Modeling, Analysis and Simulation

Journées Scientifiques des Jeunes du CERMICS, Provins

Laurent, Renato, Rutger

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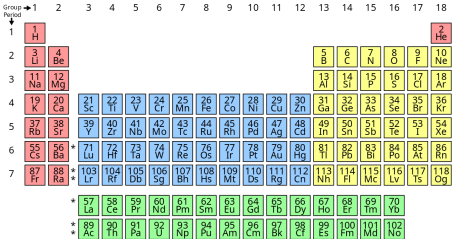
École des Ponts
ParisTech

Quantum Chemistry

Let's get Quantum



- **Chemistry:** the study of what's in the periodic table and the structures they form... ish.
- **Quantum Chemistry:** the same... but quantum !
  Why quantum ? Magnetism, superconductivity can only be understood by the modelization of matter at the atomic scale, which is the realm of quantum physics.

Schrödinger mon amour

All the information is contained in the wave function Ψ (black box) whose evolution is given by:

$$\boxed{i\frac{\mathrm{d}\Psi}{\mathrm{d}t} = H\Psi}$$

Typical Hamitlonian for a molecule: $H = -\Delta + \sum_{\text{nuc}} V_{\text{nuc}} + \sum_{i,j} V_{e_i^-, e_j^-}$ $\rightarrow$ N-body problem...

- Can we study theoreticaly this Hamiltonian ? Can we find good approximation which are easier to handle ?
- How do we discretize and numerically compute stuff ?

A bit of theory

People involved: Alfred (PhD), Eloïse (PhD), Solal (PhD), Long (Post-Doc)

What do they do ?

- Study different forms of (sometimes time-dependant) Schrödinger and question existence / unicity of solutions.
- Tools are Spectral theory, complex analysis (see Eloïse's hands-on session), Topology...

Why is it important ? One example: let's look at one spectrum of an operator A:

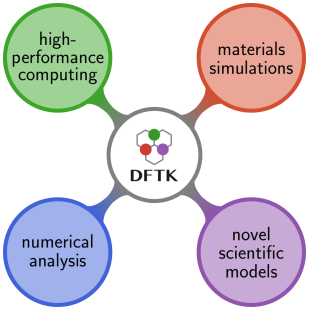
Not the same algorithm !

Numerics for ever

People involved: Gaspard (PhD), Étienne (Post-doc), Laurent (PhD)

What do they do ?

- Analyse the convergence properties of different algorithm.
- Provide missing formalism for some methods
- Provide friendly codes for mathematician



Statistical Physics

Statistical physics: macrostates and microstates

Example (sum of 2 dice):

- Macrostate of the system: sum of the dice
- Microstate: number of each die

Macrostate	Microstate
2	(1,1)
4	(2,2), (3,1), (1,3)
6	(1,5), (2,4), (3,3), (4,2), (5,1)

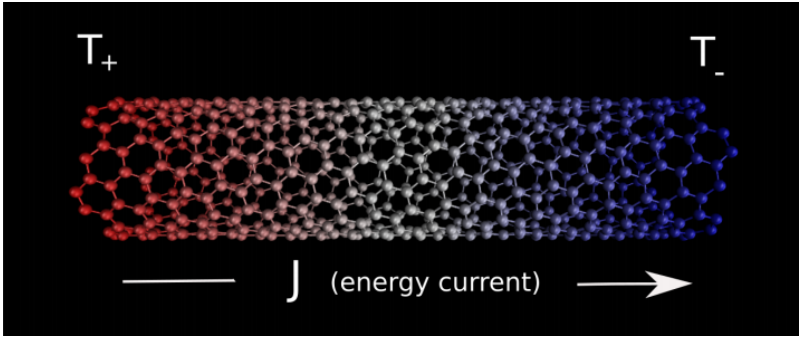
Entropy: "degeneracy of states"

$$S = -k_{\mathrm{B}} \sum_i p_i \log(p_i)$$

Statistical physics: motivation

- "numerical microscope"
- **Example (thermal conductivity):** Fourier's law

$$J = -\kappa \nabla T$$



Statistical physics: aim

not interested in location of a single particle, but instead in the overall behavior of the assembly

Statistical physics:

- Microscopic behavior $\rightarrow$ macroscopic properties via statistical ensembles
- Macrostate of the system described by a probability measure μ

Equilibrium thermodynamic properties

$$\mathbb{E}_\mu(\varphi) = \int_{\mathcal{X}} \varphi(q,p)\,\mu(dq\,dp)$$

Ergodicity: averages computed along a realization converge to averages w.r.t. μ

How do we compute these properties?

Molecular dynamics:

- Model microscopic behavior of interacting systems directly
- Integrate equations of motion

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

Hamiltonian

$$H(q,p) = \frac{1}{2} p^T M^{-1} p + V(q)$$

Statistical physics: Langevin dynamics

Langevin dynamics: stochastic perturbation of Hamiltonian dynamics

$$\begin{cases} dq_t &= M^{-1} p \, dt \\ dp_t &= \underbrace{-\nabla V(q) \, dt}_{\text{Hamiltonian}} \underbrace{- \gamma M^{-1} p \, dt}_{\text{Dissipation}} + \underbrace{\sigma \, dW_t}_{\text{Fluctuation}} \end{cases}$$

Unique invariant probability measure is the Gibbs measure

$$\mu(dq \, dp) = \frac{1}{Z} e^{-\beta H(q,p)} \, dq \, dp$$

Thermostat: T controlled by fluctuation-dissipation relation

$$\sigma = \sqrt{\frac{2\gamma}{\beta}}, \quad \text{where} \quad \beta = \frac{1}{k_{\mathrm{B}} T}$$

Statistical physics: people

MATHERIALS team

PhD students: Renato Spacek, Régis Santet, Shiva Darshan, Noé Blassel

Post-docs: Mohamad Rachid

Permanent: Gabriel Stoltz, Tony Lelièvre, Urbain Vaes, Éric Cances,

Homogenization

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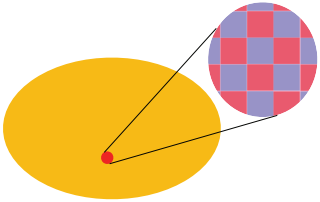

Studying a PDE $-\operatorname{div}(a^\varepsilon(\bullet)\nabla u^\varepsilon)(x) = f$ with highly oscillatory coefficients

(composite materials, nuclear reactors, subsurface flow)

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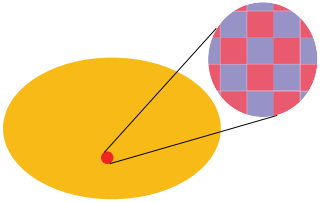

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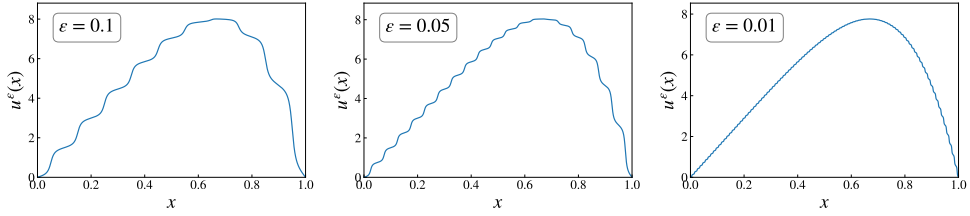
When $\varepsilon \to 0$, a dominant macroscopic behaviour seems to emerge.



Homogenization $\rightarrow$ a macroscopic model?

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Homogenization theory

- When can we characterize $\lim_{\varepsilon \to 0} u^\varepsilon$?
- E.g. periodicity assumptions: $u^\varepsilon(x) \approx u^\star(x) + \varepsilon \sum_{i=1}^{d} \partial_{x_i} u^\star(x)\, w_i\left(\frac{x}{\varepsilon}\right)$

  where the w_i resolve the microstructure and $u^\star$ solves a known PDE indep. of ε.

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Numerical homogenization (Multiscale Finite Element Method, Heterogeneous Multiscale Method, Local Orthogonal Decomposition)

- u^ε can be computed by a high-fidelty (FE) method, but this can be (too) costly
- Offline stage: resolve the microstructure locally
- Online stage: solve a low-dimensional problem for the global PDE.

Homogenization: people

Embedded in the MATHERIALS team at Inria Paris

@ CERMICS

Claude Le Bris,
PhD students: Rutger Biezemans, Albéric Lefort, Simon Ruget

@ Navier

Frédéric Legoll

other collaborations

Xavier Blanc (Université de Paris)
Alexei Lozinski (Université de Franche-Comté)