Molecular Dynamics and Monte Carlo Simulations

Moodle CH-351:
https://moodle.epfl.ch/course/view.php?id=10441

Spring Semester 2025

18 February – 27 May
Tue 11:15 - 13:00

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Course Structure (1+1)

Lectures:

(BCH 3118)

Computer Exercises:

(BCH 1113)

Lectures/exercises: each time 2h
alternating weeks

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Time Table

18.2.25	Course: intro & Chapter 1 (From QM to MM)
25.2.25	Exercise I MC determination of π
04.3.25	Course: Chapter 2 (Statistical Mechanics)
11.3.25	Exercise II: Harmonic Oscillator
18.3.25	Course: Chapter 3 (Monte Carlo Simulations)
25.3.25	Exercise III: MC
01.4.25	Course: Chapter 4 (MD Simulations 1)
08.4.25	Exercise IV: MD
15.4.25	Course: Chapter 5 (MD Simulations 2)
22.4.25	Easter Break (no courses)
29.4.25	Exercise V: MD
06.5.25	Course: Chapter 6 (MD Simulations 3)
13.5.25	Exercise VI: MD
20.5.25	mock exam & question hour
27.5.25	**Written Exam**

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Control Continue

- **computer exercises (1/2)**
- **written exam 27.5 (1/2)**

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Course Support

Documentation:

- script
- copies of slides

https://moodle.epfl.ch/course/view.php?id=10441

Recordings of previous year's lectures:

https://tube.switch.ch/channels/912e6fc9

Supplementary Literature:

- M.P. Allen and D.J. Tildesley, *Computer Simulations of Liquids*, Oxford University Press (2002) (MD)
- D. Frenkel and B. Smit, *Understanding Molecular Simulation*, Academic Press (2001) (MC)
- David Chandler, *Introduction to Modern Statistical Mechanics*, Oxford University Press (1987) (Statistical Mechanics)

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Molecular Dynamics (MD) and Monte Carlo (MC) Simulations

Aim:

Study the properties of physical, chemical and biological systems by recreating them on the computer as realistically as possible.

Molecular Dynamics & Monte Carlo Simulations:

- Simulate a system in microscopic detail to predict the macroscopic (dynamic) and thermodynamic properties of an ensemble
- The two main numerical simulations techniques in the study of condensed phase and macromolecular systems

MD&MC & Electronic Structure Methods (Quantum Chemistry):

- Make up the three main pillars of modern Computational Chemistry!

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Quiz I: Quantum Mechanics versus Classical Mechanics

1) What are the main differences between Quantum Mechanics and Classical Mechanics?

2) What are typical quantum effects that are absent in a classical system?

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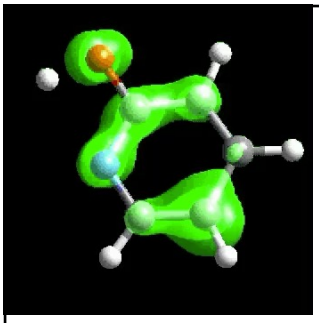

Matter: system of N atoms (N nuclei with positive charges Z_I and masses M_I and n electrons with negative charges e and masses m_e) (atomic units: $e = m_e = 1$ a.u.)

Quantum Mechanics:

System is described by (electron-nuclear) wavefunction

$$\Psi\left(\vec{r}_1, \vec{r}_2, \vec{r}_3, \cdots, \vec{r}_n, \vec{R}_1, \vec{R}_2, \vec{R}_3, \cdots, \vec{R}_N, t\right)$$

$$\Psi\left(\{\vec{r}_i\}, \{\vec{R}_I\}, t\right) = \Psi\left(\vec{r}, \vec{R}, t\right)$$

Quantum chemical electronic structure methods:
(HF, CI, MPn, CC, DFT etc.)

- Stationary states (no time dependence)
- Born-Oppenheimer approximation to separate electronic and nuclear problem

$$\Psi\left(\vec{r}, \vec{R}\right) \approx \Psi_{ele}\left(\vec{r}_1, \vec{r}_2, \vec{r}_3, \cdots, \vec{r}_n\right) \Psi_{nuc}\left(\vec{R}_1, \vec{R}_2, \vec{R}_3, \cdots \vec{R}_N\right) = \Phi(\vec{r})\chi\left(\vec{R}\right)$$

- Solve electronic Schrodinger Equ tion for fixed nuclear positions ('clamped nuclei', no dynamics of the nuclei, no temperature)

$$\hat{H}_{elec}\Psi_{elec} = E\Psi_{elec}$$

$$\hat{H}_{elec} = \hat{E}_{kin} + \hat{V}_{elec}$$

$$\hat{H}_{elec} = -\frac{1}{2}\sum_{i=1}^{n}\vec{\nabla}_i^2 - \sum_{i=1}^{n}\sum_{I=1}^{N}\frac{Z_I}{|\vec{R}_I - \vec{r}_i|} + \sum_{I=1}^{N}\frac{Z_I}{|\vec{R}_I - \vec{r}_i|} + \sum_{i>j}\frac{1}{|\vec{r}_i - \vec{r}_j|}$$

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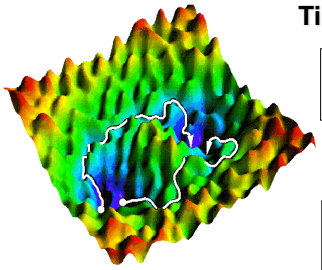
Nuclear Quantum Dynamics

Solve electronic Schrödinger Eq. for each set of nuclear coordinates

$R = (\vec{R}_1, \vec{R}_2, \vec{R}_3, ...\vec{R}_N) \Rightarrow E(R)$ potential energy surface (PES) V(**R**)



Time-Dependent Nuclear Schrödinger Eq.

$$i\hbar \frac{\partial}{\partial t} \Psi_{nu}(\vec{R}_1, \vec{R}_2, \vec{R}_3, ...\vec{R}_N, t) = \hat{H}_{nu} \Psi_{nu}(\vec{R}_1, \vec{R}_2, \vec{R}_3, ...\vec{R}_N, t)$$

Nuclear Hamilton operator:

$$\hat{H}_{nu} = -\sum_I \frac{1}{2M_I} \nabla_I^2 + V(R(t)) + \sum_{I,J} \frac{Z_I Z_J}{R_{IJ}(t)}$$

⇒ **Nuclear Quantum Dynamics**

(review: Makri, Ann. Rev. Phys. 50, 167 (1999)

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Atoms are never at rest!

- *Classical limit T>>0:*

Kinetic theory: temperature T
proportional to kinetic energy of particles E_{kin}

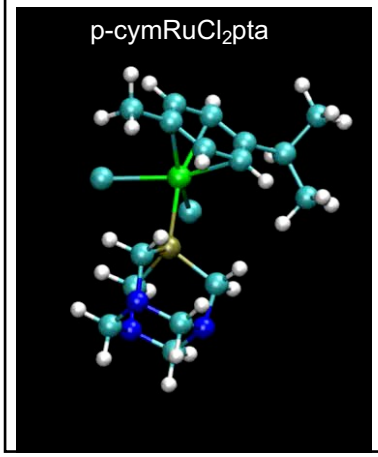
$$T = \frac{2}{3} \frac{E_{kin}}{N^{DOF} k_B} \qquad E_{kin} = \frac{1}{2} \sum_I M_I v_I^2$$

N^{DOF}: number of degrees of freedom (3N)
k_B: Boltzmann constant

- *T = 0:*

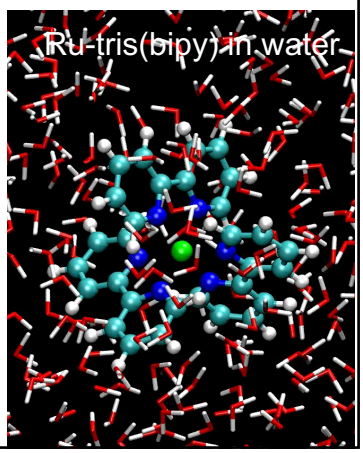
Zero point motion
Quantum Harmonic Oscillators:
Zero point energy E^{ZP}

$$E^{ZP} = \frac{1}{2} \sum_{k=1}^{3N-6} \hbar\omega_k$$



How do we incorporate finite T effects?
How do we take into account all relevant configurations to describe the thermodynamic ensemble?

-> Molecular Simulations (MD & MC)



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Chapter 1:

From Quantum Mechanics to Classical Mechanics

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Semiclassical approximation:
Treat electrons at the QM level and move nuclei classically

2) Most atoms are heavy enough so that their motion can be described with classical mechanics

• ratio of the deBroglie wavelength $\lambda = \frac{h}{\sqrt{2mE}}$ of an electron and a proton: $\frac{\lambda_{el}}{\lambda_p} = \left(\frac{m_p}{m_{el}}\right)^{1/2} \approx 40$

⇒ classical approximation is better: m↑, n↑, E↑, T↑

⇒ Works surprisingly well in many cases!

⃠ what cannot be described:
- zero point energy effects
- (proton) tunneling

⇒ quantum corrections to classical results (Wigner&Kirkwood)
⇒ classical MD extended to quantum effects on equilibrium properties and to some extend also to quantum dynamics
⇒ path integral MD and centroid dynamics

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=> Script Chapter 1

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Derivations NAC&Bohmian
(=>additional pdf)

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