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

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

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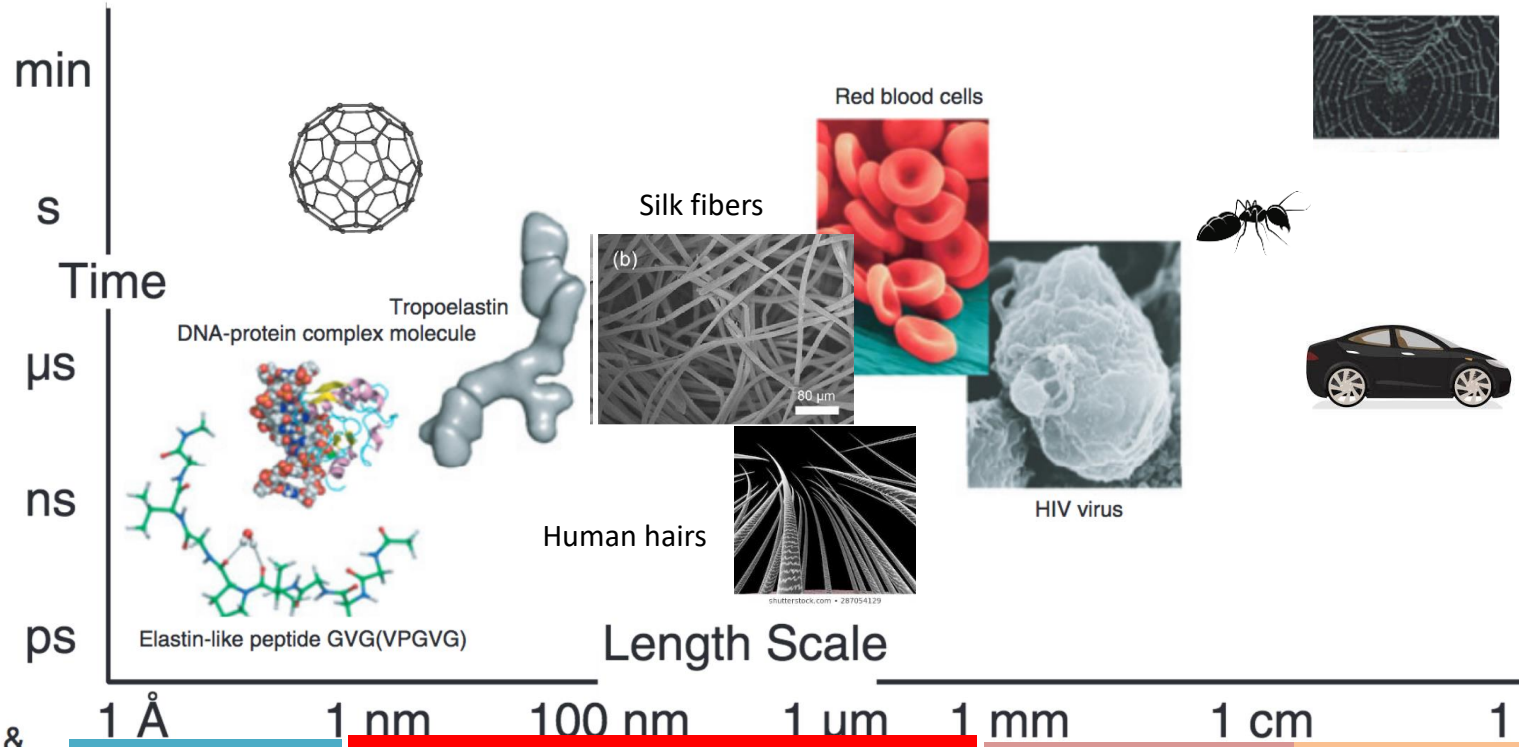
Time and length scales of materials modelling



Modeling & Computational Methods				
	Quantum mechanical models	Molecular dynamics Monte Carlo methods	Mesoscale models	Continuum models

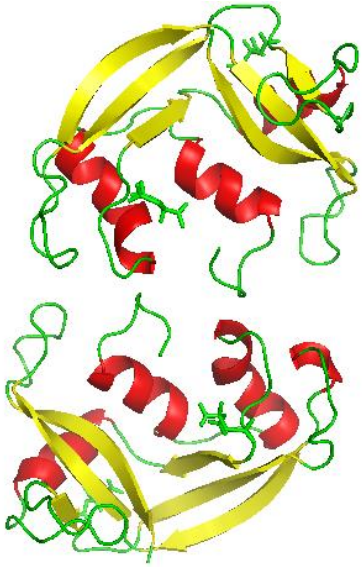
This part of the course

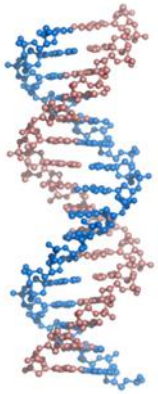
1st part of the course

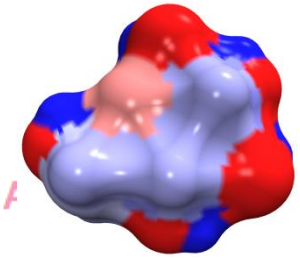
Molecular Modeling

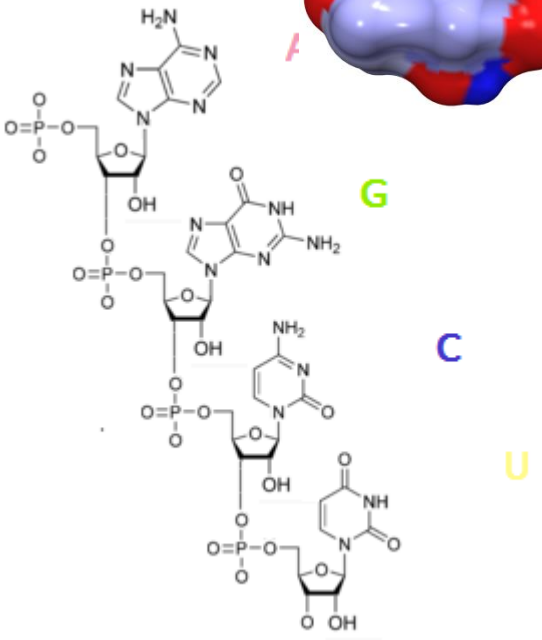
- **Molecular**: ~related to molecules
- **Modeling, or model**: simplified or idealistic description of a system or a process, often in mathematical terms, devised to facilitate calculations or predictions.
- Note: Not necessary related to computer modeling or simulations

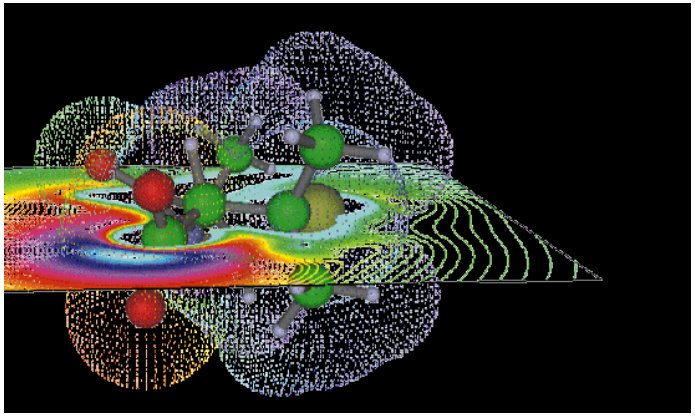
Molecular modeling

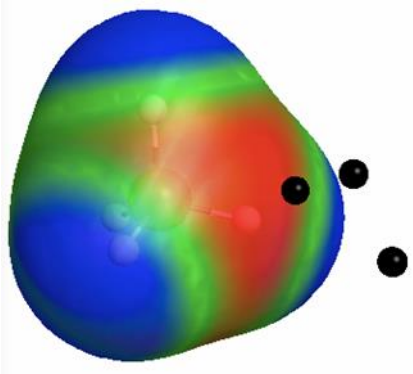












What does this 2nd part of the course cover?

- 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 for these
  - Related computer class exercises (recommended!)
  - Assignments 4-6.
- **Course book:** Andrew R. Leach, Molecular Modelling Principles and Applications, 2nd Edition, Pearson Prentice Hall.

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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?
- What technical things have been challenges in the exercises of the 1st part of the course?

Molecular modeling: From introduction to real deal

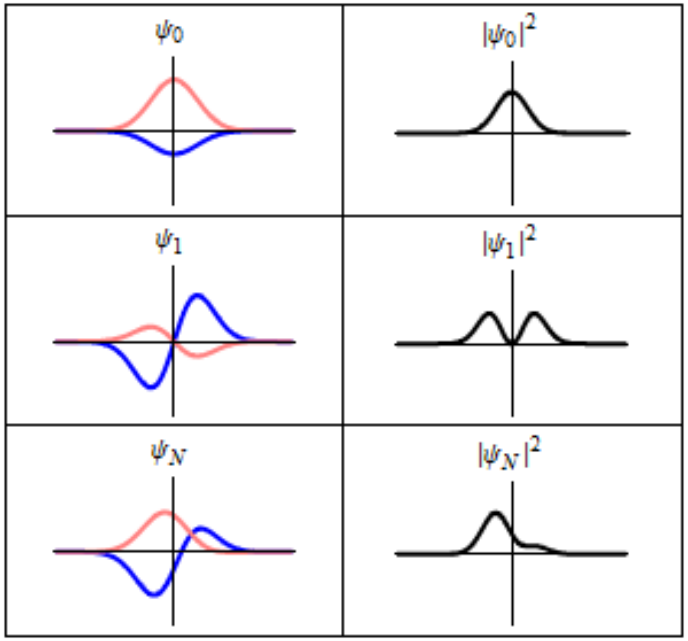
- Quantum mechanics: Schrödinger's equation

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

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

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

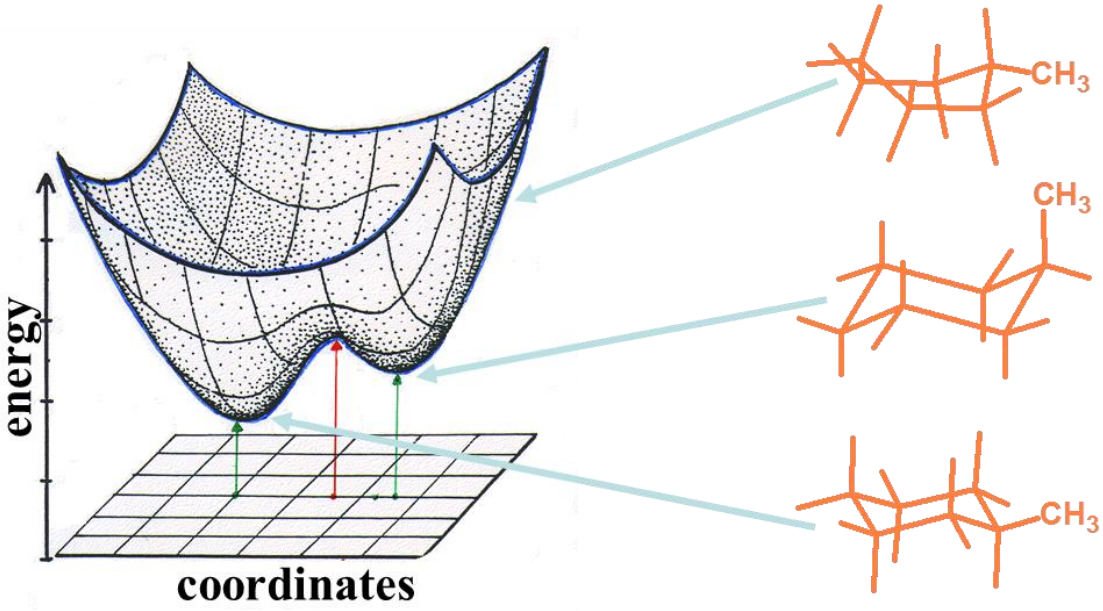
Time-dependent Schrödinger equation (general)

- 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

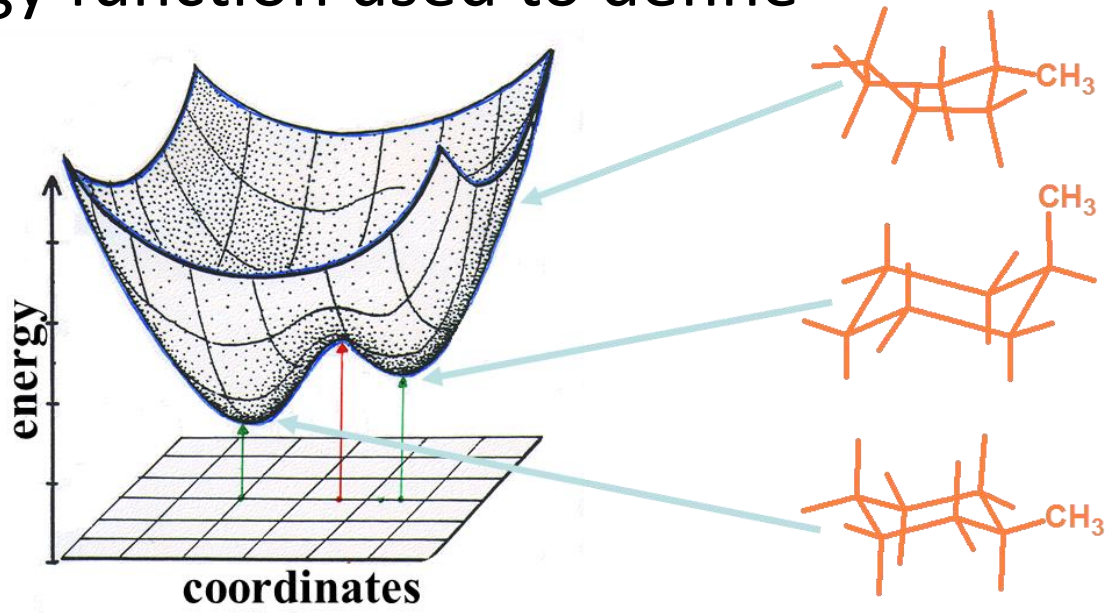
From potential energy surface to force-field

- Each point represents a molecular conformation



From potential energy surface to force-field

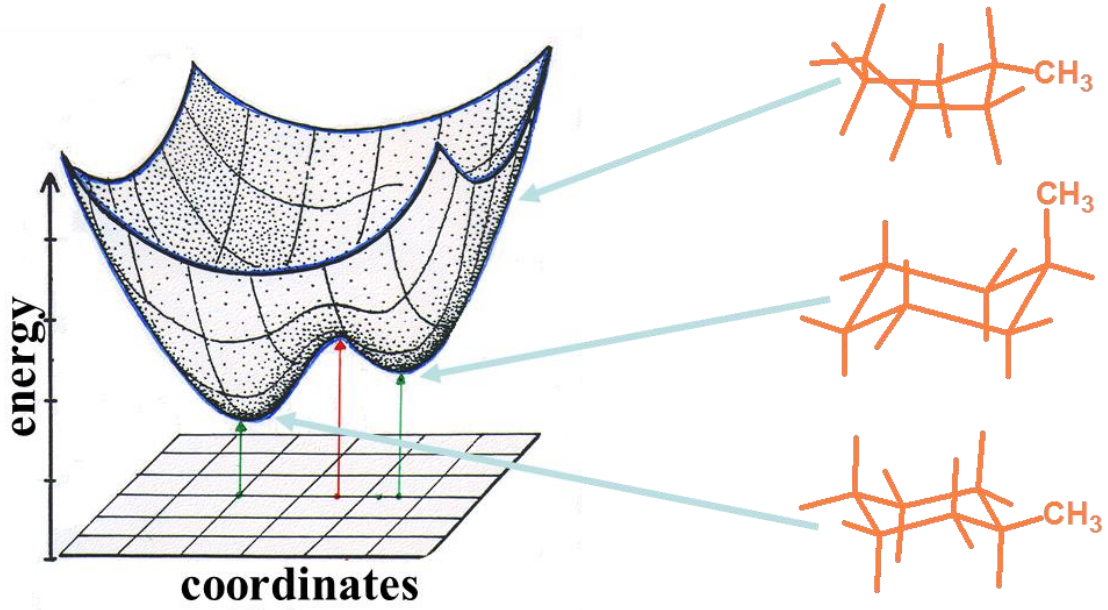
- Each point represents a molecular conformation
- In Molecular Modelling: An empirical potential energy function used to define



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"

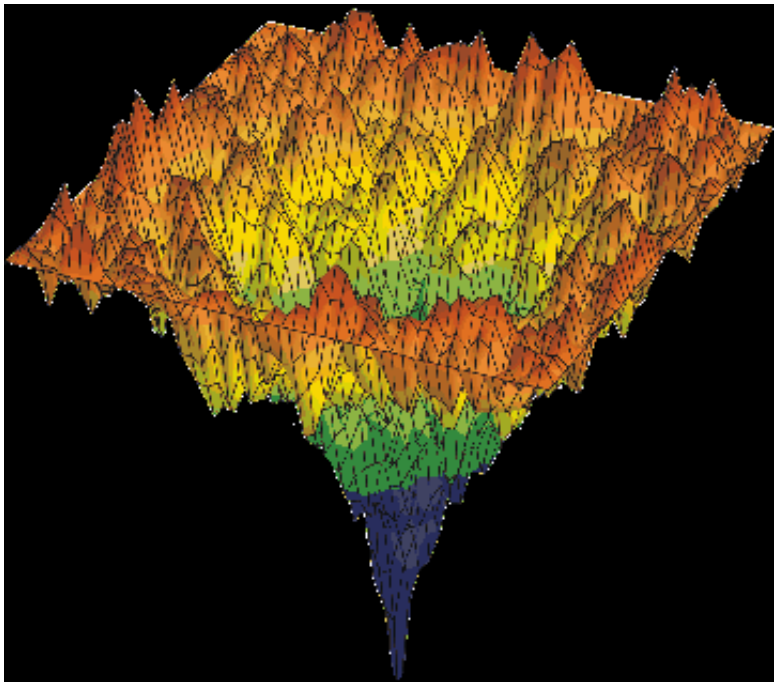
- Thermodynamics (statistical mechanics)
  - probability P of configuration A with energy E_A
    $P(E_A) = \sim e^{-E_A/k_BT}$ Boltzmann factors



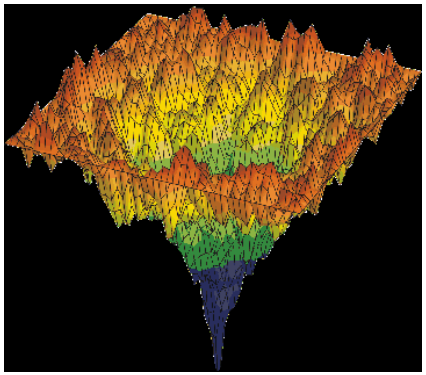
Definition: **A force-field** is an empirical potential energy function used to define the potential energy surface

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

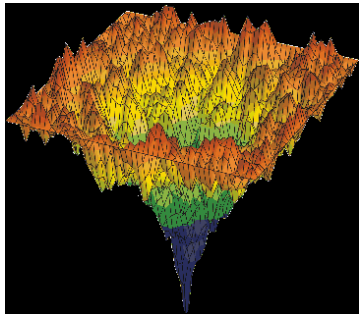


Potential energy surface



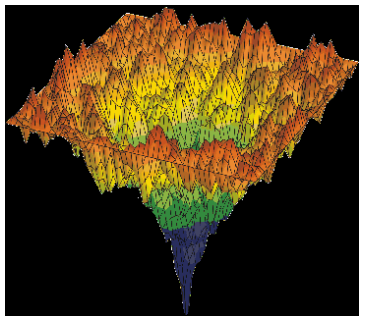
- Changes in the system energy: movements on a multidimensional surface (energy surface)
- Stationary points most interesting for modeling
  - 1st derivative of energy is zero with respect to atomic (either internal or external coordinates)
  - Force on all the particles is zero
  - Minimum energy points (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)

From potential energy surface to molecular modelling and simulations



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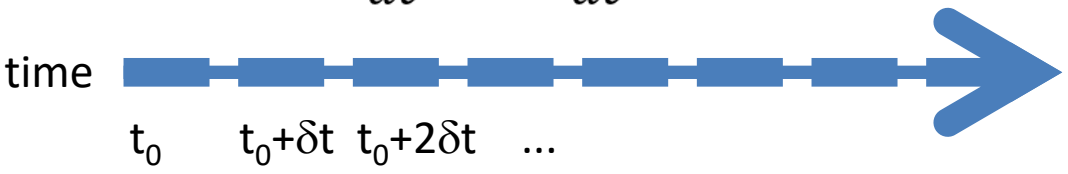
This molecular modelling course mostly

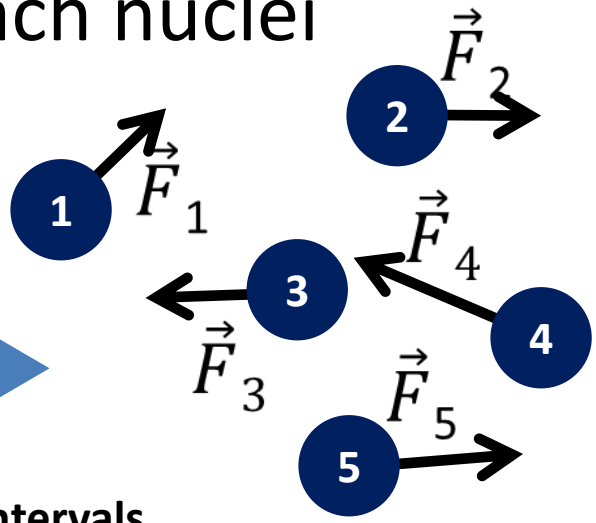
Molecular dynamics: basics

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

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

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

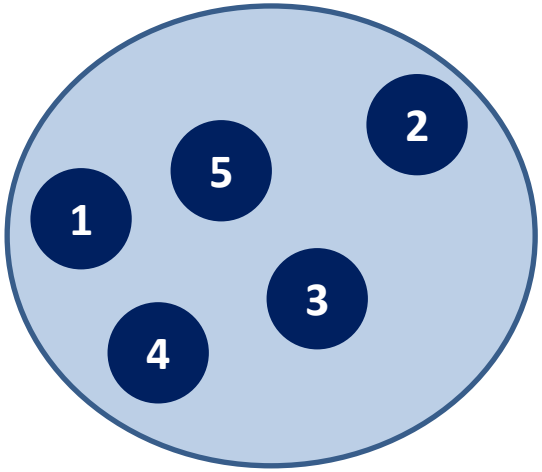




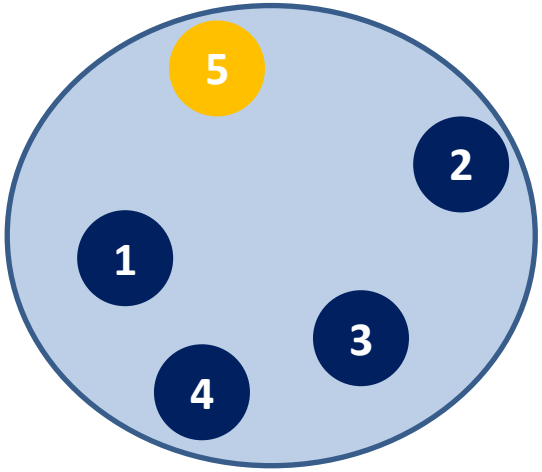
Force for each particle **calculated** at **discrete time intervals**
Particle **positions updated** assuming particle moves with this force (acceleration) in the direction of force for the entire (short) time interval
New forces calculated with updated positions
loop-as-long-as-wanted (typically as long as possible)

Monte Carlo basics

- Potential energy functional E (function of nuclei positions) -> 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 E1



Energy E2

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

Movies for visualizing molecular modelling

- Materials simulations (metals, surfaces, shear flows, liquids, some molecular materials...)
  - http://lammps.sandia.gov/movies.html
- Biomolecules
  - http://www.ks.uiuc.edu/Gallery/Movies/
- Visualization (very biological)
  - Inner life of a cell
    http://www.youtube.com/watch?v=wJyUtbn0O5Y
  - From DNA to protein
    http://www.youtube.com/watch?v=D3fOXt4MrOM