

Métodos numéricos para escoamentos em nano e microescalas

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MOLECULAR DYNAMICS

Statistical Physics

- *Molecular simulations generate information at microscopic level.*
- *How to connect this microscopic information (atomic positions and velocities) into macroscopic observable (temperature, pressure, heat capacity ...) ?!*

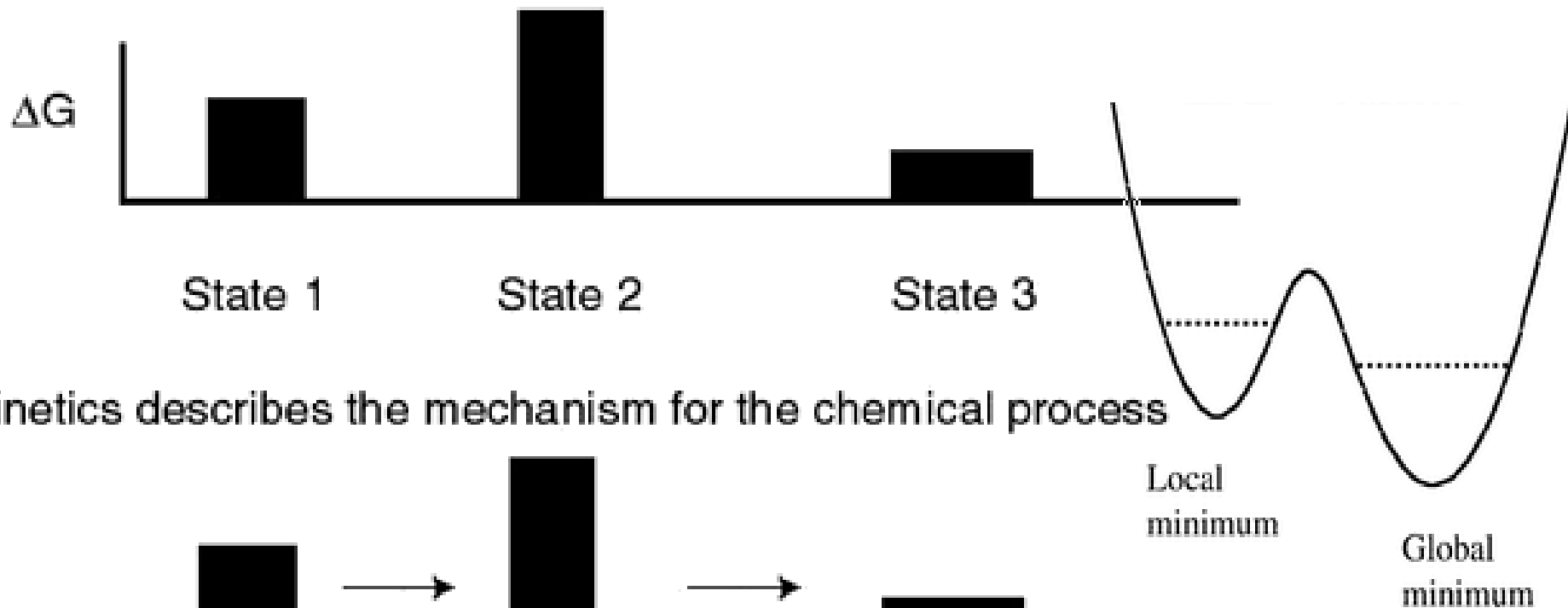
Procedure

- Goal: *explore the macroscopic properties of a system through microscopic simulations*
- Path: *through Statistical mechanics*
rigorous mathematical approach that relates macroscopic properties with the distribution and motion of atoms and molecules of the N-body system.

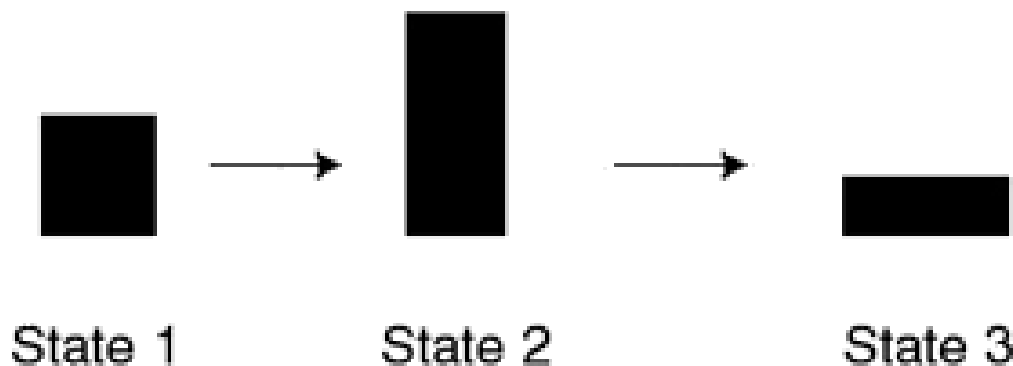
Explore both thermodynamic and or kinetic phenomena

Thermodynamics, Kinetic and Dynamics

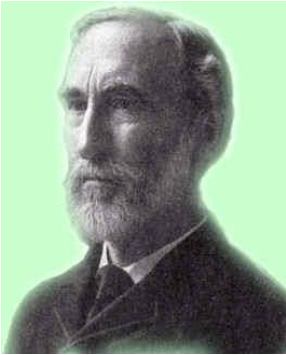
Thermodynamics describes the driving force for chemical processes



Kinetics describes the mechanism for the chemical process

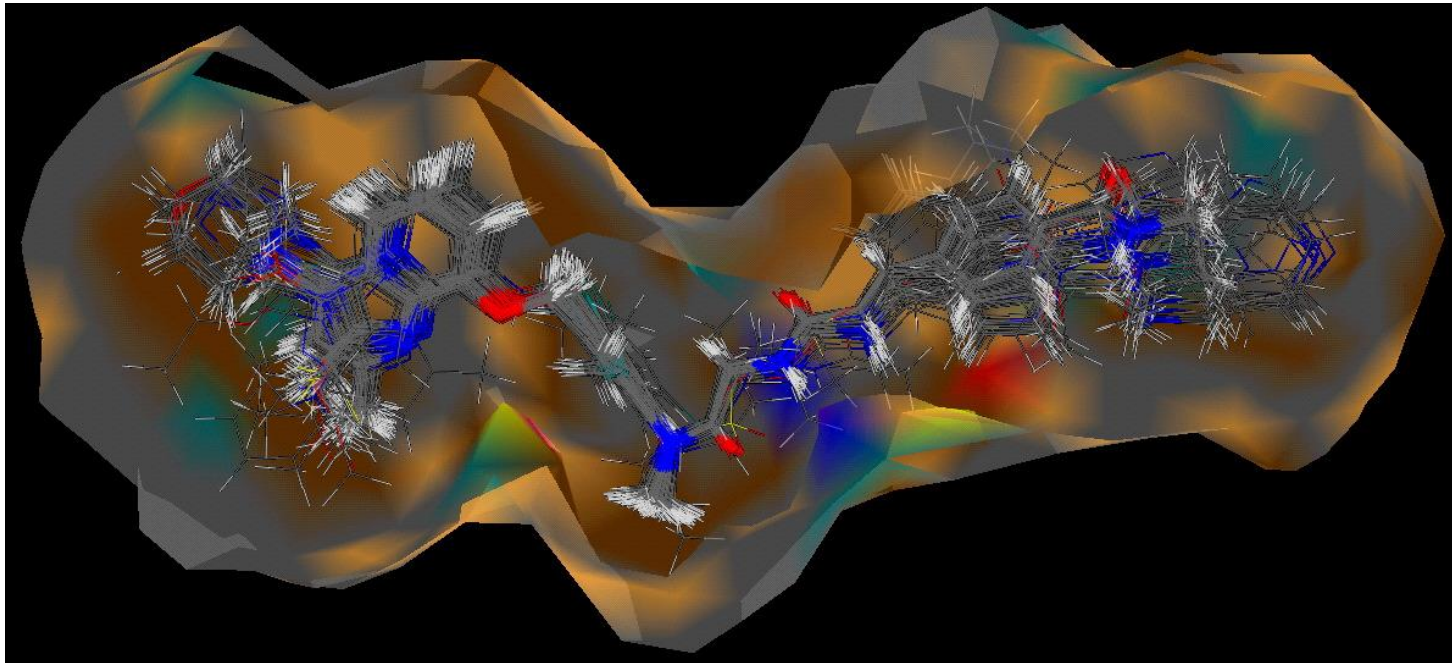


Microscopic state and ensemble



- Microscopic state: defined by the atomic positions (r) and momenta (p).

Phase space: r and p coordinates in a multidimensional space.



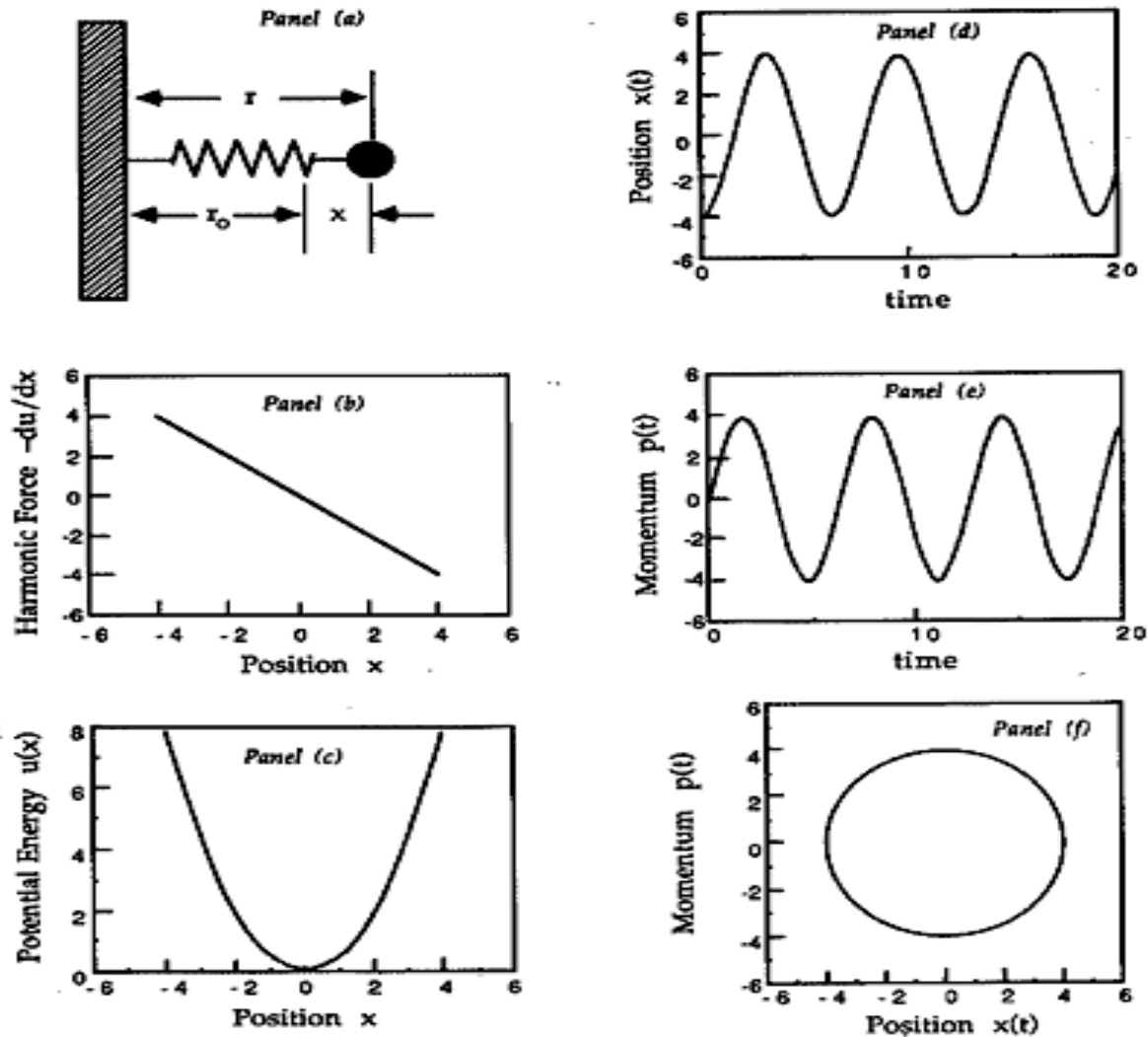
Please, could you be more clear ?!

SURE !

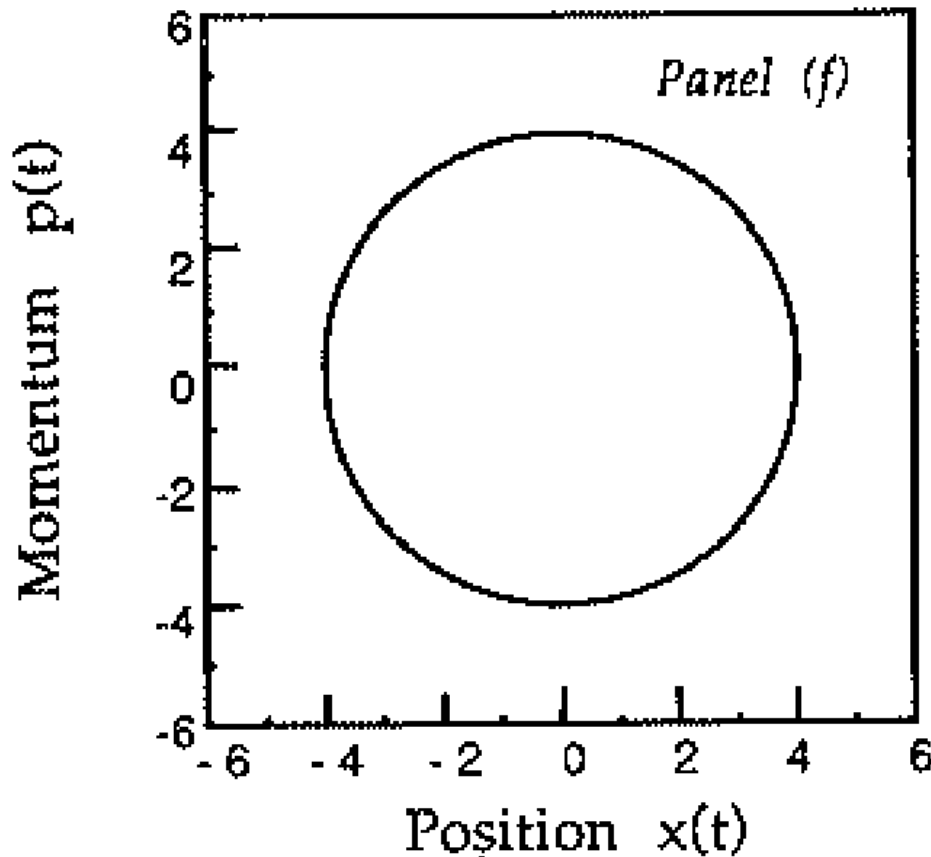
Let me take the most simple case possible:

The 1-D HARMONIC OSCILATOR

Harmonic oscillator - phase space



Harmonic oscillator - phase space



Now, for us :

we have more than 10^{23} particles,

we would have a phase space of 6×10^{23} dimensions !!!



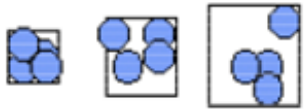

Ensembles



- Ensemble: is a collection of all possible systems which have different microscopic states **BUT** have **AN IDENTICAL** macroscopic or thermodynamic state.

- ◆ Each microscopic state has some probability.
- ◆ Distribution function describes everything.

Ensembles

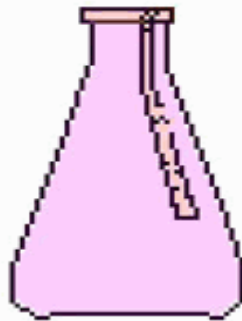
Name	All states of:	Probability distribution	Schematic
Microcanonical (EVN)	given EVN	$\pi_i = \frac{1}{\Omega}$	
Canonical (TVN)	all energies	$\pi(E_i) = \frac{1}{\Omega} e^{-\beta E_i}$	
Isothermal-isobaric (TPN)	all energies and volumes	$\pi(E_i, V_i) = \frac{1}{\Delta} e^{-\beta(E_i + PV_i)}$	
Grand-canonical (TVμ)	all energies and molecule numbers	$\pi(E_i, N_i) = \frac{1}{\Xi} e^{-\beta(E_i + \mu N_i)}$	

SO WHAT ?!

***Phase space, Ensemble, Microcanonical, Canonical,
bla bla bla ...***

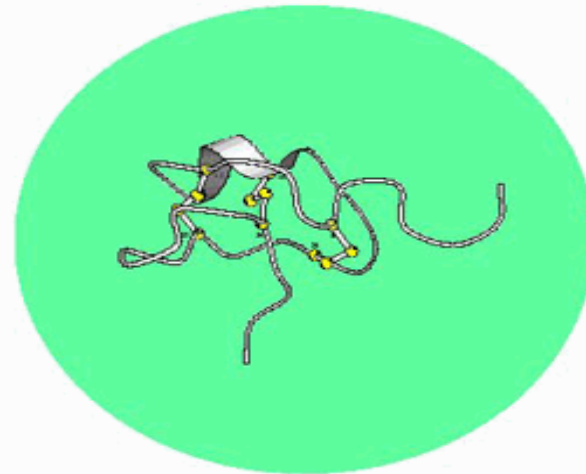
Where is the relation with bridges, buildings, cars, real life ?

Experiment



Macroscopic

Molecular Simulation



Microscopic

PAY ATTENTION

Next:

The most important slides of this course !

Average in an ensemble

PROBABILITY (define the conditions of the systems)

$$\langle D \rangle = \int P(\mathbf{p}^N, \mathbf{r}^N) D(\mathbf{p}^N, \mathbf{r}^N) d\mathbf{p}^N d\mathbf{r}^N$$

OBSERVABLE: physical property that we are interested in ...

Time average

$$\bar{D} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t D(t') dt'.$$



OBSERVABLE: physical property that we are interested in ...

The most important slide of this course

Ensemble average = Time average

$$\langle \mathbf{A} \rangle_{\text{NVT}} = \lim_{t_{\text{sim}} \rightarrow \infty} \frac{1}{t_{\text{sim}}} \int_{t_0}^{t_0 + t_{\text{sim}}} \mathbf{A}(t) dt$$

Remember !!!

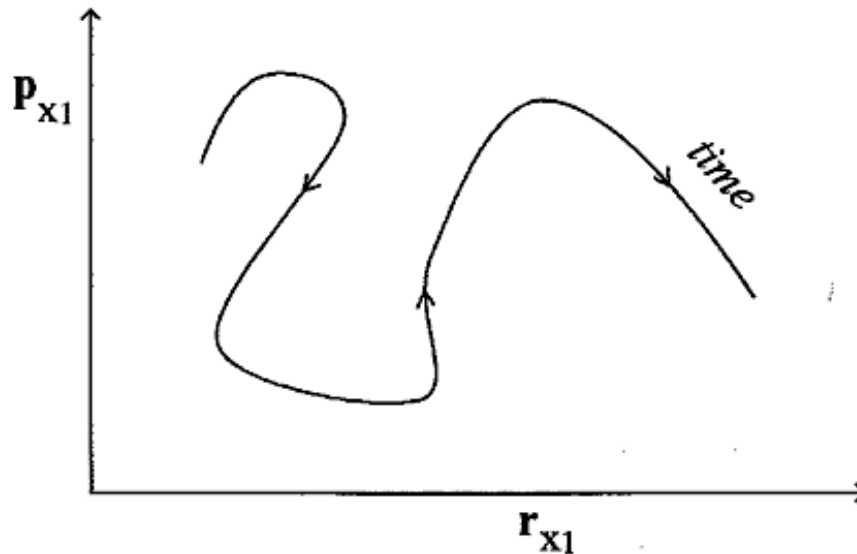
Ensemble average = Time average

$$\langle \mathbf{A} \rangle_{\text{NVT}} = \lim_{t_{\text{sim}} \rightarrow \infty} \frac{1}{t_{\text{sim}}} \int_{t_0}^{t_0 + t_{\text{sim}}} \mathbf{A}(\tau) d\tau$$

Molecular simulations

Molecular simulation provides the way to:

- 1) Calculate time averages of an observable*
- 2) Visit the most important points in the phase space.*



Knowing the phase space and time averages, one knows the macroscopic properties.

Figure 5.1: Motion of a point in a two-dimensional phase space. The diagram only maps the temporal evolution of two coordinates, $r_{x1}(t)$ and $p_{x1}(t)$, out of the $6N$ coordinates, $r_{x1}(t), r_{x2}(t), \dots, r_{xN}(t), p_{x1}(t), p_{x2}(t), \dots, p_{xN}(t)$. The arrows indicate the continuous increase of time.

Equilibrium properties

Nstep	Etotal kJ/mol	Upot kJ/mol	Virial kJ/mol	Temp K
20	-4.8215	-6.0300	2.0563	96.90
40	-4.8216	-5.9691	1.1320	92.01
60	-4.8216	-5.9057	-.0485	86.93
80	-4.8216	-5.9630	.8602	91.52
100	-4.8218	-5.9696	.9501	92.04

Temperature: 92.3979 ± 3.2927 [K]

Potential: $-5.9739 \pm .0409$ [kJ/mol]

Total Energy: $-4.8215 \pm .0017$ [kJ/mol]

Translational Energy: $1.1523 \pm .0411$ [kJ/mol]

Virial: $1.0893 \pm .6904$ [kJ/mol]

Pressure: 143.1503 ± 71.6967 [bar]

Stochastic x Deterministic



Stochastic ←————→ Deterministic



Metropolis
Monte Carlo

Force-biased
Monte Carlo

Brownian
Dynamics

Langevin
Dynamics

Molecular
Dynamics

Molecular Dynamics

3) Dynamics

How to solve the classical equations of motion for all particles in different conditions (Temperature, Pressure and any other thermodynamical parameters) ?.

Solution:

Given by Sir Isaac Newton over 300 years ago !!

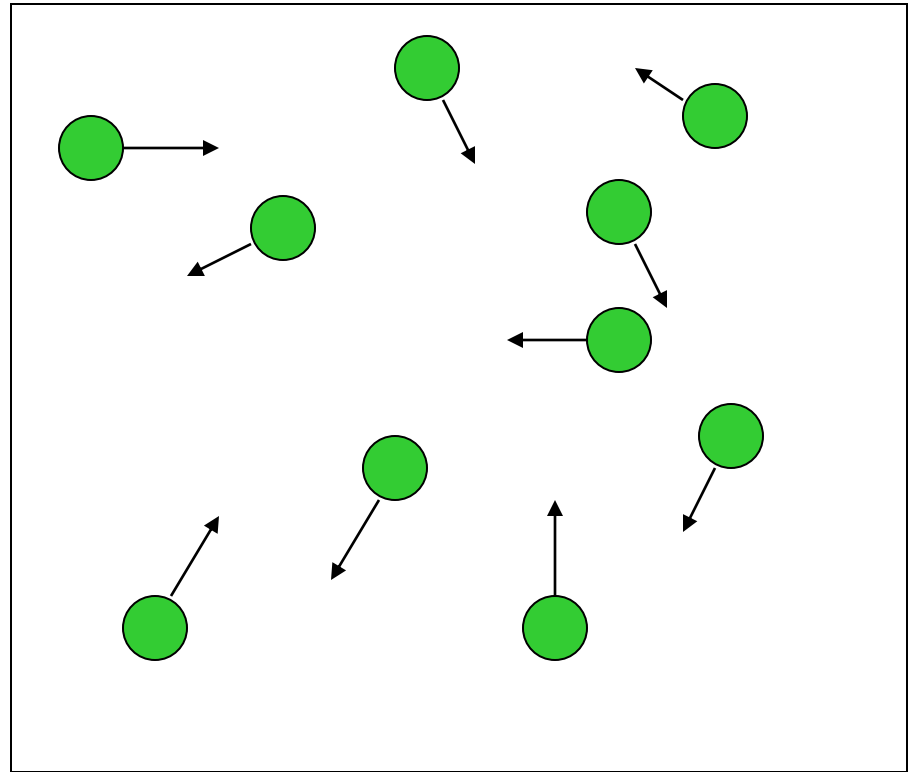
$$m \frac{d^2 \vec{r}_i}{dt^2} = -\nabla_i V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

We have to solve the Newton's motion equation in time for each of the i th particle in the system.

Molecular Dynamics

Newton's equations
of motion

$$m \frac{d^2 \vec{r}_i}{dt^2} = -\nabla_i V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$



Molecular Dynamics

The properties can be obtained by sampling the system at a given ensemble (NPT, NVT, NVE, gran-canonical, ...)

$$\langle \mathbf{A} \rangle_{\text{NVT}} = \int d\Gamma \rho_{\text{NVT}} \mathbf{A}(\Gamma)$$
$$\rho_{\text{NVT}}(\Gamma) = \frac{e^{-\beta \mathcal{H}(\Gamma)}}{Z_{\text{NVT}}}$$

where

$$\left\{ \begin{array}{l} \beta = \frac{1}{k_B T} \\ \mathcal{H} = \mathbf{K} + \mathbf{V} \\ Z_{\text{NVT}} = \int d\Gamma \rho_{\text{NVT}} \end{array} \right.$$

Ergodic Hypothesis

$$\langle \mathbf{A} \rangle_{\text{NVT}} = \lim_{t_{\text{sim}} \rightarrow \infty} \frac{1}{t_{\text{sim}}} \int_{t_0}^{t_0 + t_{\text{sim}}} \mathbf{A}(\tau) d\tau$$

Molecular Dynamics

- **What is molecular dynamics ?**
- Computer simulation technique that allows one to predict the time evolution of a system of interaction particles (atoms, molecules, granules, etc.)
- **Steps:**
 - 1) Set the system of interest:
 - a) Initial conditions
(initial positions and velocities of all particles)
 - b) Interatomic potential
(to describe the forces between the particles)

Schematic diagram of a basic MD code

Define initial positions and velocities $\vec{r}_i(t_0)$ and $\vec{v}_i(t_0)$

Calculate forces at current time t_n :

$$\vec{F}_i = -\vec{\nabla}_i U(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_{N_{at}})$$

Solve equations of motion for all particles in the system over a short timestep Δt .

$$\vec{r}_i(t_n) \rightarrow \vec{r}_i(t_{n+1}) \quad \vec{v}_i(t_n) \rightarrow \vec{v}_i(t_{n+1})$$
$$t_{n+1} = t_n + \Delta t$$

Calculate desired physical quantities, write data to trajectory file

Is $t_{n+1} > t_{\max}$?

Write to the disc final atomic configuration & finish

Piece of the code

Program MolDyn

! This a very simple Molecular Dynamics code
call init

10 call force
call integrator
time = time + dt
call sample
if (time.lt.maxtime) goto 10

stop
end

Building your own code

- **Subroutines**
- **Init**: to initialize the system to be simulated
- **Force**: to calculate the forces
- **Integrator**: to solve numerically the equation of motion
- **Sample**: to analyse and accumulate the trajectory
- **Variables**
- **time** = instant of time of the simulation
- **dt** = time step to solve the equations of motion
- **maxtime** = maximum time wanted

Limitations of the MD technique (I)

- 1) Classical description of interatomic interaction
 - Electrons are not present explicitly
(Potential energy surface)
 - PES is approximated by an analytic function that gives the potential energy U as a function of coordinates.
 - Forces comes from the gradient of a PES.

Limitations of the MD technique (II)

- 2) In classical MD the Schrodinger equation for nuclei is replaced with the Newton equation.

How good is this approximation ?

Quantum effects are significant when the de Broglie wavelength Λ is larger than the inter-particle distance.

$$\lambda_{dB} = \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{1/2}$$

2. Classical description of atomic motion (continued)

For the thermal motion we can use the thermal de Broglie wavelength:

$$\Lambda_{th} = \frac{h}{\sqrt{2\pi m k_B T}}$$

For T = 300 K we have

- $\Lambda_{th} = 1 \text{ \AA}$ for a H atom
- $\Lambda_{th} = 0.19 \text{ \AA}$ for a Si atom
- $\Lambda_{th} = 0.16 \text{ \AA}$ for an Ar atom
- $\Lambda_{th} = 0.07 \text{ \AA}$ for a Au atom

Typical interatomic spacing in solid-state materials is $d \sim 1\text{-}3 \text{ \AA}$. Therefore:

- The wave nature of electron dominates over the particle behavior, electrons can not be considered within classical approximation.
- All atoms, except for the lightest ones such as H, He, Ne, can be considered as “point” particles at sufficiently high temperature ($d \gg \Lambda$) and classical mechanics can be used to describe their motion.

Interatomic interactions

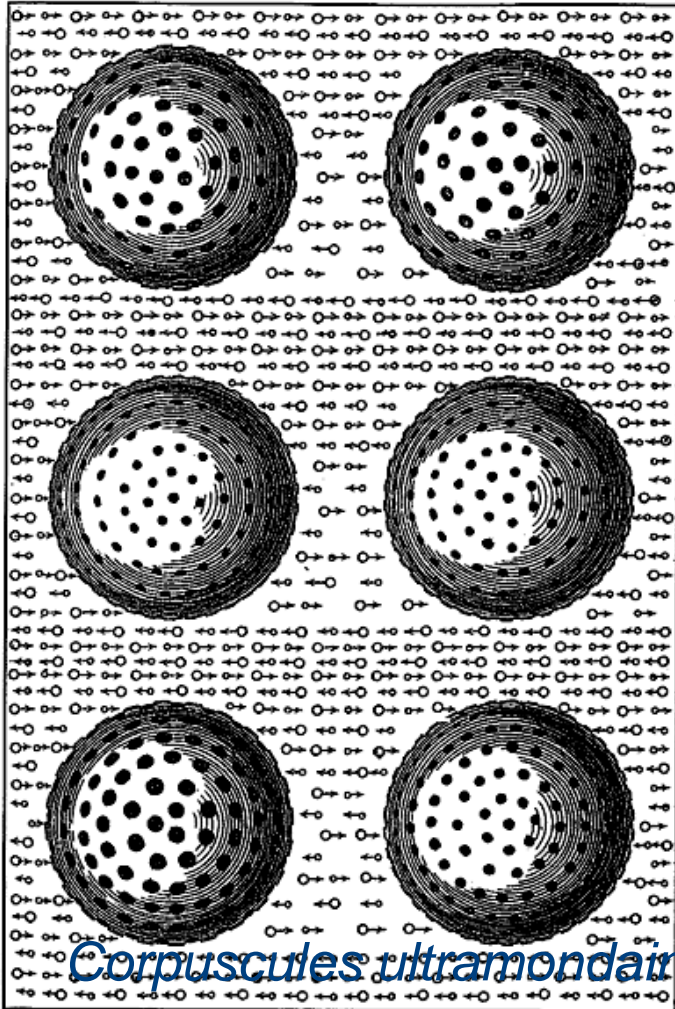
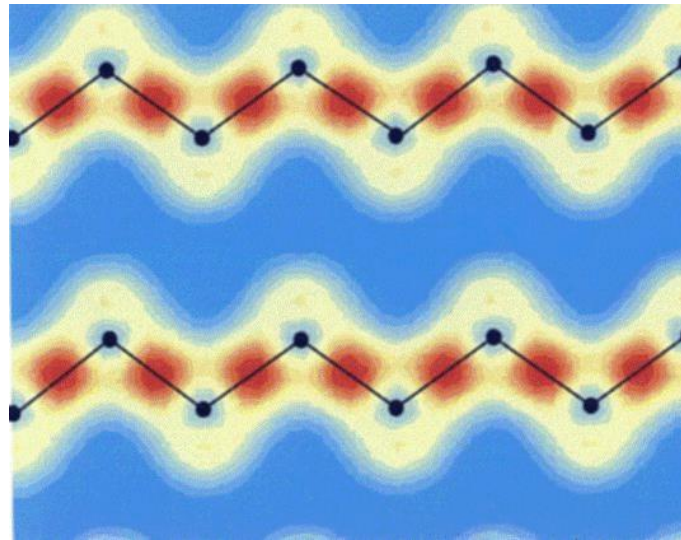
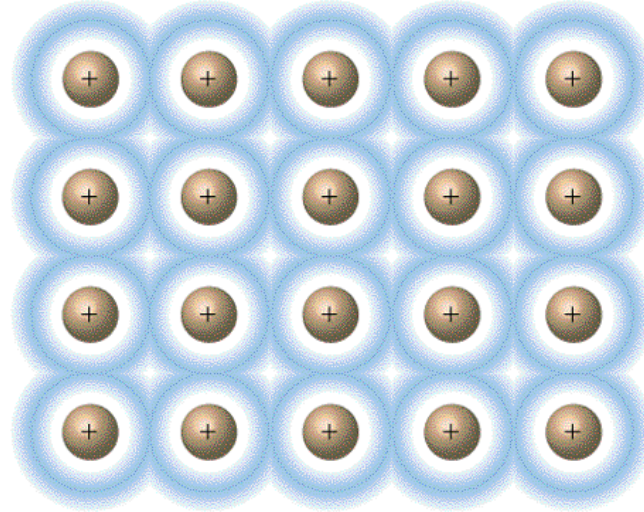
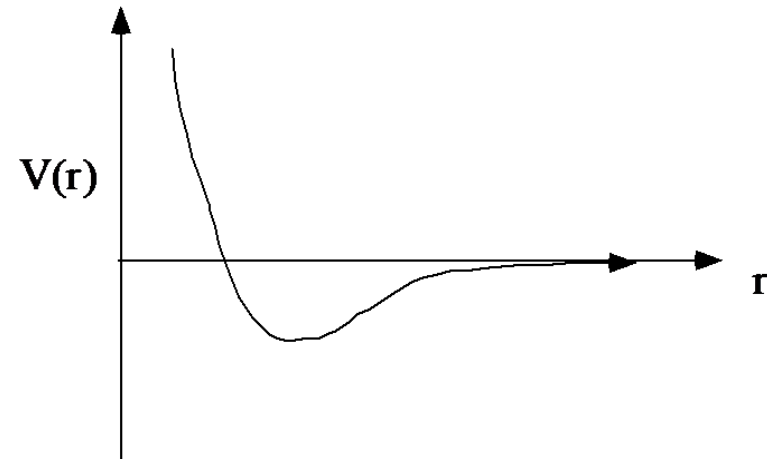
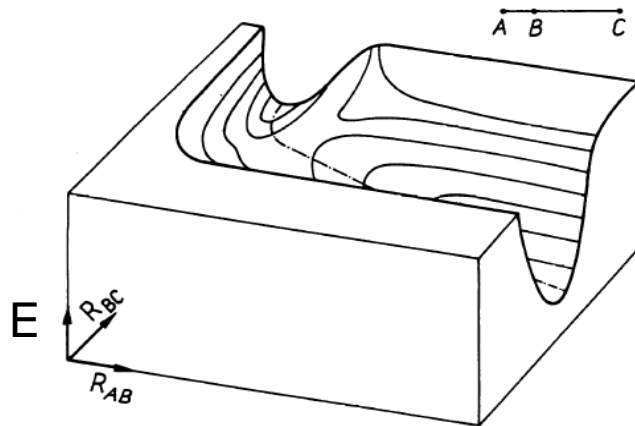
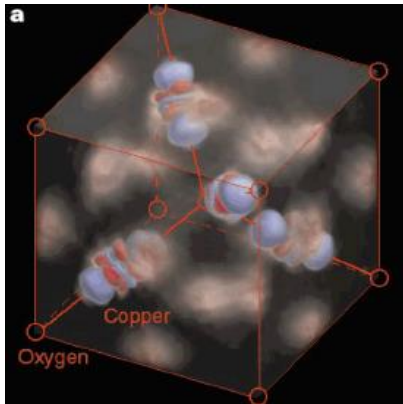


Fig. 2.2 Le Sage's picture of attraction between particles of matter [249].



What does atomistic modeling involve?

- Atomic scale modelling of materials (interaction between atoms)
- **ENERGY** can be calculated by:
 - *quantum mechanical* calculation of energy as a function of structure.
 - *effective potentials* (analytical functions of the energy as a function of geometry which can be “parameterized” using experimental or quantum mechanics data
Lennard-Jones, Morse, etc. (**physicists**), embedded-atom method, etc. (**materials scientists**), force fields (**chemists**), reactive potentials,...



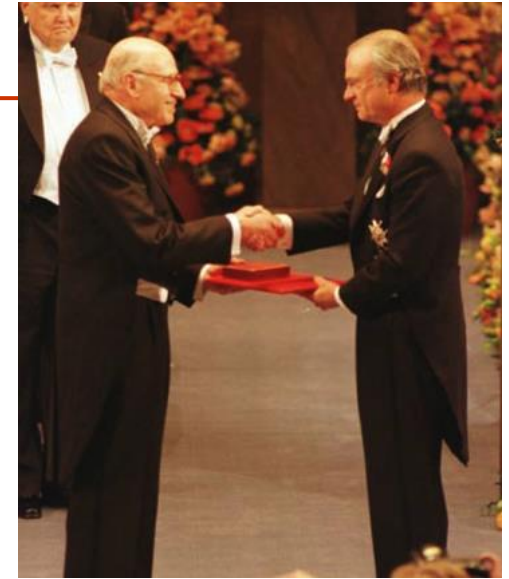
First principles calculations

Numerically solving Schrodinger's equation:

Density Functional Theory (DFT)

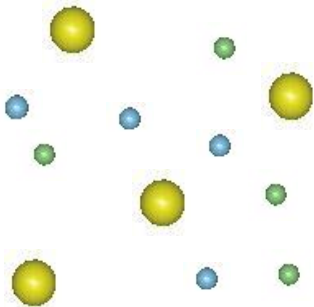
Pseudopotentials

Quantum-Espresso, SIESTA, VASP and Gaussian



Kohn - Nobel Prize 99

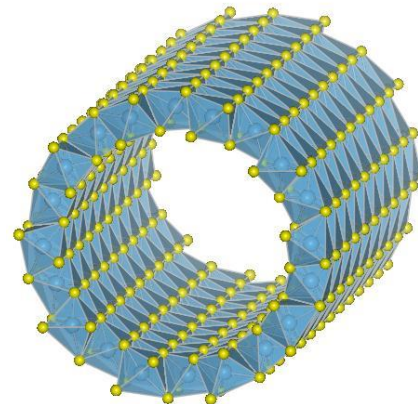
Composition



$$Hy = Ey$$



Structures



Properties

Thermodynamics

Lattice Parameters

Elastic constants

Electronic Structure

Kinetics

Tailoring interatomic potentials

- Strategy**
- Assumption: DFT accuracy is OK
 - Effective potential fitted to DFT
 - Improve functional form for effective potential

- Goal**
- Construct effective potential with “DFT accuracy”
 - More accurate and less computationally expensive

EDIP (Environment Dependent Interatomic Potential) (Justo et al. - PRB 97)

Tangney-Scandolo Potential (MgO and SiO₂) (Tangney & Scandolo JCP 03)

Potentials Guest-Frameworks (Miranda & Scandolo)

Potentials for nanostructure systems (Miranda & Ceder)

Luke, use the mass times
acceleration! or the Hellmann
- Feynman theorem



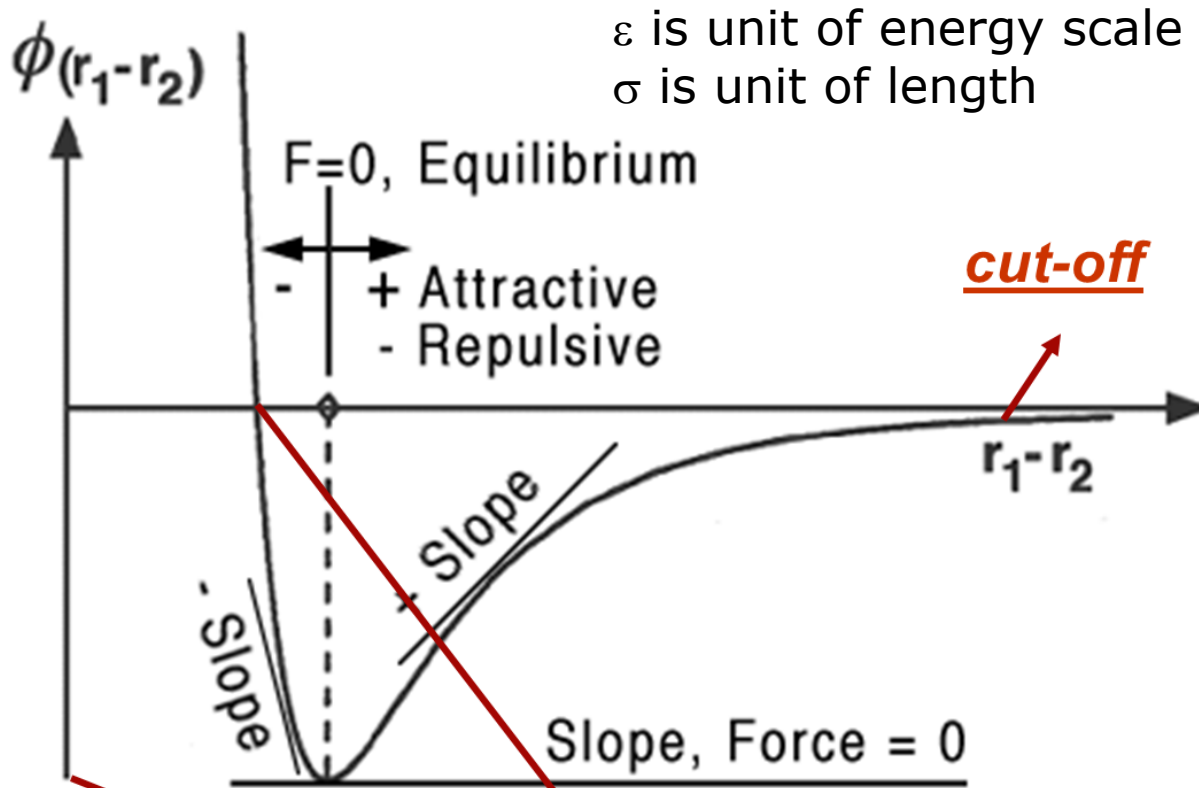
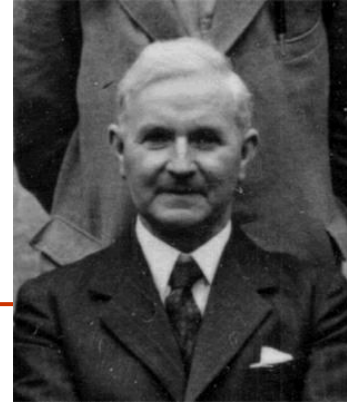
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Lennard-Jones:

A simple two-parameter form



When expressing Temperature, Pressure and Density in renormalized units all LJ systems are identical

$$\text{Temperature: } \frac{\varepsilon}{k_B}$$

$$\text{Pressure: } \frac{\varepsilon}{\sigma^3}$$

$$\text{Density: } \frac{1}{\sigma^3}$$

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

Part 2 - Forces

```
subroutine force
do 10 i = 1,N-1
  do 20 j = i+1,N
    xij = x(i) - x(j)
    r2 = xij**2 + yij**2 + zij**2
    if (r2.gt.cutoff) goto 20
    urep = sigma**12/r2**6
    uatt = sigma**6/r2**3
    uij = 4.*epsilon*(urep - uatt)
    wij = -24.*epsilon*(2.*urep - uatt)
    upot = upot + uij
    virial = virial + uij
    f(i) = f(i) - xij*wij/r2
    f(j) = f(j) + xij*wij/r2
20  continue
10  continue
return
end
```

Lennard-Jones potential

- The L-J potential is approximate. The form of the repulsion term has no theoretical justification;
- The repulsion force should depend **EXPONENTIALLY** on the distance,
- But the repulsion term of the L-J formula is more convenient due to the ease and efficiency of computing r^{12} as the square of r^6 .
- The attractive long-range potential, however, is derived from **DISPERSION** interactions (London).

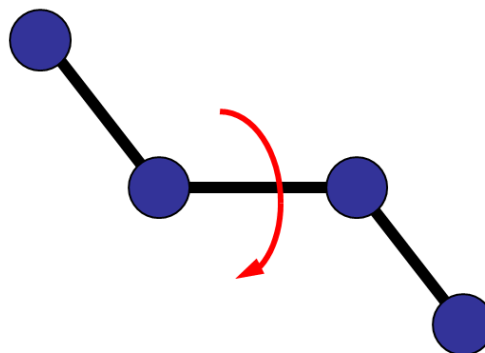
Potentials for complex molecules

Potential Energy

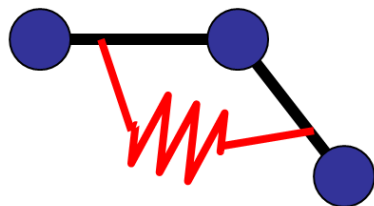
Empirical Force Field (e.g., CHARMM, OPLS, Amber, (MMFF))



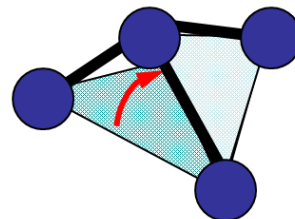
Bond



Dihedral



Angle



Improper
dihedral

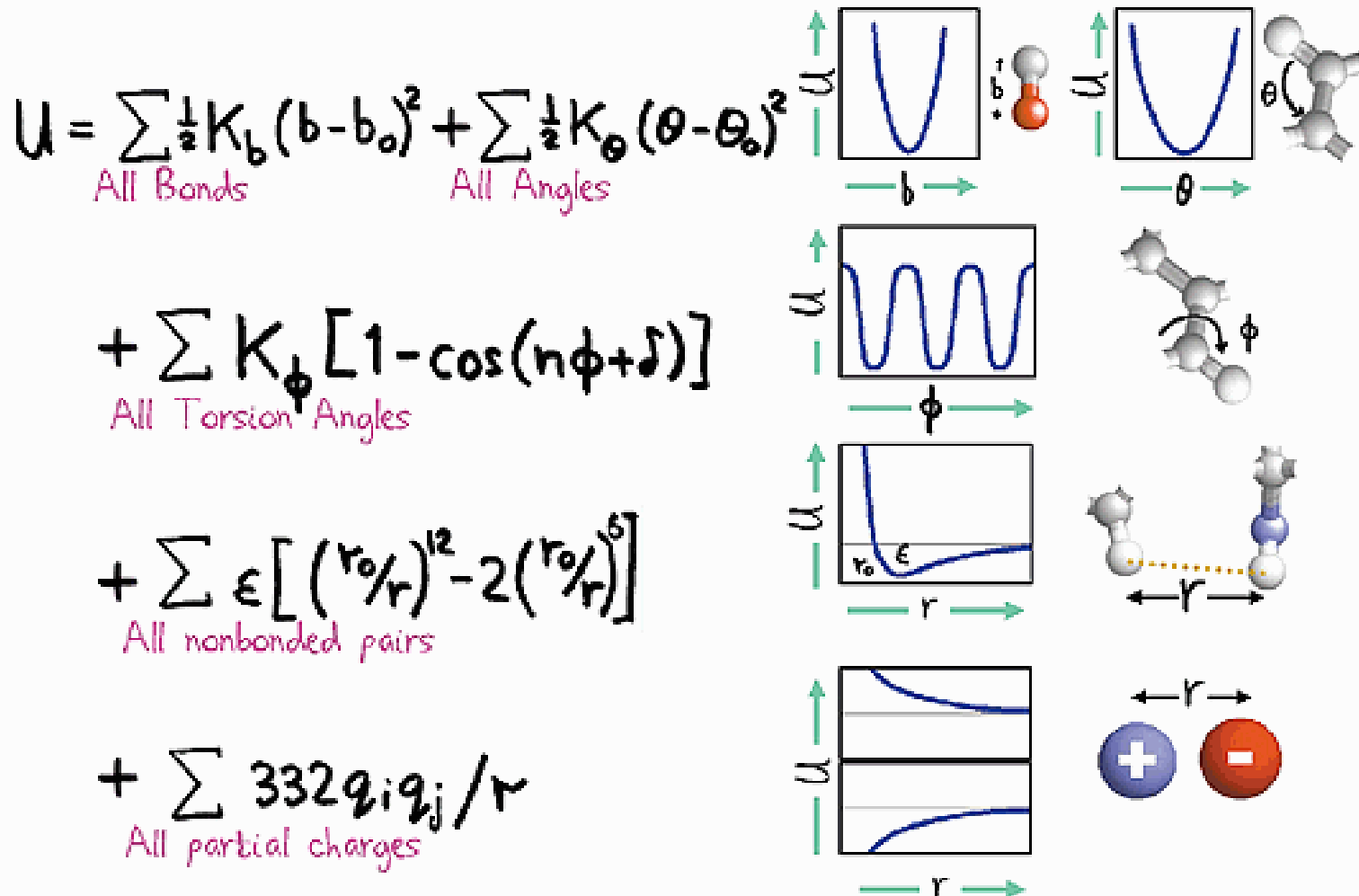


VDW

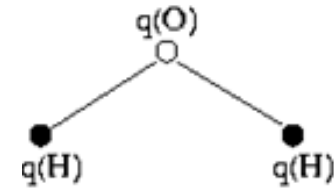
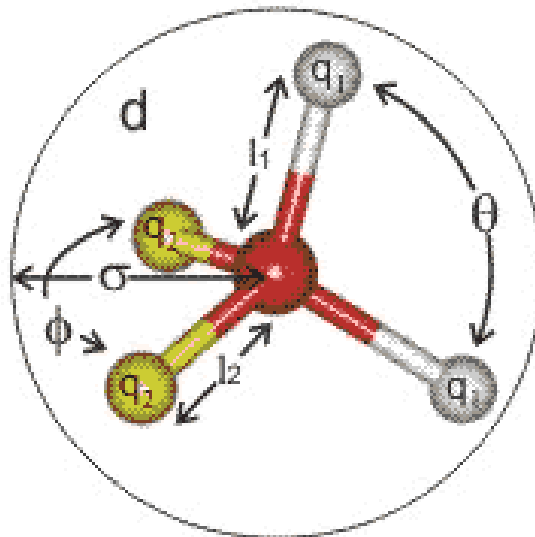
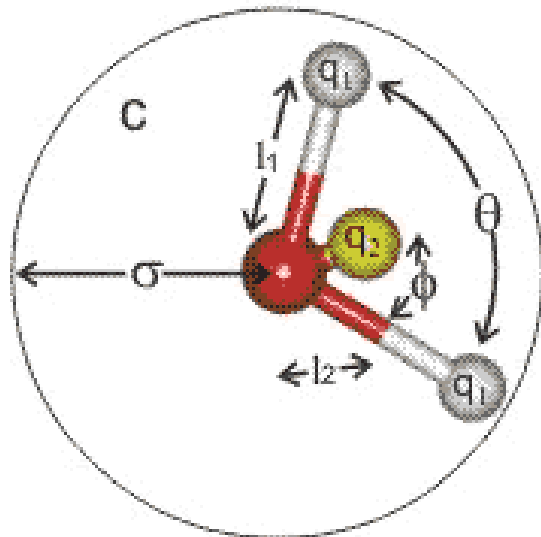
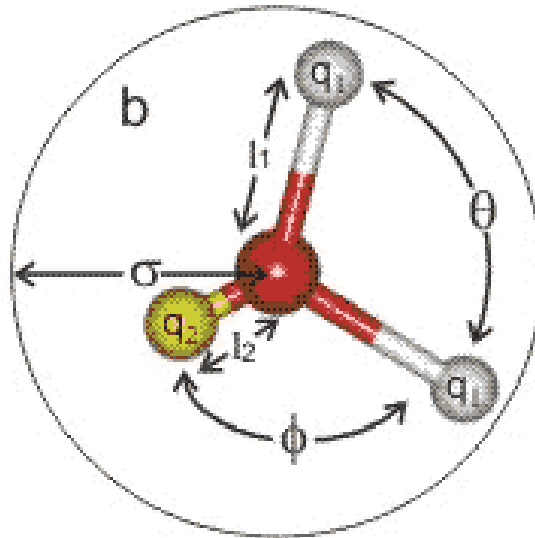
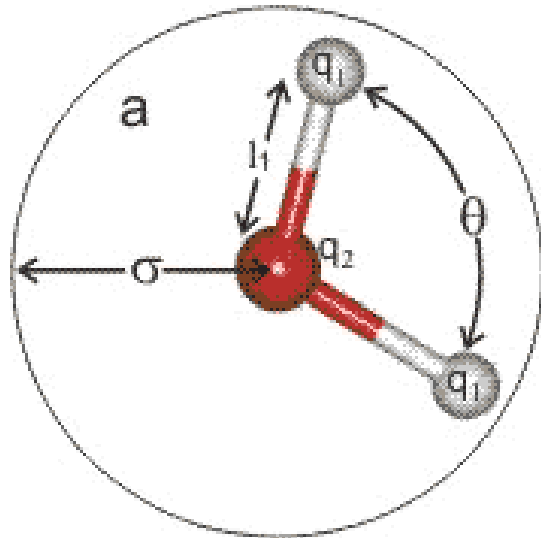
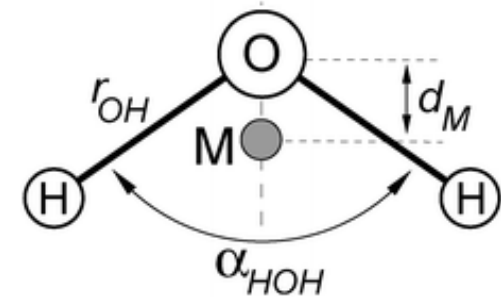


Coulombic

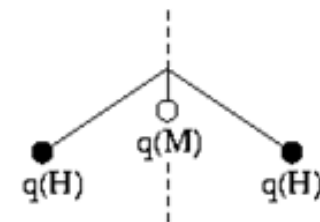
Potentials for complex molecules



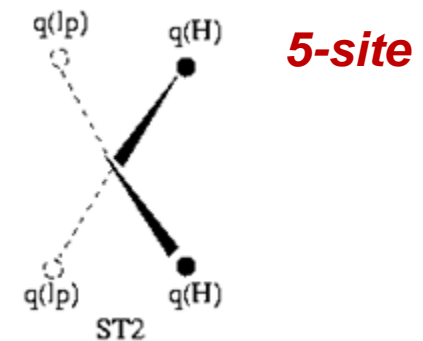
Potentials for “simple” molecules but complex systems



SPC, SPC/E, TIP3P



TIP4P, BF



ST2

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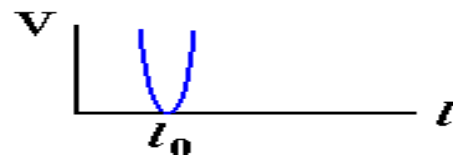
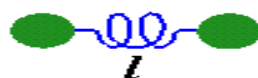
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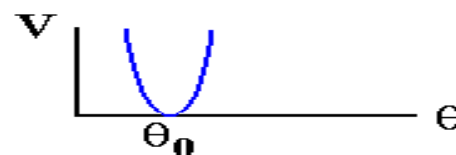
Potentials for complex molecules

Empirical Potential Energy Function

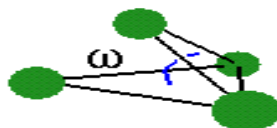
Bonds



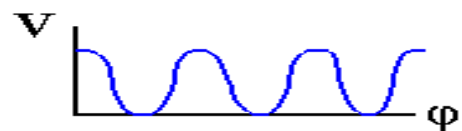
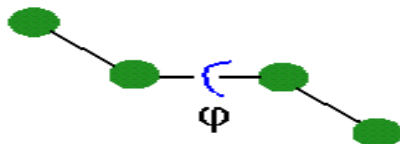
Angles



Improper
Dihedrals



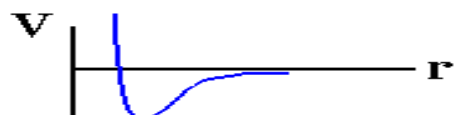
Torsions



Electrostatics



van der Waals



Tailoring interatomic potentials

- Strategy
- Assumption: DFT accuracy is OK
 - Effective potential fitted to DFT
 - Improve functional form for effective potential

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Schematic diagram of a basic MD code

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Calculate forces at current time t_n :

$$\vec{F}_i = -\vec{\nabla}_i U(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_{N_{at}})$$

Solve equations of motion for all particles in the system over a short timestep Δt .

$$\vec{r}_i(t_n) \rightarrow \vec{r}_i(t_{n+1}) \quad \vec{v}_i(t_n) \rightarrow \vec{v}_i(t_{n+1})$$
$$t_{n+1} = t_n + \Delta t$$

Calculate desired physical quantities, write data to trajectory file

Is $t_{n+1} > t_{\max}$?

Write to the disc final atomic configuration & finish