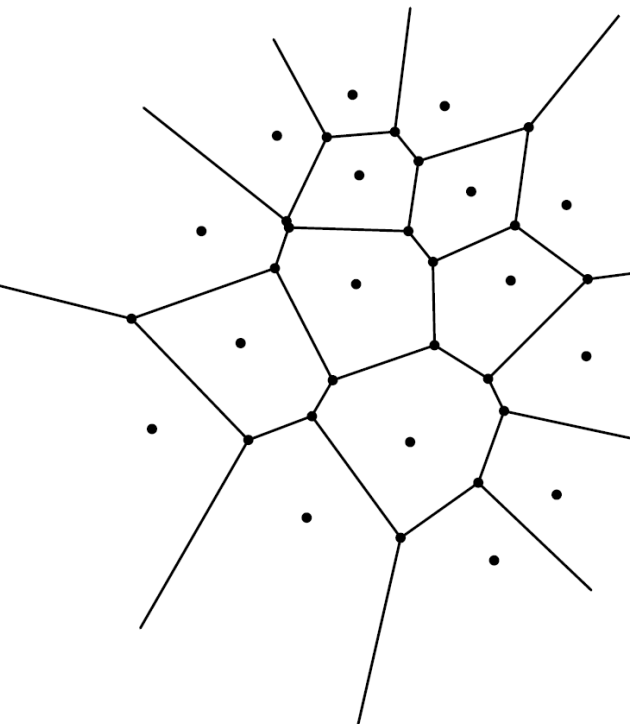


Wigner-Seitz cells are only a special type of **Voronoi cells**

Constructed in exactly the same way, but this time for a generic (no translational invariance) set of points

That's what you need to characterise your disordered system:

A (probability density) distribution of the volume of the **Voronoi polyhedra** (3D)



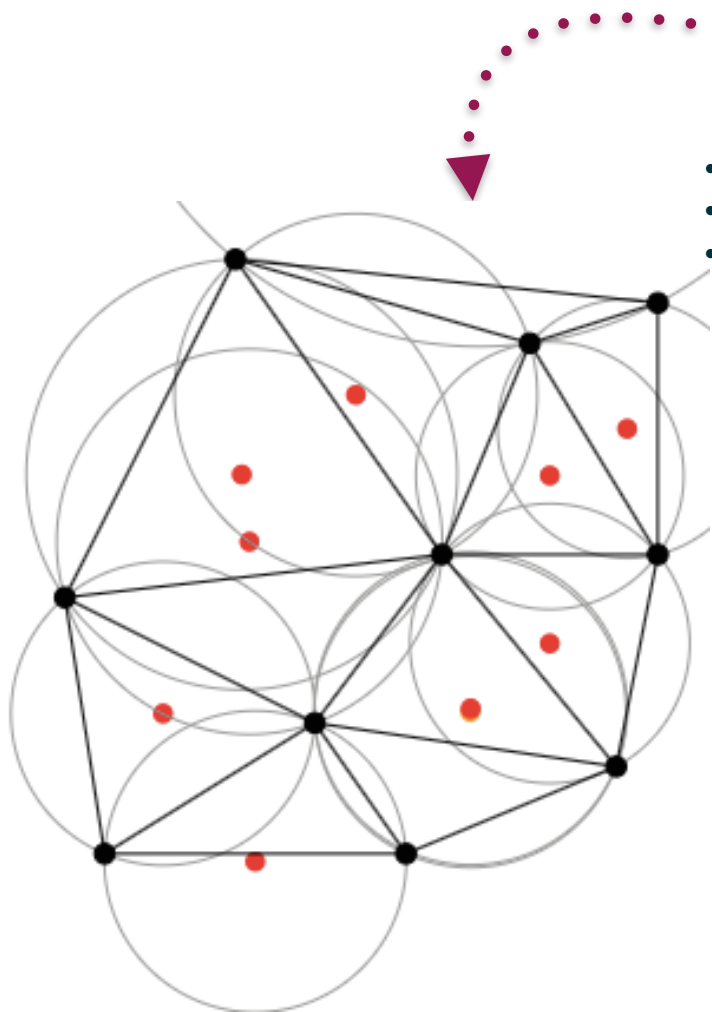
And there's more!

What if you take the "inverse" (the dual graph) of the Voronoi tessellation?

Delaunay triangulation

In 2D:

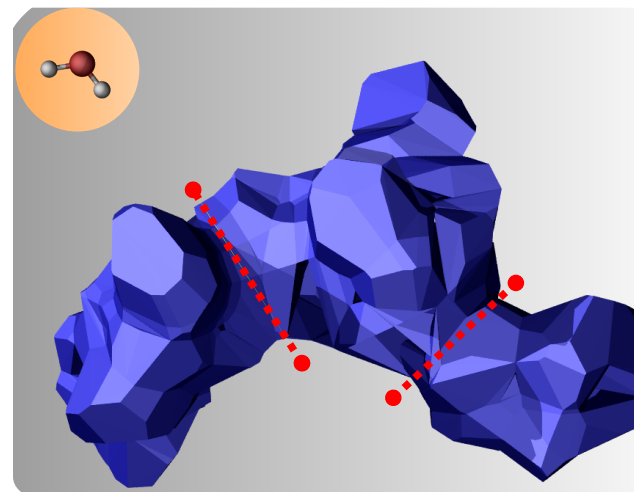
- **Red points:** they define the Delaunay tessellation
- **Black points:** the actual set of 2D points you want to tessellate
- For each circumcircle of the triangle centred around every red point, there are no black points inside



In 3D:

Delaunay *simplexes*
(non-necessarily-regular tetrahedra)

They take into account the empty space within your system



Structural disorder

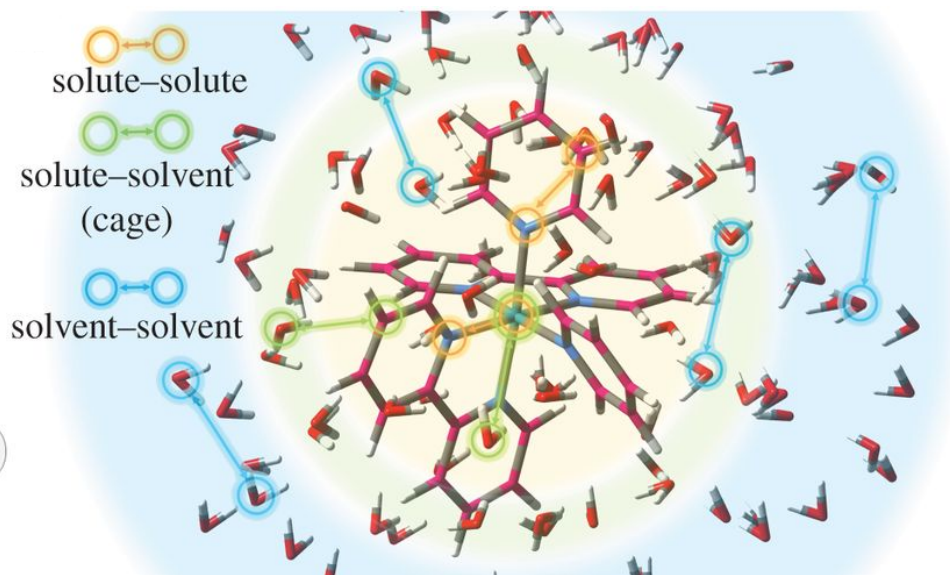
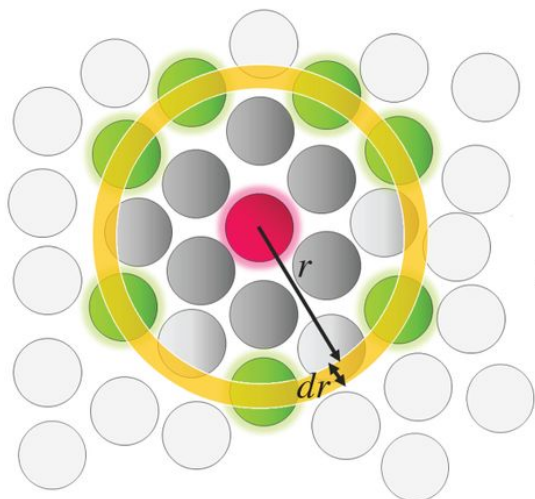
Short-range order

The topology of your disordered system is only half of the story.
You need a measure of the short-range order of your system



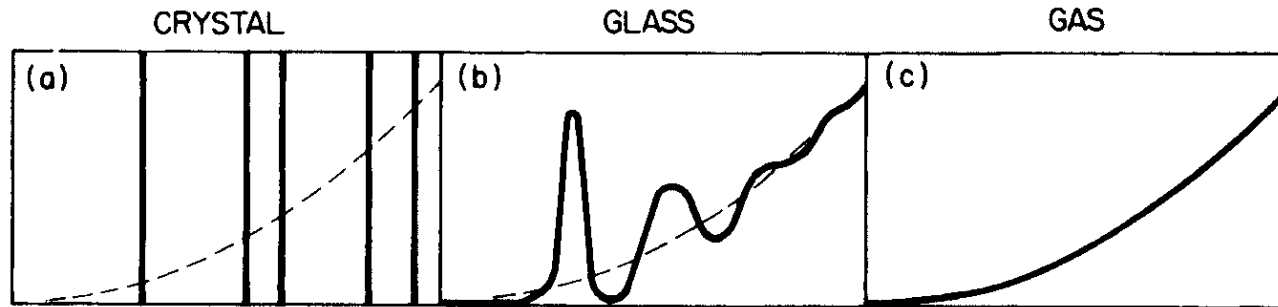
Simplest option: the radial distribution function

$$g(r) = \frac{1}{4\pi r^2 N \langle \rho \rangle} \sum_{i=1}^N \sum_{k=1, k \neq i}^N \langle \delta(r - (|\mathbf{r}_k - \mathbf{r}_i|)) \rangle$$



Structural disorder

Short-range order



- Can be derived via statistical mechanics
- Related to the structure factor (the quantity experiments deal with - unless they actually manage to *count* the particles...) via Fourier transform
- The integral of the $g(r)$ gives the coordination number
- Ill defined for non-homogeneous system - there are workarounds, though...

$$S(q) = 1 + \frac{1}{N} \left\langle \int_V d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} \sum_{k=1, k \neq i}^N \delta(r - (|\mathbf{r}_k - \mathbf{r}_i|)) \right\rangle$$

Short range order (radial distribution function)
+
Topology (Voronoi tessellation)

!! Ensemble average !!

What about crystalline order within a disordered network?

Fingerprint of your disordered system

Goodbye Bloch

Disordered systems  Bloch theorem? Forget about it!

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{Cr}(\mathbf{r}) \right] |\psi(\mathbf{r})\rangle = E |\psi(\mathbf{r})\rangle, \quad V_{Cr}(\mathbf{r}) = V_{Cr}(\mathbf{r} + \mathbf{R}_{Lattice})$$

NOPE

Disordered systems

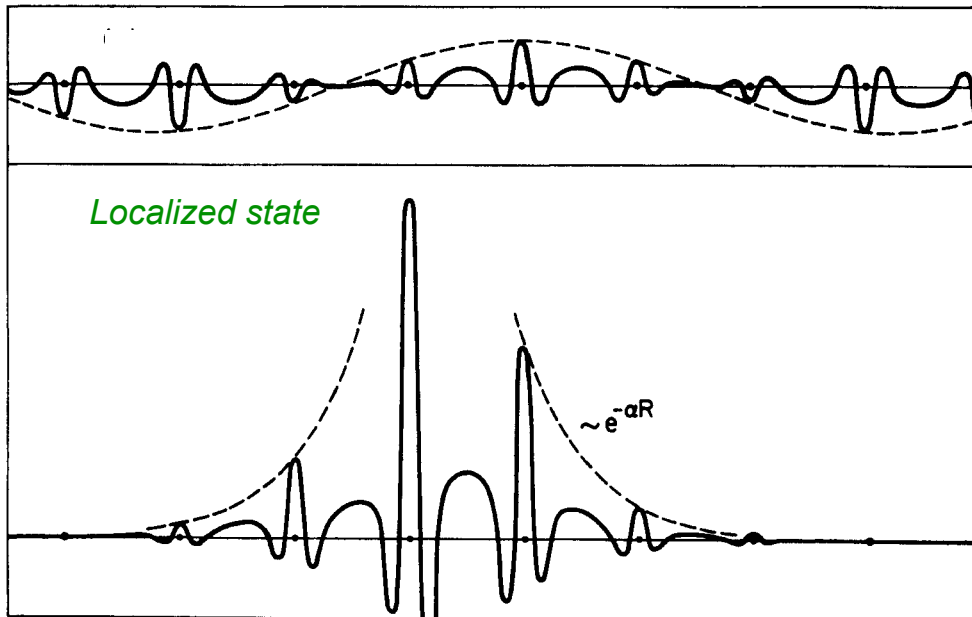
- You don't have a periodic potential anymore
- No more plane waves extending throughout the whole system
- Band diagrams are (almost) no more



In addition to extended states:
Localized electronic states

Extended states still exists -possibly-,
 but you cannot label them by quantised
 wave vector values as in crystals

Bloch-like, extended state



Basically the whole of $|\Psi|^2$ is concentrated
 in a small region of the system
 (can be a bunch of atoms)



Decays exponentially with distance

Localized states in crystals?

Localized states



In crystals: extrinsic states
In amorphous solids or liquids: ***intrinsic states***



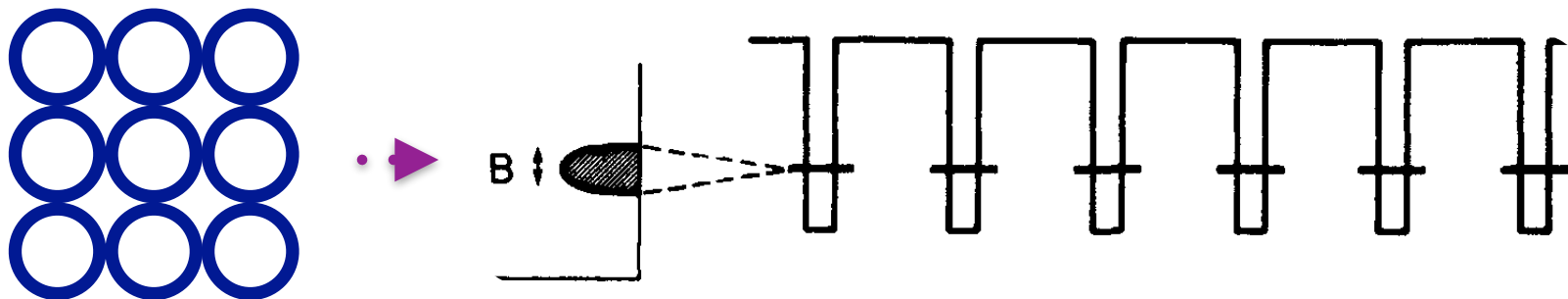
Continuous spectrum

The Anderson localisation → delocalisation transition

Let us start from a sort of tight-binding picture:

The band structure is obtained as a superposition of localised states, one for each atom

In a crystal, at every atom correspond a single potential well
All the wells have the same depth - all sites are equivalent

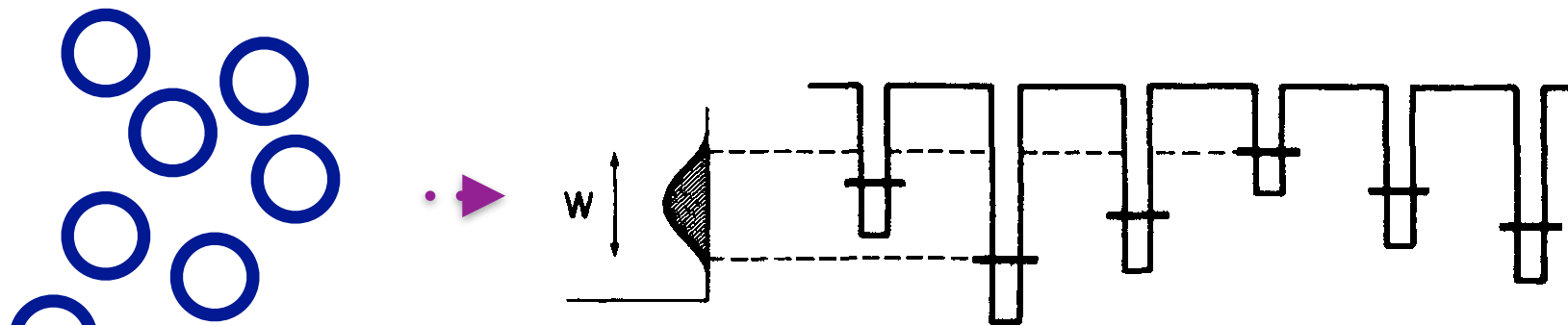


B is the bandwidth of the crystalline states - in the absence of disorder

Electronic structure

The Anderson Hamiltonian

In e.g. an amorphous solid the well depths vary from site to site in a random way
The sites are **not** equivalent anymore



W is the width of the distribution the well depths

Quantifies the energy range of the disorder-induced spatial fluctuations of the potential energy

Not impossibly disordered
Extended states persist



Now, it's all about W/B



All the states in the valence band are localised

The Anderson Hamiltonian:

$$\hat{\mathcal{H}}_{Anderson} = \sum_{i=1}^{N_{Sites}} E_{Random,i} c_i^\dagger c_i + \sum_{j=1, j \neq i}^{N_{Sites}} T_{i,j} c_i^\dagger c_j$$

Randomly chosen from an energy distribution of width W

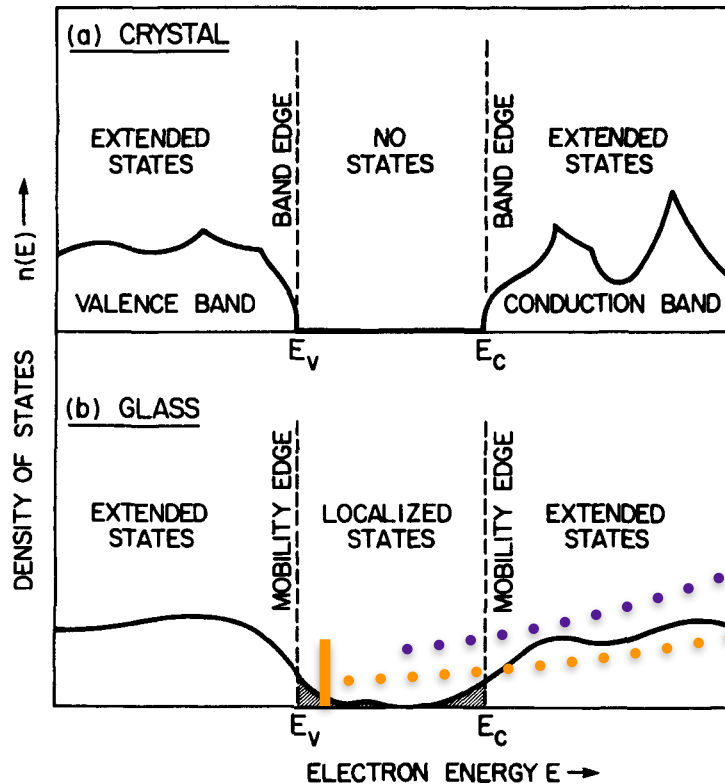


*Hopping integral:
Measures the coupling between different sites*





- Even in disordered system there *is* a valence band - and possibly an energy gap (some glasses are transparent, after all...)
- Even if the degree of disorder is not that large, **states in the tails of the band are localised**



Pseudogap
Possibly too large for a (visible light) photon...

Defects -or, particularly localised states

DFT can get these!
(Large models, no periodicity, ensemble averages...)

Dynamical properties

Still equilibrium properties!

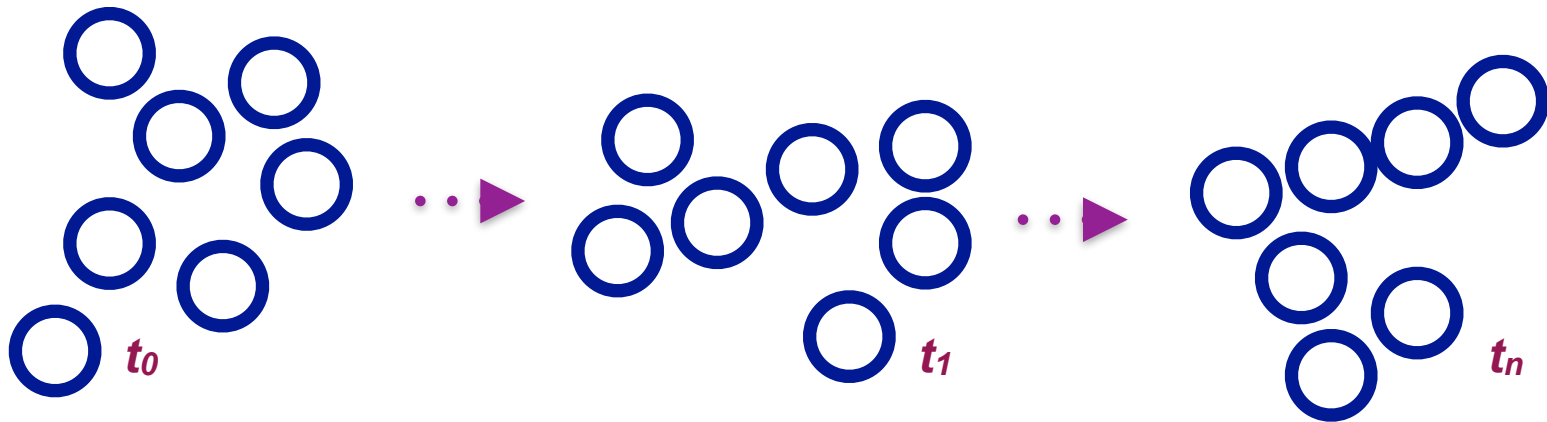
Think about a metallic liquid.

In addition to structural properties (topology, short range order...),
one is usually interested in dynamical properties as well

An example: the diffusion coefficient

A single number that tells you a lot about your system

(it's not about mobility alone, the diffusion coefficient is an essential ingredient in many situations...)



The diffusion coefficient is a **transport coefficient**. And it's not the only one out there:

- Diffusion (in response to a concentration gradient)
- Viscosity (in response to external stress)
- Thermal conductivity (in response to a temperature gradient)
- Electrical conductivity (in response to an external electric field)

All of these quantities refer to **equilibrium properties** of the system,
which however can be **calculated by looking at the dynamics of the system in time**

Or, by actually introducing the perturbation by hand → non equilibrium MD

Dynamical properties

Green-Kubo relations

All these transport coefficients can be obtained within the same formalism:
the Green-Kubo relations

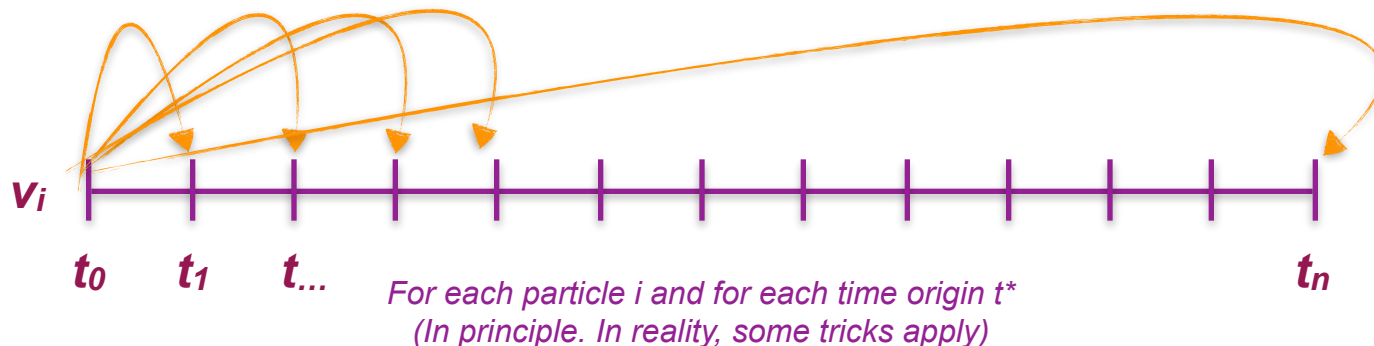
$$\gamma \propto \int_0^\infty \langle p(t^\dagger) \cdot p(t^*) \rangle dt$$

Transport coefficients are related to the time integral of an autocorrelation function

For instance, for the diffusion coefficient:

$$\mathcal{D} = \int_0^\infty \langle v(0) \cdot v(t) \rangle dt$$

Ensemble average over all the particles and all the time windows



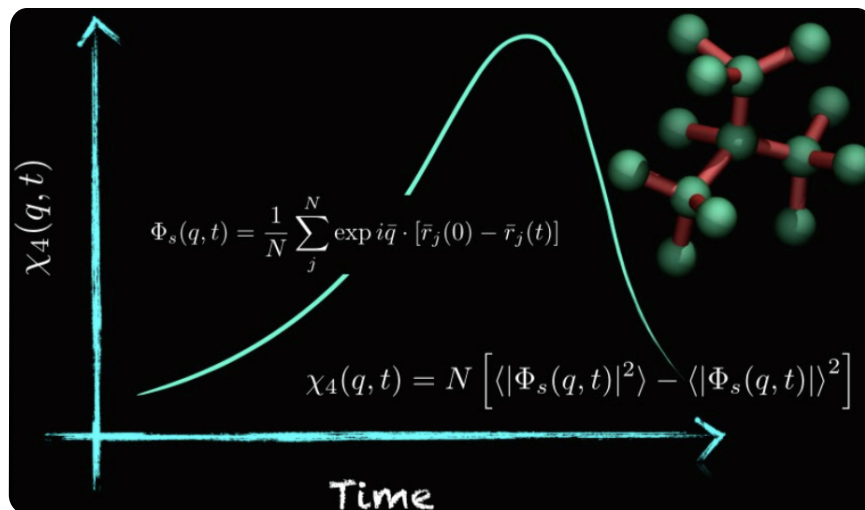
Dynamical properties

Green-Kubo relations

Autocorrelation functions are equilibrium properties of the system



They measure the correlation of some property (for example the velocity) at time t^* and t^\dagger , along the whole **equilibrium** trajectory



They contain an awful lot of information about the dynamics of your system
(just from the density and the velocities: mobility, structural relaxation, dynamical heterogeneities...)



- The ergodic hypothesis needs to hold (you truncate the integral at a certain time)
- All of this work *exclusively* within linear response theory



The perturbation you apply to the system is small enough so that you can leave out second order terms

It's our old friend the Liouville equation again!

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

Recall the equilibrium case:

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

And the Liouville equation becomes:

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

If you don't specify a particular ensemble,
any function of the Hamiltonian is a solution of the equilibrium Liouville equation

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



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

Dynamical properties

Linear response theory

This time, we introduce a generic perturbation
(can be a concentration gradient, a temperature gradient, an electric field...)

The ensemble distribution function will be:

$$f(x, t) = f_0(\mathcal{H}(x)) + \Delta f(x, t)$$

*Unperturbed ensemble distribution
function - it satisfies the equilibrium
Liouville equation*

And similarly the Liouville operator becomes:

$$\dot{x} \cdot \nabla \Rightarrow (\dot{x}_0 + \Delta \dot{x}(t)) \nabla$$

$$\dot{x} \cdot \nabla f_0(\mathcal{H}(x)) = 0$$

Leave out the second order term...

$$\left(\frac{\partial}{\partial t} + \dot{x}_0 \nabla \right) \Delta f(x, t) = -\Delta \dot{x}(t) \nabla f_0(\mathcal{H}(x))$$

Of course, a similar quantum case exists...

This is the “linearized” non-equilibrium Liouville equation, which ultimately leads to the Green-Kubo formalism
(Other derivations exist...)

The key point:

Within linear response theory, a non-equilibrium average can be generated entirely within an equilibrium calculation

Ab initio MD is (slowly) getting there!

