

CHEM-E4115
Computational Chemistry I (5cr)
2nd part: molecular modelling

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2nd part: molecular modelling

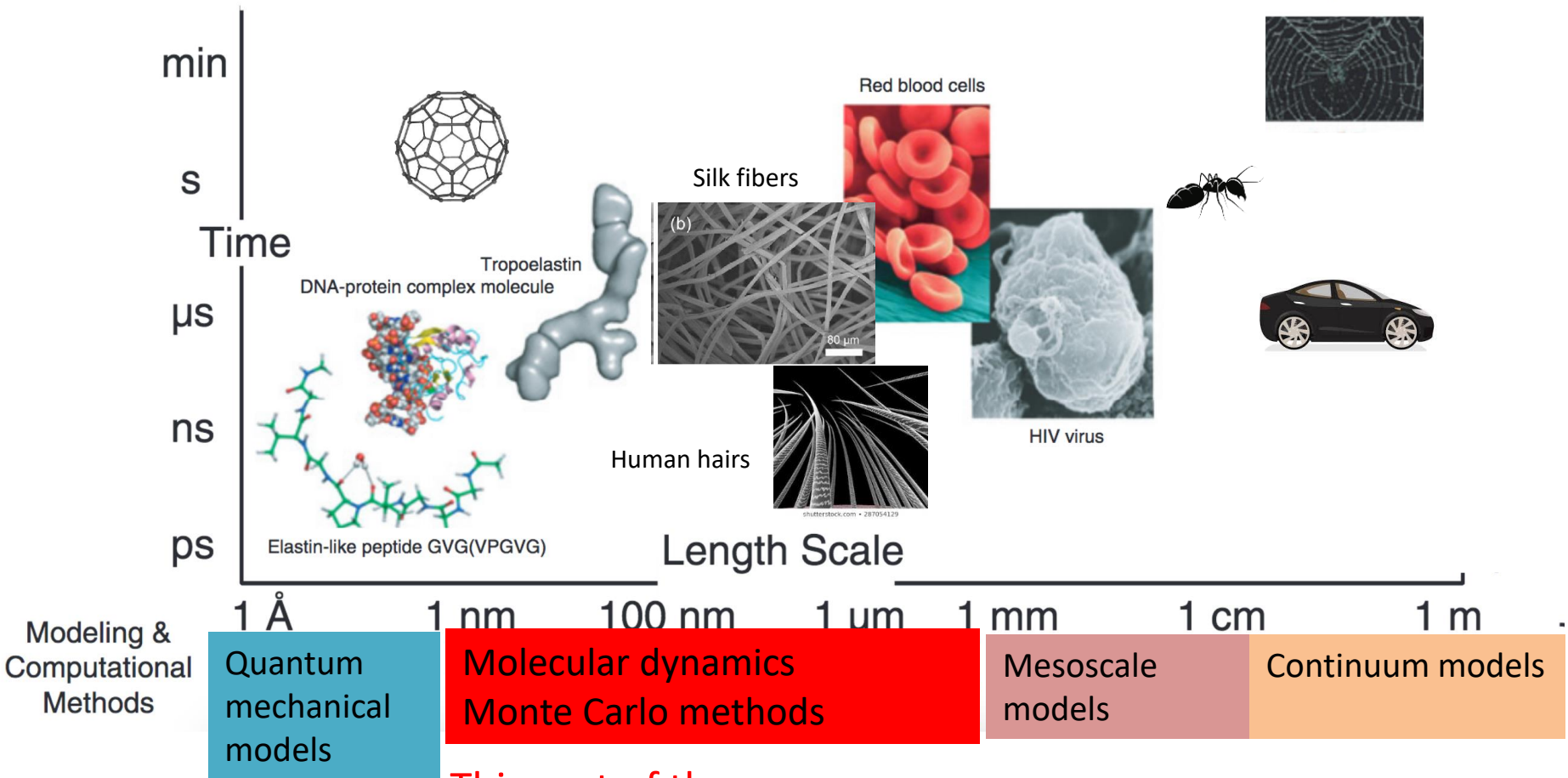
- Practical things
 - Official course news and info forum is MyCourses announcements
 - Course completion: computer class exercises and independent assignments

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Time and length scales of materials modelling



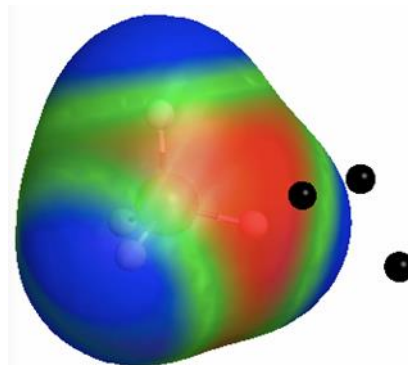
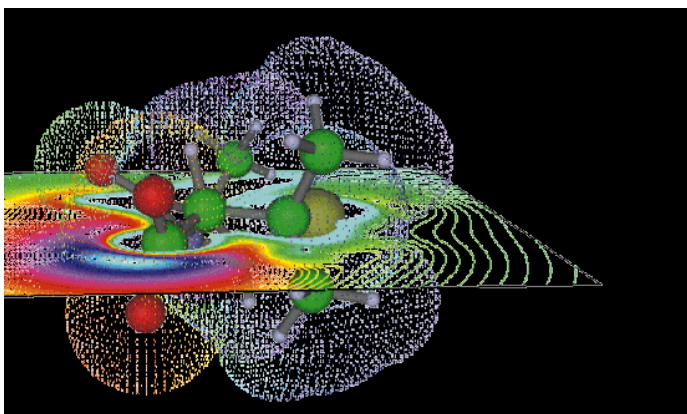
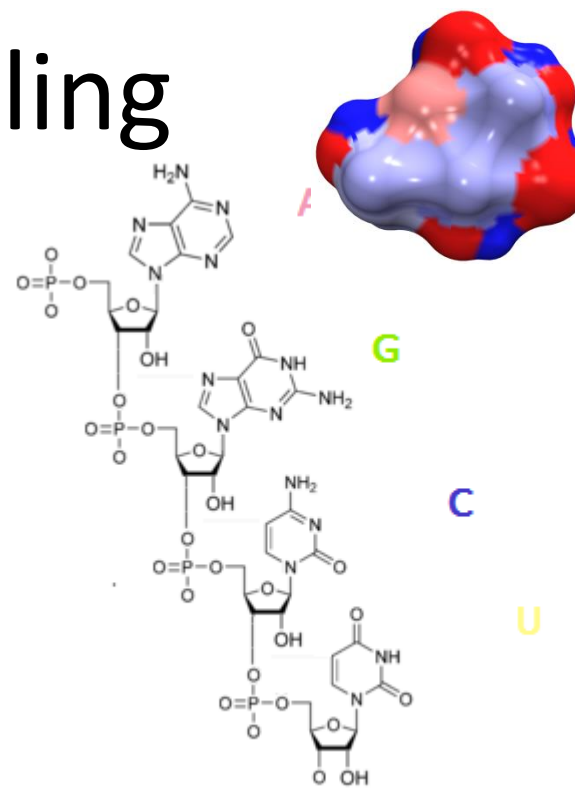
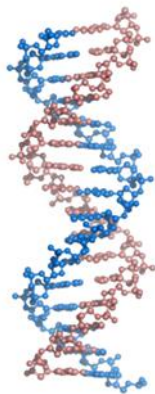
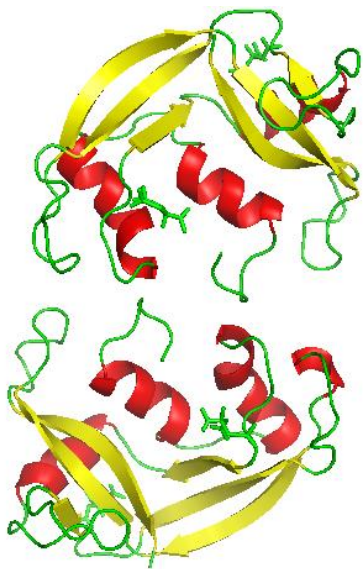
1st part of the course

This part of the course

Molecular Modeling

- **Molecular:** ~related to molecules
- **Modeling, or model:** simplified or idealistic description of a system or a process, often in mathematical terms, devised to facilitate calculations or predictions.
- **Note:** Not necessary related to computer modeling or simulations

Molecular modeling



What does this 2nd part of the course cover?

- Empirical molecular modelling (also called "classical" models)
 - **Most common simulation methodology** in molecular modelling (molecular dynamics methods, Monte Carlo methodology, some glimpses to extensions and quantum chemistry when appropriate)
 - Atomistic and molecular level coarse-grained molecular models, force-field construction basics
 - Related computer class exercises (recommended!) & Assignments 4-6.
- **Book level text for this part of the course:**
 - Daan Frenkel and Berend Smit, Understanding molecular simulation : from algorithms to applications, 2nd or 3rd Edition
 - Available as e-book via Aalto Library, a couple of physical copies of book available
 - Comprehensive but technical reading material
 - Andrew R. Leach, Molecular Modelling Principles and Applications, 2nd Edition.
 - A few physical copies of book available. Clear, comprehensive presentation of basics at a not too mathematical level. Book is outdated at level of what can be done.
 - Basics of molecular dynamics and Monte Carlo covered (separately) in most basic course books

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Computational Chemistry I (5op)

2nd part: molecular modelling

- What is your background? What are your interests and aims with this course?
- Have you ever done any molecular modelling (except priorly on this course)? If yes, what? Which software?

Molecular modeling: From introduction to real deal

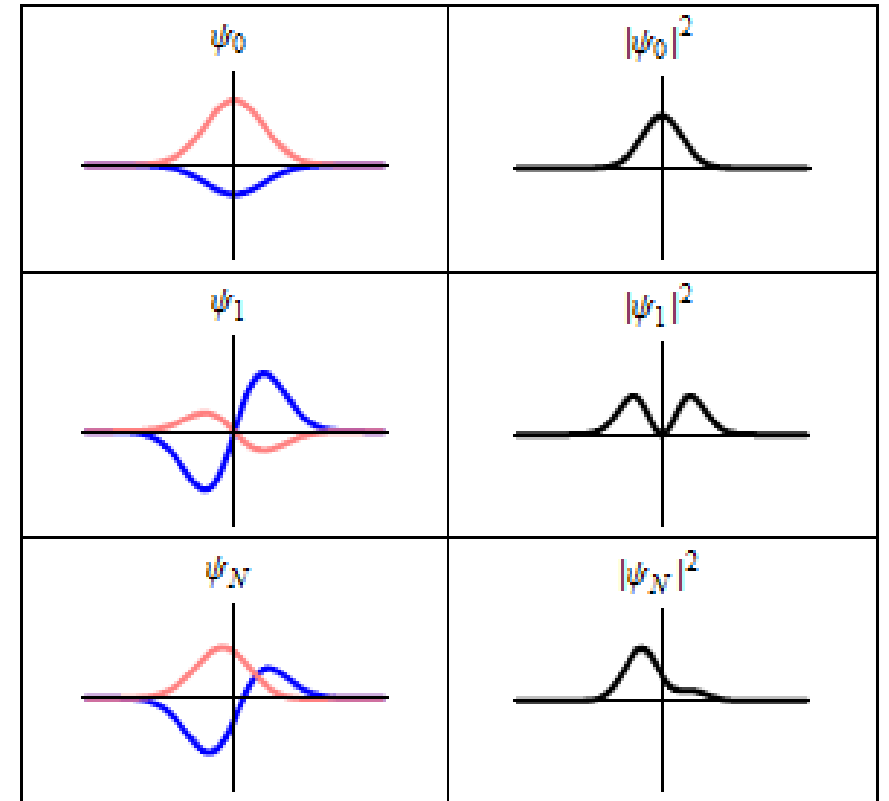
- Quantum mechanics: Schrödinger's equation

$$i\hbar \frac{\partial}{\partial t} \psi = \hat{H}\psi$$

Time-dependent
Schrödinger
equation (general)

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V \right] \Psi = i\hbar \frac{\partial}{\partial t} \Psi$$

Schrödinger's equation:
Single non-relativistic
particle



3 wavefunction solutions to the Time-Dependent Schrödinger equation for a harmonic oscillator.

http://en.wikipedia.org/wiki/Schr%C3%B6dinger_equation

Molecular modeling:

From course introduction to real deal

- Quantum mechanics: Schrödinger's equation

$$i\hbar \frac{\partial}{\partial t} \psi = \hat{H}\psi$$

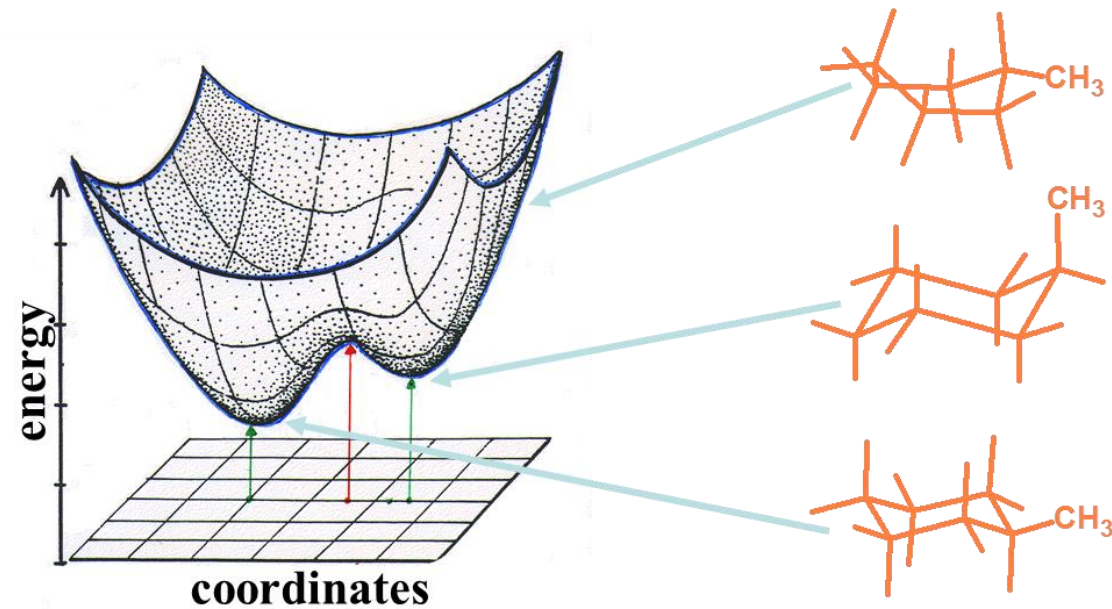
Time-dependent Schrödinger equation (general)

- Born-Oppenheimer approximation:
 - Electrons and nuclei motion treated separately
 - Consequently energy of a molecule in ground (electronic) state can be considered as a function of the nuclear coordinates only
 - If one or several of the nuclei move, this energy changes

 Potential energy surface

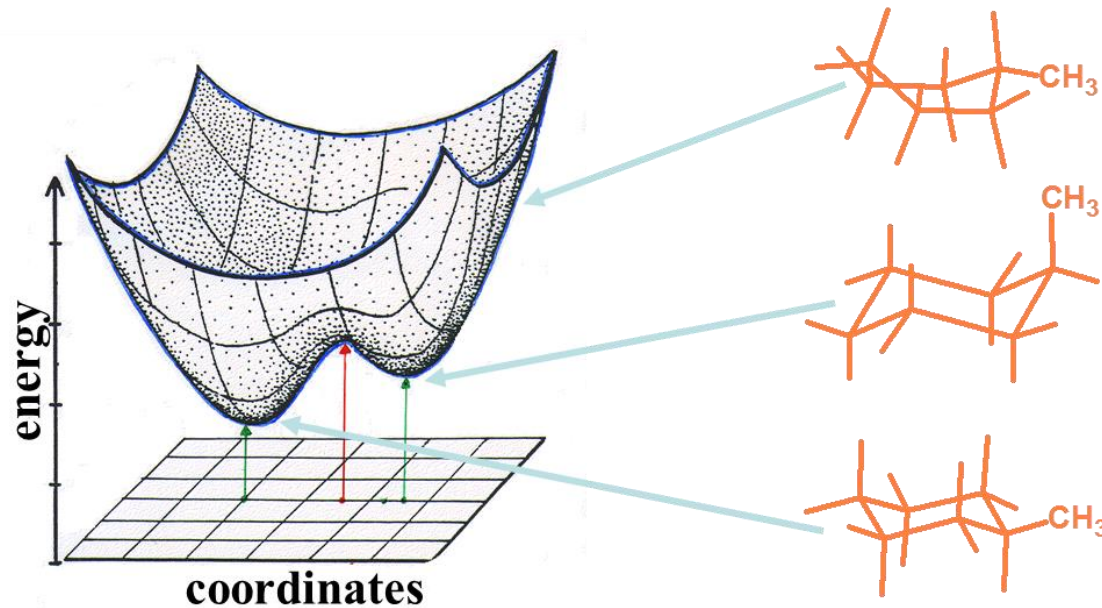
From potential energy surface to force-field

- Each point represents a molecular conformation



From potential energy surface to force-field

- Each point represents a molecular conformation
- In Molecular Modelling: An empirical potential energy function used to define



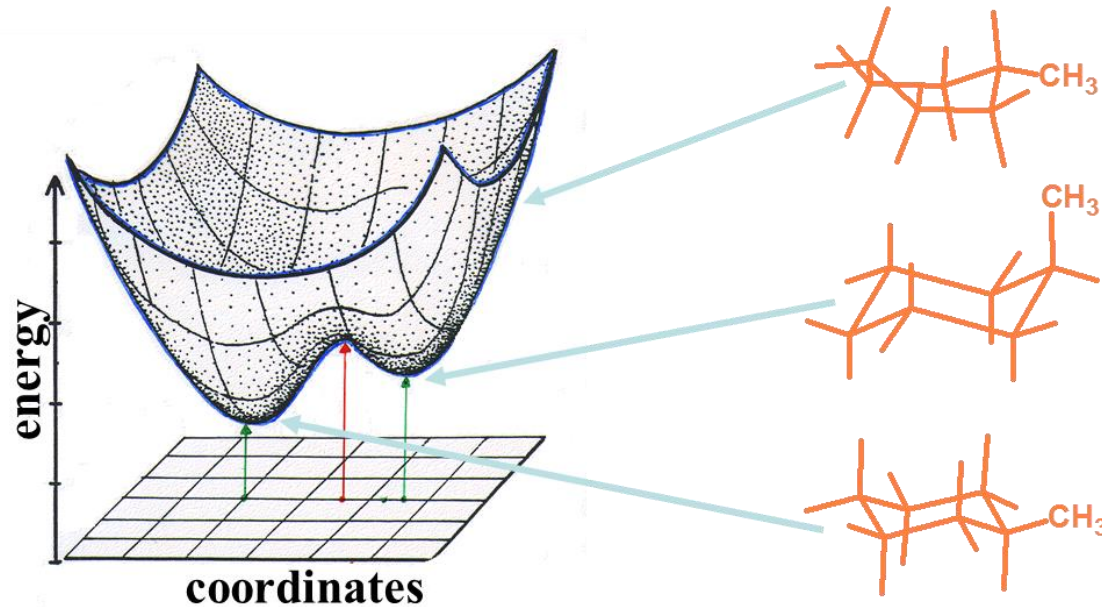
Definition: **A force-field** is an empirical potential energy function used to define the potential energy surface

Force-field and connection to molecular conformations existing in “reality”

- Thermodynamics (statistical mechanics)

- probability P of configuration A with energy E_A $P(E_A) = \sim e^{-E_A/k_B T}$

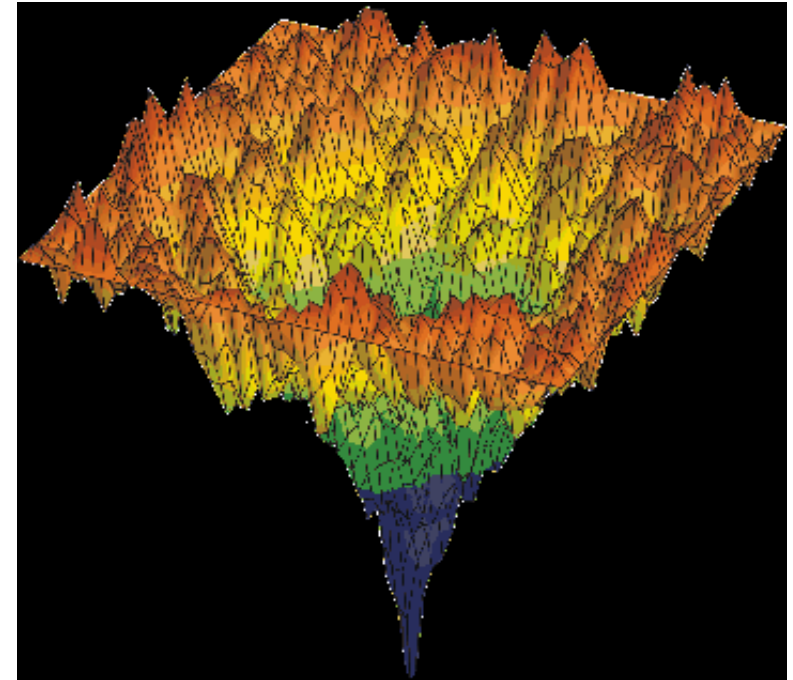
Boltzmann factors



Definition: **A force-field** is an empirical potential energy function used to define the potential energy surface

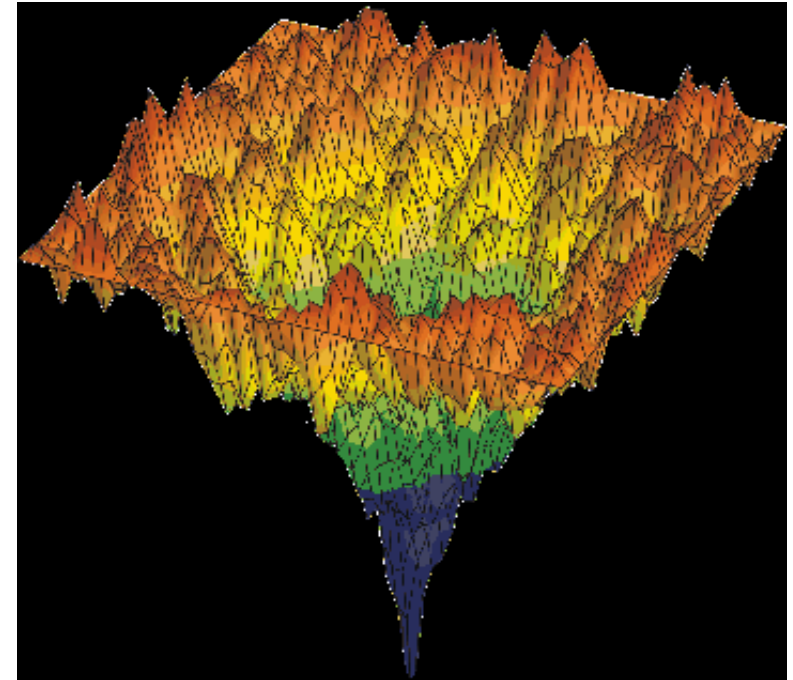
Potential energy surface

- Simple for simple molecules, not so simple for more complex systems...
- Needed in molecular modelling
 - Accurate force-field
 - A calculation method to numerically “solve” force-field predicted response of molecular system
 - Exact solutions not feasible except for very simple molecules



Potential energy surface

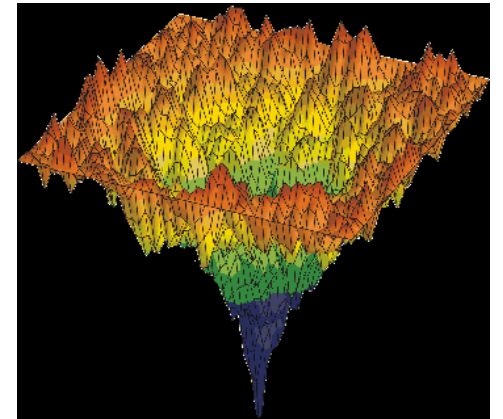
- Changes in the system energy: movements on a multidimensional surface (energy surface)
- Stationary points most interesting for modeling
 - 1st derivative of energy is zero with respect to atomic coordinates (either internal or external coordinates)
 - Force on all the particles is zero
 - Minimum energy points (stable structures) one type of stationary point
 - Later, more on methodology how to find stationary points
- Later, more on constructing potential energy surfaces (force-fields)



From potential energy surface to molecular modelling and simulations

- Global minimum energy configuration
- $T > 0$ also higher internal energies
- Assumed: sampling of the potential energy landscape such that all points are visited according to their Boltzmann weight (Ergodic sampling); true as long as simulation long enough

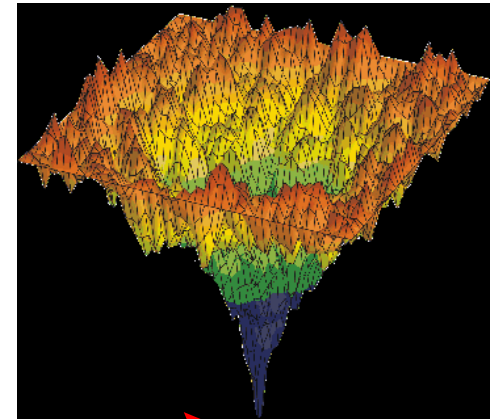
- Typical methodology: **This molecular modelling course mostly**
 - Minimum energy configuration determination (no dynamics, just potential energy surface)
 - Molecular dynamics (deterministic dynamic sampling of the potential energy surface)
 - Monte Carlo (stochastic sampling of the potential energy surface)



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Molecular dynamics: basics

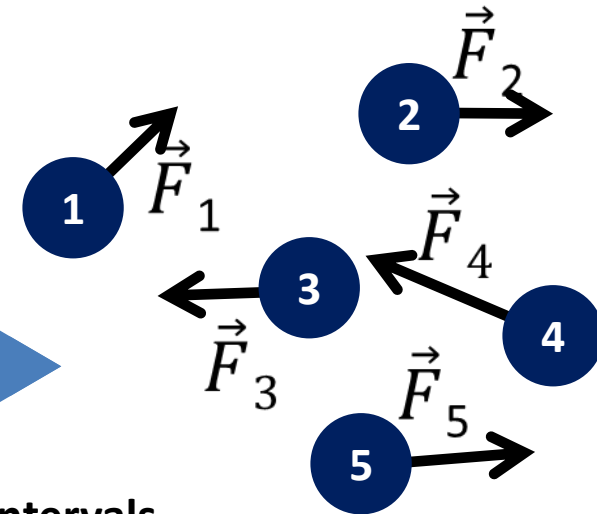
- Potential energy functional E (function of nuclei positions) \rightarrow Force on each nuclei

$$\vec{F} = -\nabla E$$

$$\vec{F} = m\vec{a} = m\frac{d\vec{v}}{dt} = m\frac{d^2\vec{r}}{dt^2}$$

time

t_0 $t_0+\delta t$ $t_0+2\delta t$...



Force for each particle **calculated** at **discrete time intervals**

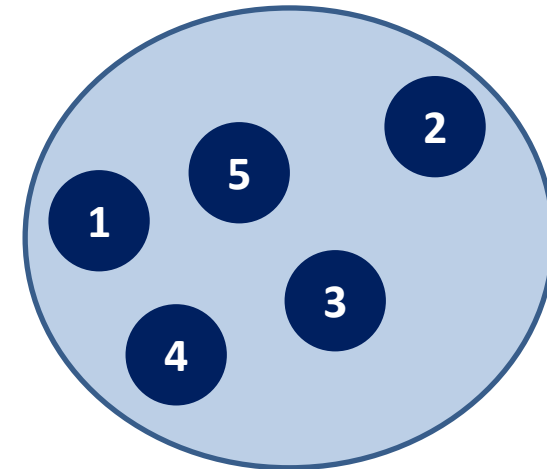
Particle **positions updated** assuming particle moves with this force (acceleration) in the direction of force for the entire (short) time interval

New forces calculated with updated positions

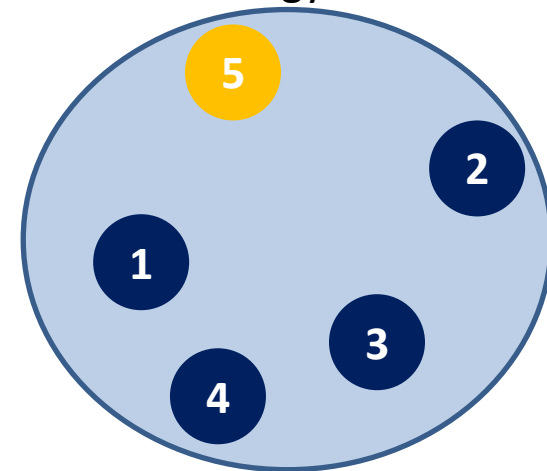
loop-as-long-as-wanted (typically as long as possible)

Monte Carlo basics

- Potential energy functional E (function of nuclei positions) \rightarrow probability of configuration
- Configurations sampled with some "random" algorithm (typically random number generator based trial moves) and new configuration accepted based on its energy (Metropolis Monte Carlo)
 - high energy configurations accepted with low probability, low energy configurations with high
 - Boltzmann distribution
 - Average over a large set provides physically measurable property
 - No deterministic dynamics



Energy E_1



Energy E_2

Summary :

Molecular modelling

- Molecular model: a representation of real molecule
- Molecular modelling methodology
 - Minimum energy configuration determination (no dynamics, just potential energy surface)
 - Molecular dynamics (deterministic dynamic sampling of the potential energy surface)
 - Monte Carlo (stochastic sampling of the potential energy surface)
- Molecular visualization: how to use visualization to better understand molecules and molecule groups