
Practicing Molecular Simulations

**Lecture 3.
Modeling interactions.**



Lucyna Firlej

Potential Energy Surface (PES).

Fundamental to everything is the **Schrödinger equation**

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

- wave function $\Psi(R, r, t)$
 - nuclear coordinates* (pointing to R)
 - electronic coordinates* (pointing to r)
- Hamiltonian operator $H = K + U = -\frac{\hbar}{2m} \sum \nabla_i^2 + U$
- time independent form : $H\Psi = E\Psi$

Born-Oppenheimer approximation

- electrons relax very quickly compared to nuclear motions
- nuclei move in presence of **potential energy** obtained by solving electron distribution for fixed nuclear configuration
 - (it is still very difficult to solve for this energy routinely)*
- usually nuclei are heavy enough to treat classically

Moving on Potential Energy Surface.

Solution of Schrödinger equation (in Born-Oppenheimer approx) :

$$\Psi(r,R) \approx \psi(r|R) \Theta(R)$$

Equation of motion for electrons

$$(K_e + V) \psi(r, R) = E_e(R) \psi(r, R)$$



PES

Equation of motion for nuclei:
(motion on the PES)

quantum

$$(K_n + E_e(R)) \Theta(R) = E_T(R) \Theta(R)$$

classical (MD, MC)

$$m \frac{d^2 R}{dt^2} = -\nabla E_e(R)$$

Contributions to PES

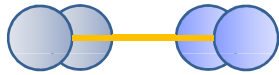
Total pair energy breaks into a sum of terms:

$$E_p(\mathbf{R}) \Rightarrow U(\mathbf{r}^N) = U_{str} + U_{bend} + U_{tors} + U_{cross} + U_{vdW} + U_{el} + U_{pol}$$

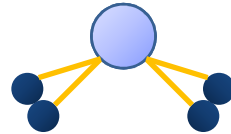
PES

intramolecular only

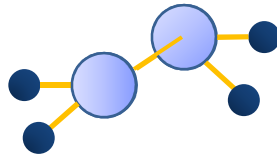
- U_{str} - stretch



- U_{bend} - bend



- U_{tors} - torsion



- U_{cross} - cross (mixed)

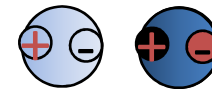
- U_{vdW} - van der Waals



- U_{el} - electrostatic



- U_{pol} - polarization



taken from Dr. D. A. Kofke's lectures on Molecular Simulation, SUNY Buffalo
<http://www.eng.buffalo.edu/~kofke/ce530/index.html>

Intermolecular forces.

short range

interaction energy exponentially decays with molecular separation

at small intermolecular distance, an overlap of the molecular wave functions causes electronic exchange or repulsion

non pair - additive

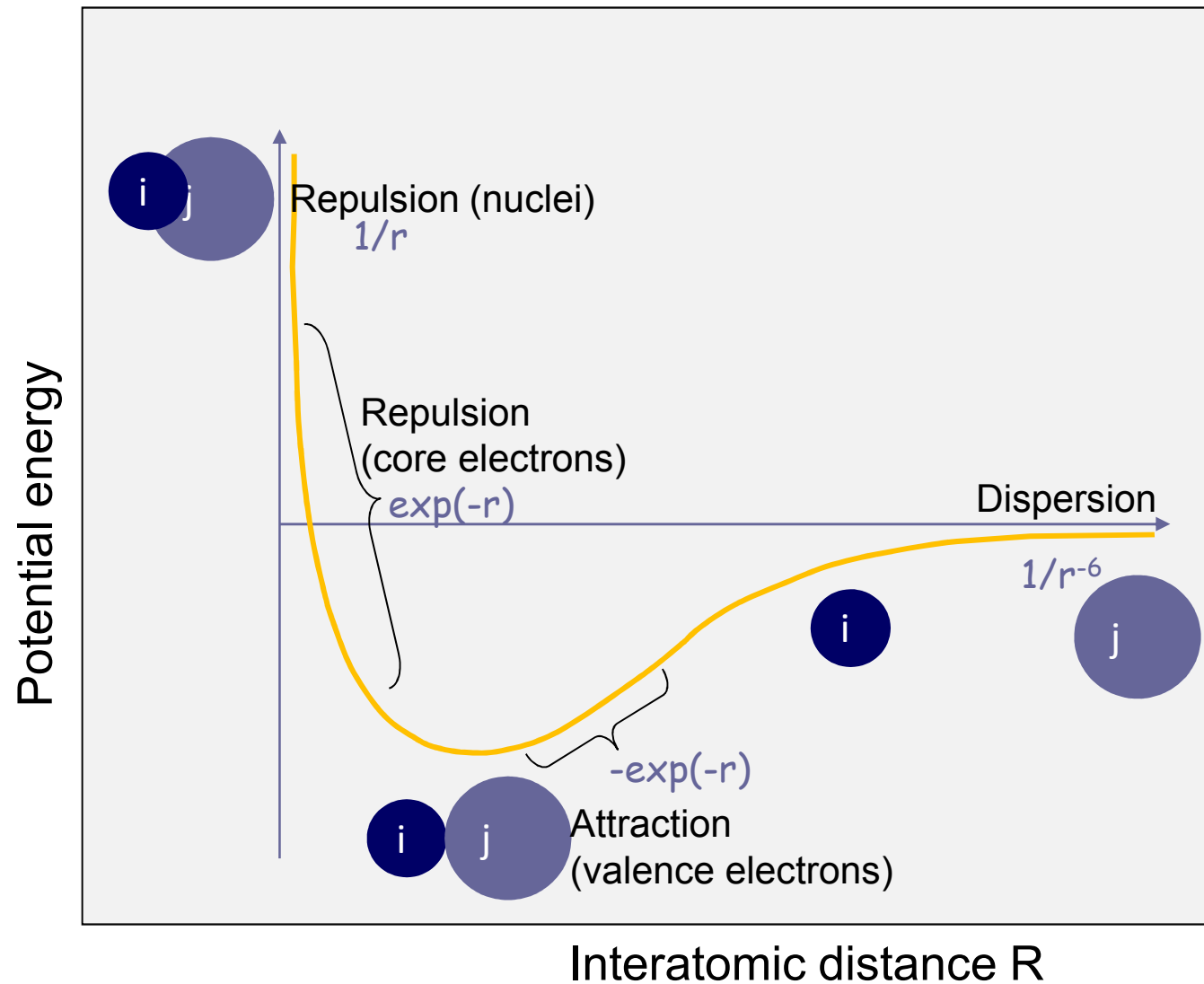
long range

interaction energy is proportional to some inverse power of molecular separation

- **electrostatic**: from static charge distribution (attractive or repulsive)
- **induction**: from distortion caused by molecular field of neighbors (always attractive)
- **dispersion**: from instantaneous fluctuations caused by electron movement (always attractive)

In theory, it is possible to calculate the intermolecular interactions from first principles (*ab initio*). In practice, only for small systems.

General shape of potential energy



Dispersion (VdW) forces.

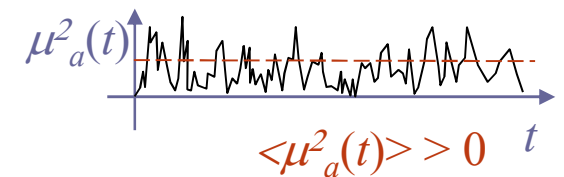
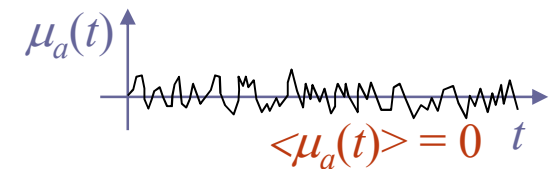
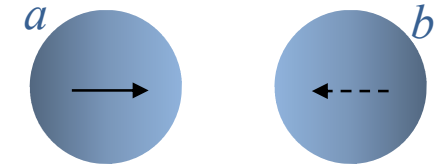
- Short-range attractive (van der Waals) forces present for all types of molecules.
- Quantum mechanical origin (London 1930)

$$u_{dis}(r) = E_{tot} - E_a - E_b = -\frac{C_6}{r^6} - \frac{C_8}{r^8} - \frac{C_{10}}{r^{10}} \dots \approx -\frac{C_6}{r^6}$$

- They arise from fluctuations in the molecular charge cloud.
- these produce a fluctuating dipole $\mu_a(t)$,
- which induced a dipole in a neighboring molecule b

$$u_{dis}(t) = -\frac{1}{2} \alpha_b E^2 \approx -\frac{1}{2} \alpha_b \mu_a^2(t) r^{-6} \approx -\frac{C_6}{r^6}$$

- expand electrostatic interaction in a multipole series.
- treat oscillating electron cloud as a simple harmonic oscillator.
- solve Schrödinger equation: it gives C_6 , C_8 , C_{10}



Repulsion (overlap) forces.

- No simple theory exists.
- For simple molecules, can be approximated by

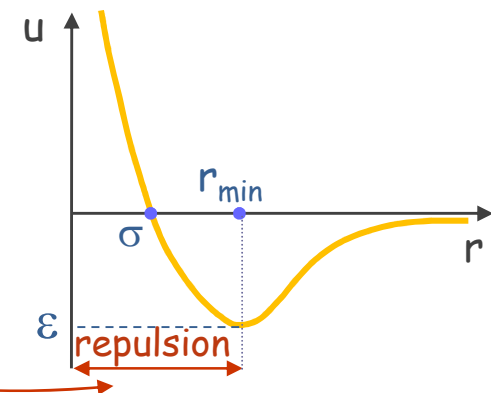
$$u_{\text{overlap}}(r) \approx A(r) e^{-Br}$$

↑
inconvenient to use.
often approximate by

$$u_{\text{overlap}}(r) \approx Ar^{-n} \quad \text{with } n = 8 \text{ to } \infty$$

Example: Lennard-Jones potential

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

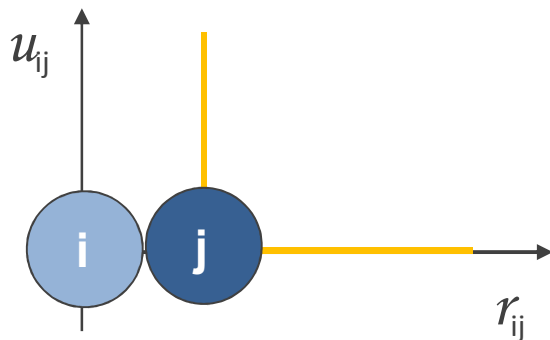


The hard & soft sphere potentials.

Hard-sphere potential :

$$u_{ij}(r) = \begin{cases} \infty & \text{for } r_{ij} \leq \sigma \\ 0 & \text{for } r_{ij} > \sigma \end{cases}$$

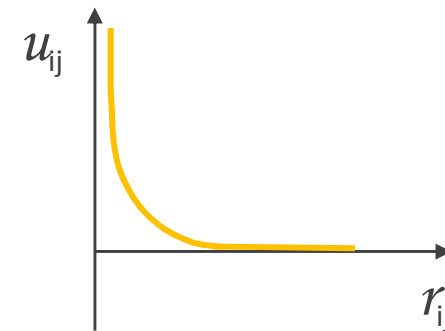
$\sigma = 2R = \text{hard sphere diameter}$



- attractive interaction totally absent;
- cannot predict even qualitatively the properties of real fluids

Soft-sphere potential :

$$u_{ij}(r) = \begin{cases} \varepsilon \left(\frac{\sigma}{r_{ij}} \right)^{12} & \text{for } r_{ij} \leq \sigma \\ 0 & \text{for } r_{ij} > \sigma \end{cases}$$

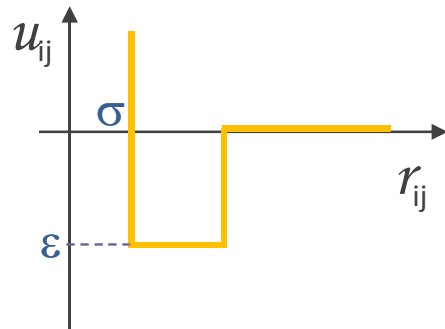


- attractive interaction still absent;
- can predict some properties of real fluids (e.g., melting lines)

Hard sphere + attractive therm potentials.

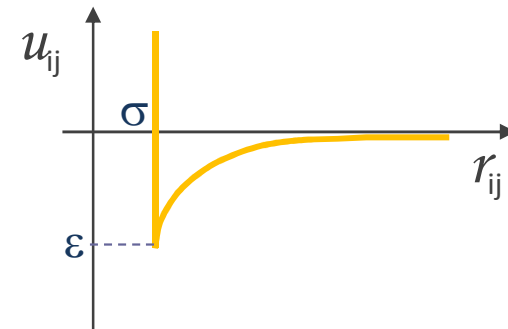
Square-well potential:

$$u_{ij}(r) = \begin{cases} \infty & \text{for } r_{ij} \leq \sigma \\ -\varepsilon & \text{for } \sigma < r_{ij} \leq \lambda\sigma \\ 0 & \text{for } r_{ij} > \lambda\sigma \end{cases}$$



$\lambda\sigma$ – a multiple of sphere radius R
 ε - measure of attractive interaction

More realistic modifications
of square-well potential:



Shuterland potential:

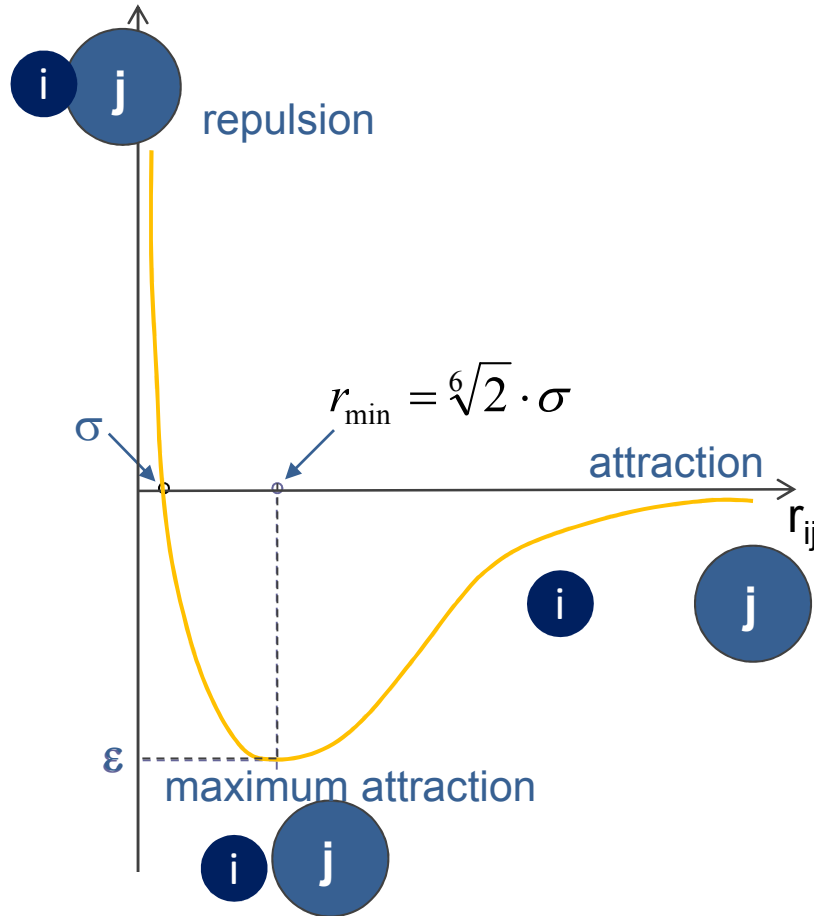
$$u_{ij}(r) = \begin{cases} \infty & \text{for } r_{ij} \leq \sigma \\ -Cr_{ij}^{-6} & \text{for } r_{ij} > \sigma \end{cases}$$

Yukawa potential:

$$u_{ij}(r) = \begin{cases} \infty & \text{for } r_{ij} \leq \sigma \\ -\frac{\varepsilon\sigma}{r_{ij}} \exp\left[-z\left(\frac{r_{ij}}{\sigma} - 1\right)\right] & \text{for } r_{ij} > \sigma \end{cases}$$

C, z – adjustable constants

Lennard-Jones potential: repulsion+ dispersion.



$$u_{ij}(r) = \varepsilon \left[\left(\frac{m}{n-m} \right) x^{-n} - \left(\frac{n}{n-m} \right) x^{-m} \right]$$

no theoretical justification

dispersion term

n, m – constants

$x = r/r_{\min}$,

r_{\min} – separation corresponding to minimum energy

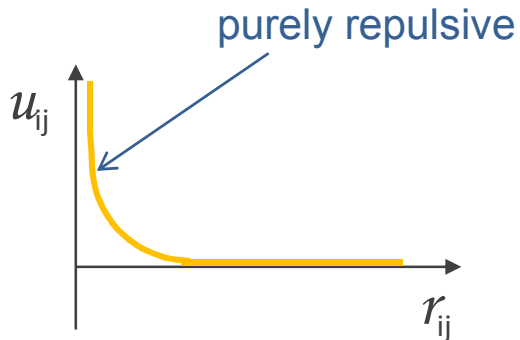
$$\sigma = r_{\min} \left(\frac{m}{n} \right)^{1/(n-m)}$$

The most common form of LJ potential is obtained for $n = 12$ and $m = 6$

$$E_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$

Modifications of LJ potential.

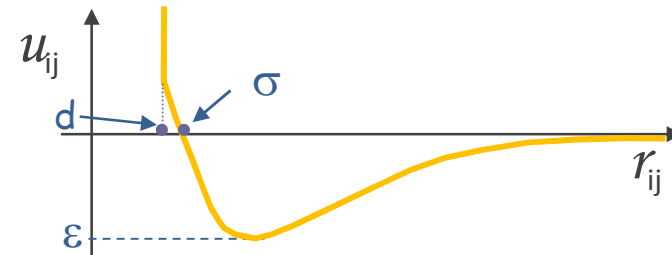
Hard-spheres LJ potential:



$$u_{ij}(r) = \begin{cases} 4\varepsilon \left[2\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] + \varepsilon & \text{for } r \leq \sqrt[6]{2} \cdot \sigma \\ 0 & \text{for } r > \sqrt[6]{2} \cdot \sigma \end{cases}$$

Kihara truncated potential:

LJ potential is truncated at the distance d corresponding to *absolutely impenetrable core of molecules*



$$u_{ij}(r) = \begin{cases} \infty & \text{for } r \leq d \\ \varepsilon \left[\left(\frac{\sigma-d}{r-d}\right)^{12} - \left(\frac{\sigma-d}{r-d}\right)^6 \right] & \text{for } r > d \end{cases}$$

Egelstaff potential:

(better approximation of dispersion forces)

$$u_{ij}(r) = \varepsilon \left[2\left(\frac{r_{\max}}{r}\right)^{12} - 2\left(\frac{r_{\max}}{r}\right)^9 - \left(\frac{r_{\max}}{r}\right)^6 \right] \quad \text{for } r > d$$

Born-Mayer (6-exp) potential.

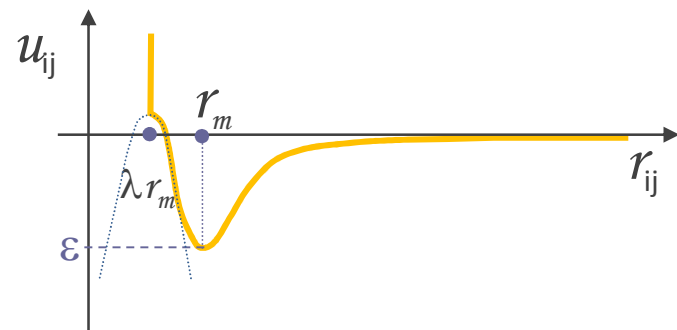
After LJ, the most widely used form of a pairwise potential

1932 – the repulsion between atoms should have an exponential dependence on r , because of the electron waves function overlap:

$$u_{ij}(r) = A \exp(-Br) - \frac{C}{r^6}$$

the most widely used modification is

$$u_{ij}(r) = \begin{cases} \infty & \text{for } r_{ij} \leq \lambda \\ \frac{\varepsilon}{1 - \frac{\sigma}{\alpha}} \left\{ \frac{\sigma}{\alpha} \exp\left[-\alpha \left(1 - \frac{r_{ij}}{r_m}\right)\right] - \left(\frac{r_m}{r_{ij}}\right)^6 \right\} & \text{for } r_{ij} > \lambda r_m \end{cases}$$



Damping functions.

In general, the repulsion-dispersion interaction can be represented as

$$u_{REP}(r) = \gamma(1 + ar) \exp(a_0 + \frac{a_1}{r} + \frac{a_2}{r^2})$$

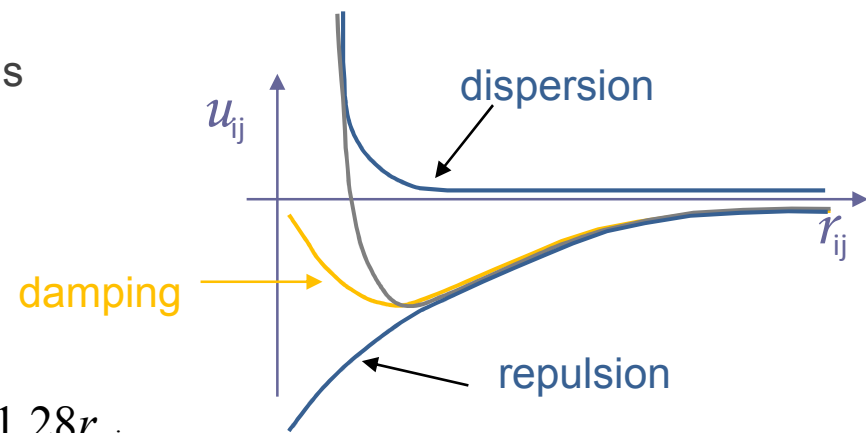
a_i - constants, fitted using *ab initio* data
(charge distribution on molecule)

$$u_{DISP}(r) = f(r) \left(\frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} \right)$$

As the dispersion dominates at small distances, often we should introduce a damping function $f(r)$ which artificially reduced the dispersion term

- we can have a global damping for all terms of dispersion
or
- we can damp separately each term

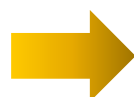
$$f(r) = \begin{cases} 1 & \text{for } r \geq 1.28r_{\min} \\ \exp\left[-\left(-1.28r_m / r - 1\right)^2\right] & \text{for } r < 1.28r_{\min} \end{cases}$$



General requirements for potentials.

Accuracy: reproduce properties of interest as closely as possible
(at present, the best semi-empirical potentials have greater accuracy than explicit solutions of Schrödinger equation)

Transferability: applicable to situations for which the potential function was not fit
(different symmetry, charge state changes, variable temperature, transfer from bulk to surface, different compounds)



There is no real justification
for transferability of potential between compounds!

Computational efficiency: force calculations are generally the most time consuming part of a simulation:

Different applications may emphasize different aspects of potentials:

- chemistry - **accuracy** (accurate reaction rates require very accurate barrier estimation)
 - statistical mechanics - **efficiency** (many-body dynamics may result from simple potentials)
 - biochemistry - **all three** (reasonable structures with approximate forces)
-

Force Fields Methods.

in principle, it is possible to calculate the intermolecular interactions from the first principles (*ab initio*),

but

in practice, it is too expensive to solve QM electronic energy for every nuclear configuration



instead, we define energy using simple empirical formulas:
“**force fields**” or “**molecular mechanics**”

Today, force fields constitute the only way to describe complex molecules (like polymers or proteins).

Force fields are usually written in terms of pairwise additive interatomic potentials.

Many body interactions.

The potential energy of **N** interacting particles can be evaluated as:

$$E_{pot} = \sum_i^N u_1(r_i) + \underbrace{\sum_i^N \sum_{j>i}^N u_2(r_i, r_j)}_{\text{interactions between pairs of particles}} + \underbrace{\sum_i^N \sum_{j>i}^N \sum_{k>j>i}^N u_3(r_i, r_j, r_k)}_{\text{interactions between particle triplets}} + \dots$$

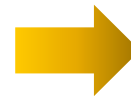
effect of an external field

many body interactions

interactions between particles

- Typically, it is assumed that **only two-body term is important** (E_{pot} is truncated after the second term)
- In some particular cases three-body term should be considered (chemistry, biochemistry)

Evaluation of E_{pot} is the most time-consuming step in simulations





$$t \sim N^m$$

m – number of interactions

Components of a Force Field.

Any force field contains the necessary building blocks for the calculation of energy and force:

- a list of atom types
- a list of atomic charges
- rules for atom-types
-  - functional forms of the components of the energy expression
-  - parameters for the function terms
- rules for generating parameters that have not been explicitly defined (for some force fields)
- a defined way of assigning functional forms and parameters (for some force fields)

Force fields.

There are several potentials “ready to use”, which were optimized to model specific properties of matter.

OPLS – **O**ptimized **P**otential for **L**iquid **S**imulations
(contains 6-12 potentials and electrostatic terms)

ECEPP – **E**mpirical **C**onformational **E**nergy **P**rogram for **P**eptides
(6-12 potentials + electrostatic terms + hydrogen bonding + torsion)

AMBER – **A**ssisted **M**odel **B**uilder with **E**nergy **R**efinement
(6-12 potentials + electrostatic terms + hydrogen bonding + torsion + bond & angle terms)

CHARMM – **C**hemistry of **H**arvard **M**acromolecular **M**echanics
(6-12 potentials + electrostatic terms + torsion + bond & angle terms + out-of-plane bending) no hydrogen bonding

MM3 – **M**olecular **M**echanics (? the more complete)

UFF – **U**niversal **F**orce **F**ield (potentials are determined from general rules based only on elements, their hybridization and connectivity)

CFF – Force Field based on quantum mechanics
(it emphasizes the importance of cross-interactions)

Classical Force Fields.

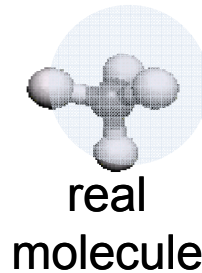
Simple, fixed algebraic form for every type of interaction.
Variable parameters depend on types of atoms involved.

Example: CHARMM* force field:

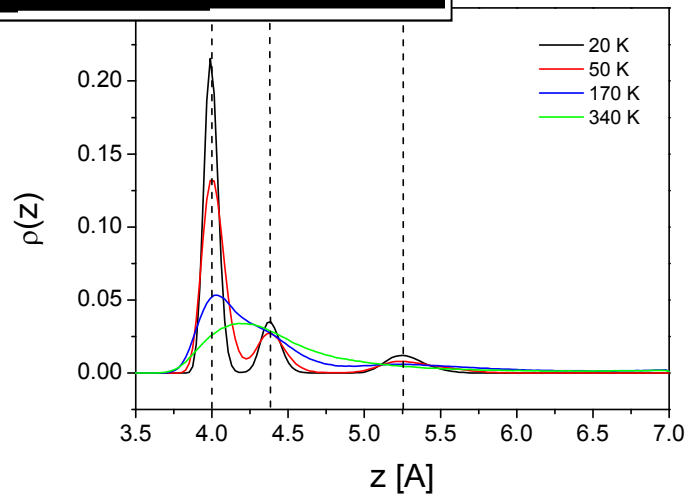
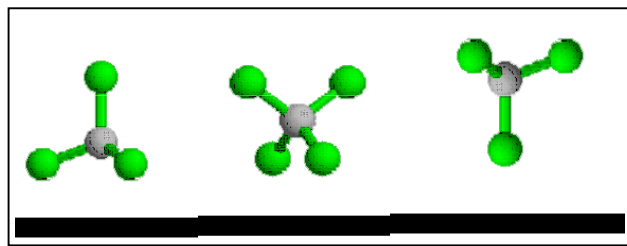
$$\begin{aligned}
 U(\vec{R}) = & \underbrace{\sum_{\text{bonds}} k_i^{\text{bond}} (r_i - r_0)^2}_{U_{\text{bond}}} + \underbrace{\sum_{\text{angles}} k_i^{\text{angle}} (\theta_i - \theta_0)^2}_{U_{\text{angle}}} + \\
 & \underbrace{\sum_{\text{dihedrals}} k_i^{\text{dihe}} [1 + \cos(n_i \phi_i + \delta_i)]}_{U_{\text{dihedral}}} + \\
 & \underbrace{\sum_i \sum_{j \neq i} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]}_{U_{\text{nonbond}}} + \sum_i \sum_{j \neq i} \frac{q_i q_j}{\epsilon r_{ij}}
 \end{aligned}$$

Concept of superatom.

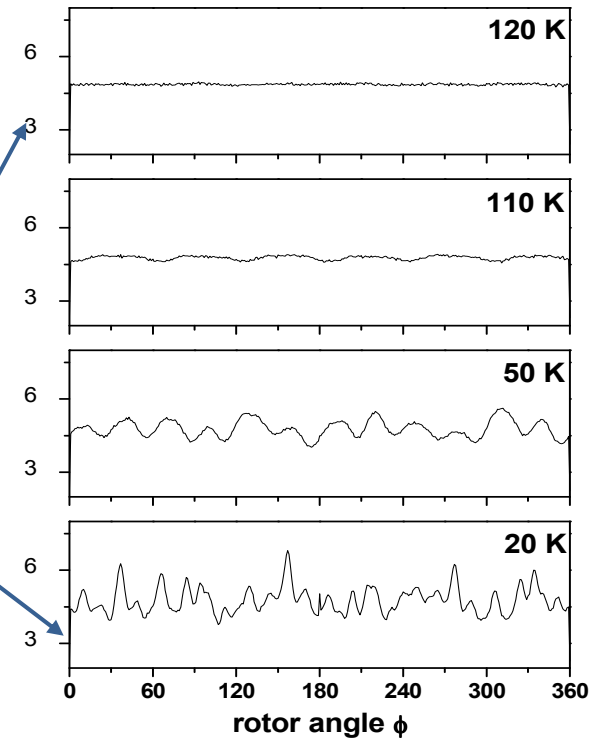
Atoms
or
molecules of fluid ?



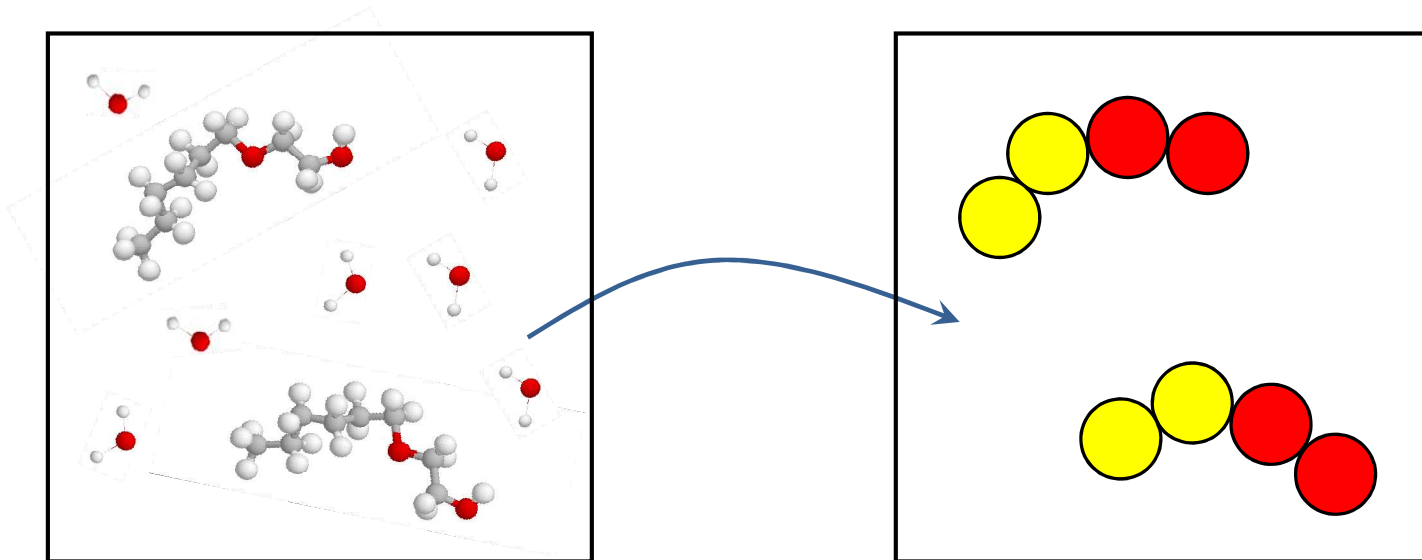
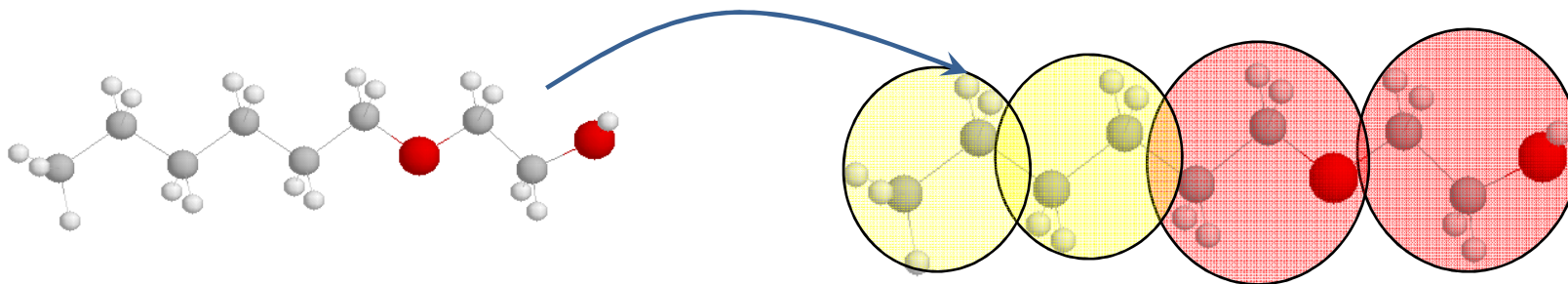
Example: CCl_4 adsorbed on smooth graphite surface



order-disorder
phase transition



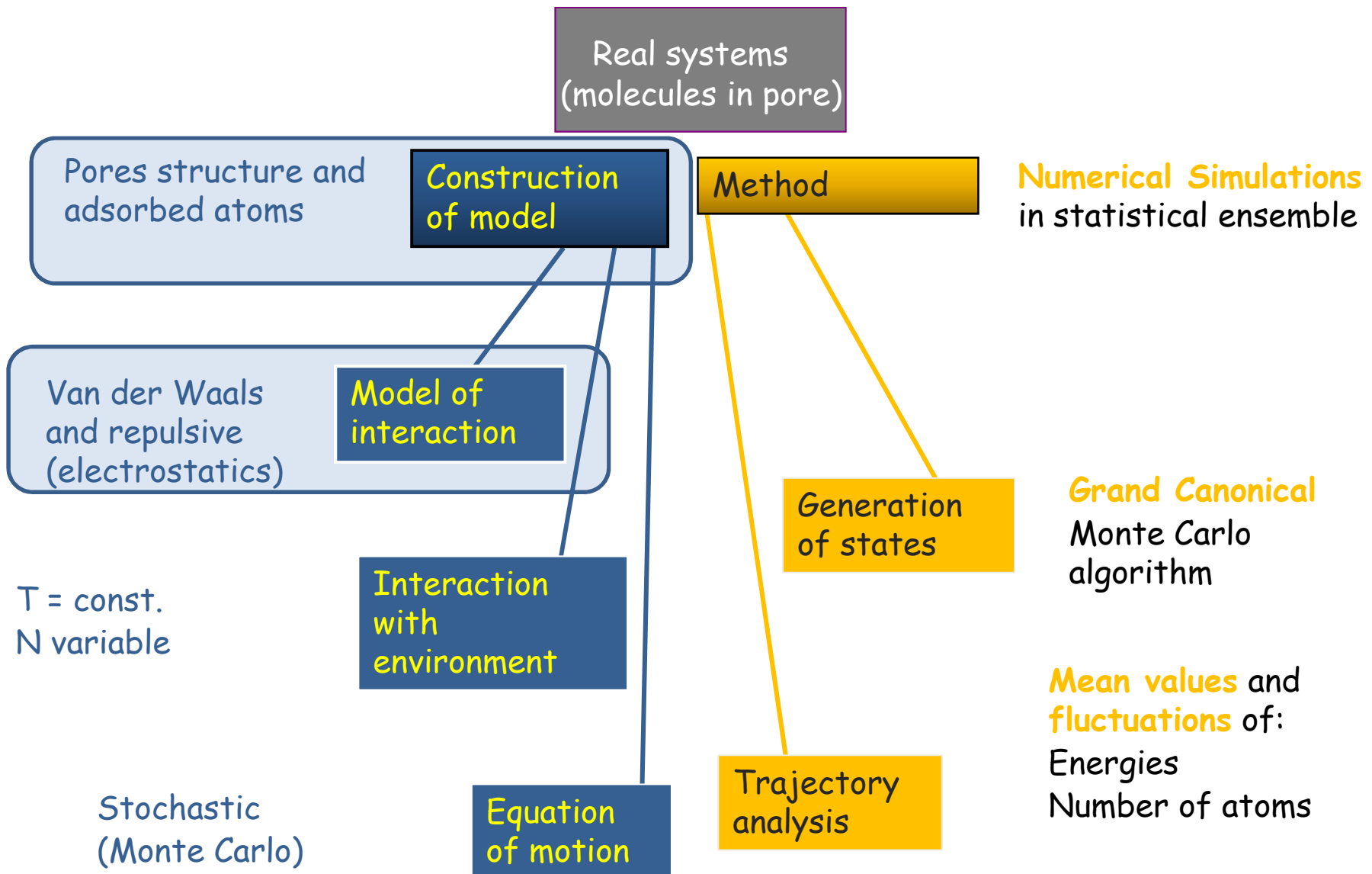
Coarse graining procedure.



original system

effective system

Numerical simulations: how?



2nd step: modeling CH₄ – CH₄ interaction.

We will work at temperatures 80, 110, 140 and 180 K.
At these temperatures methane is rotating isotropically,
and can be approximated by a spherical superatom.

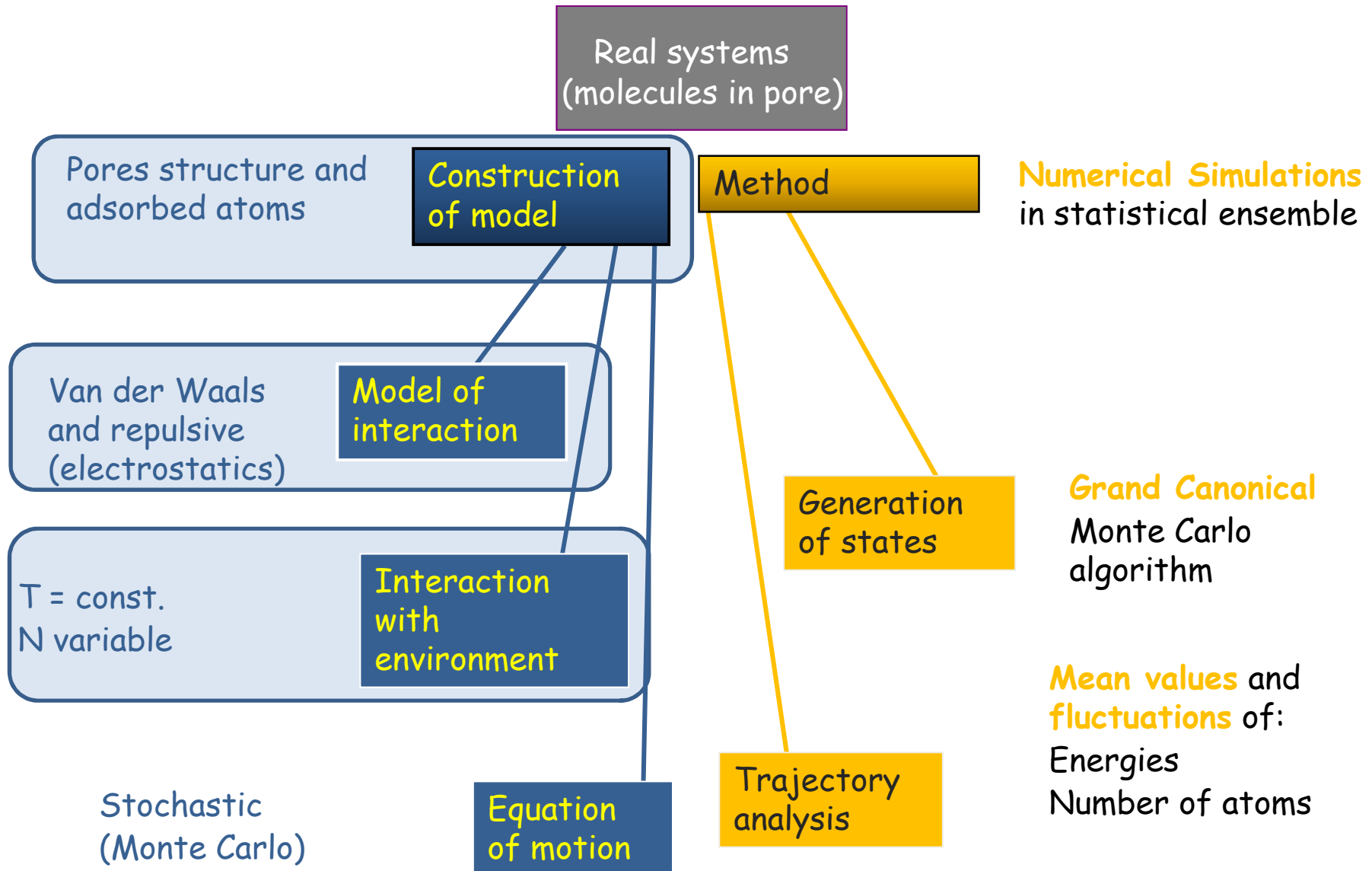
The CH₄ molecule is electrically neutral – no electrostatic component of interaction!

The interaction between two CH₄ superatoms will be modeled by LJ potential with $\varepsilon = 148$ K, $\sigma = 3.73$ Å.

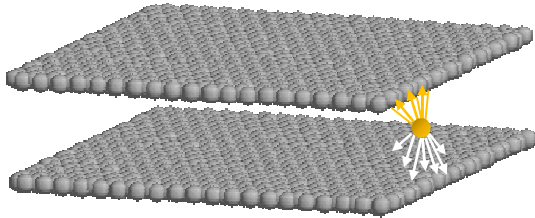
Our MC code will not calculate the CH₄ - CH₄ interaction on the fly, but use the precalculated matrix $(r_{ij}, E(r_{ij}))$, where $E(r_{ij})$ is expressed as the polynomial of r_{ij} .

- To do:**
1. read and understand the code [spline.f](#)
 2. calculate and plot LJ potential for CH₄ - CH₄ interaction.
 3. notion of cutoff: when the CH₄ - CH₄ interaction becomes negligible?

Numerical simulations: how?

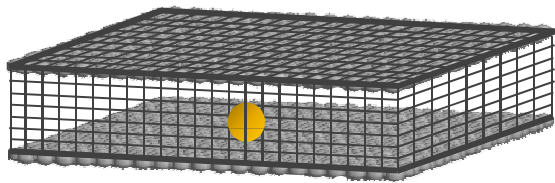


3rd step: modeling CH₄ – pore wall interaction.



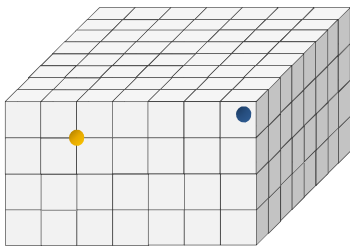
We need to calculate the interaction of CH₄ molecule with the atoms in the pore wall (within cutoff distance)

Warning: Periodic Boundary Conditions (PBC) must be in place!



The simplest way to calculate the distribution of energy in any heterogeneous space is to divide this space in small cubes, and calculate the energy at each cube's corner.

In such a way we obtain a grid (a matrix $[x, y, z, E(x,y,z)]$) of energy of CH₄ adsorbed inside the pore



Warning: bilinear extrapolation should be used to calculate the interaction at any (x,y,z) location.

3rd step: modeling CH₄ – pore wall interaction.

To do:

1. Write the code to calculate the grid of CH₄ superatom interaction inside the pore of width H 10 Å.
 - $\epsilon_{CC} = 28.2$ K, $\sigma_{CC} = 3.4$ Å
 - mixing rules: $\epsilon_{CMet} = \sqrt{\epsilon_{CC} \cdot \epsilon_{MetMet}}$, $\sigma_{CMet} = (\sigma_{CC} + \sigma_{MetMet})/2$
 - step of the grid $\Delta x = \Delta y = \Delta z = 0.2$ Å
2. Plot (contour plot) the CH₄ PES in the middle of the pore.
Determine the corrugation of PES in the middle of the pore.
3. Write the code to calculate the map of minimum of CH₄ energy inside the pore, and, for each point of the surface, the distance of this minimum from the pore wall. Again, it will be a map. Determine the corrugation of this minimum energy surface, and compare with that from the previous exercise.
4. Write the code that calculate the average interaction energy of CH₄ with the pore wall, depending on the distance from the pore wall only.

