Introduction to model potential Molecular Dynamics

A 3hour course at ICTP

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Outline

Model potential molecular dynamics... as simple as possible

1. how to calculate forces...
2. how to numerically calculate trajectories...
3. from time evolution to thermodynamics (optimizations and equilibrium calculations)

Definitions (I)

The dynamics is the study of the time evolution of a system $x(t)$ as a result of the forces acting on it.

Molecular Dynamics

Molecular dynamics (MD) is the computer simulation of the physical movements of molecules and atoms of a system under study.

Definitions II

The molecular constituents are treated classically when the De Broglie length λ is smaller than the interatomic distances (i.e. $\sqrt{2mk_BT}/\hbar >> (N/V)^{\frac{1}{3}}$, where T is the temperature N/V the density).

For **classical particles** the **Newton equations** of motion can be used to calculate the molecular trajectories $x(t)$:

$$m\ddot{x}(t) = F(x)$$

Definitions (II)

Molecular:
refers to atomic constituents: $x(t)$ is the molecular or atomic trajectory (i.e. position as a function of time)

potential:
refers to the fact that atomic forces $F(x)$ are obtained by interatomic potential that are functions of the atomic positions $U(x)$

model:
refers to the fact that the interatomic potential is and “effective” potential calibrated on suitable set of physical properties of the system rather than obtained from first-principles

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Potential

For an isolated (non dissipative) system the interatomic forces only depends on the particle position $F(x)$ and are conservative (i.e. the work do not depend on the path) so derivable from an interatomic potential $U(x)$

$$F = -\nabla U(x)$$

First-principles molecular dynamics: Forces explicitly taking into account electrons (for example, within DFT methods) (Newton's equation are still used fot the motion of the molecular constituents)
Model potential molecular dynamics: Forces are derived $F = -\nabla U(x)$ by an analytic potential $U(x;\alpha)$ depending on empirical parameters α that are calibrated on experiments or on first-principles calculations.

Interatomic potential: General requirements

What requirements should be satisfied by an interatomic potential (internal forces):

- not explicitly dependent on time $U(x_1, x_2, ...)$
- translational invariant (only depending on pair vectors) $U(x_1 - x_2, x_1 - x_3, \ldots, x_i - x_j)$
- rotational invariant (only dependent on scalar products and tensors)

$$U(x_{ij}) = F(\vec{x}_{ij} \cdot \vec{x}_{ij}, \vec{x}_{ij} \cdot \vec{x}_{kl}, \vec{x}_{ij} \cdot \vec{x}_{kl} \times \vec{x}_{pq})$$

- sum of two-body, N-body term

$$U = U(0) + \sum \frac{\partial U}{\partial x_{ij}}(0) x_{ij} + \frac{1}{2} \sum \frac{\partial^2 U(0)}{\partial x_{ij} \partial x_{kl}} x_{ij} x_{jk}$$

$$U = U(0) + \sum U(x_{ij}, x_{jk}) ...$$

Interatomic potential: General requirements

sum of two-body, N-body term

$$U = \frac{1}{2}\sum \frac{\partial^2 U(0)}{\partial x_{ij}\partial x_{kl}} x_{ij}x_{jk} + ...$$

$$U = \sum U_2(x_{ij}^2) + \sum U_3(x_{ij}, x_{ik}) + ...$$

Lennard-Jones potential

Two-body potential 12-6

$$U(\vec{x}_1, ..., \vec{x_N}) = \sum_{ij} U_2^{LJ}(r_{ij})$$

where

$$U_2^{LJ}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^p - \left(\frac{\sigma}{r_{ij}} \right)^q \right]$$

$p = 12$ and $q = 6$ in the 12-6 Lennard-Jones potential.
The minimum energy is found at $r_{ij}^0 = \sigma(2^{\frac{1}{6}}) = 1.122\sigma$;
ϵ is a measure of the cohesive energy since $U(r^0) = -\epsilon$;
The lengths σ is such that $U_2^{LJ}(\sigma) = 0$

Forces are calculated by deriving the potential.

Lennard-Jones

We define $x_{ij} = x_i - x_j$, and the modulus $r_{ij} = |\vec{x_i} - \vec{x_j}|$ so that the forces can be calculated:

$$F_i = -\frac{dU}{d\vec{x_i}} = -\frac{\partial U(r_{ij})}{\partial r_{ij}} \cdot \frac{dr_{ij}}{d\vec{x_i}}$$

$$\frac{\partial U(r_{ij})}{\partial r_{ij}} = 4\epsilon \left[-\frac{12}{r_{ij}} \left(\frac{\sigma}{r_{ij}} \right)^p + \frac{6}{r_{ij}} \left(\frac{\sigma}{r_{ij}} \right)^q \right]$$

$$= 4\epsilon \left[-\frac{p}{\rho^{p+1}} + \frac{q}{\rho^{q+1}} \right] \frac{1}{\sigma}$$

where $\rho = r_{ij}/\sigma$
Furthermore,

$$\frac{\partial r_{ij}}{\partial \vec{x_i}} = \frac{\vec{x}_{ij}}{r_{ij}} = \frac{x_i - x_j}{r_{ij}}$$

Lennard-Jones forces

Once the derivation of the single two-body component has been performed that it is possible to consider the overall potential:

$$U(r_{ij}, r_{ik}) = \sum_{i<j} U(r_{ij})$$

So when deriving it is obtained that

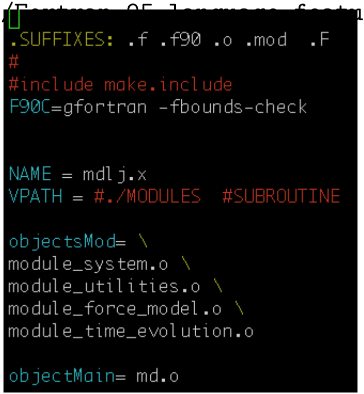
$$\frac{d}{d\vec{x}_k} U = \sum_{i<j} \frac{dU(r_{ij})}{d\vec{x}_k} = \sum_{i<j} \left[\delta_{ik} \frac{dU(r_{ij})}{d\vec{x}_k} + \delta_{jk} \frac{dU(r_{ij})}{d\vec{x}_k} \right] =$$

$$\sum_{i<j} \left[\delta_{ik} \frac{dU(r_{ij})}{d\vec{x}_i} - \delta_{jk} \frac{dU(r_{ij})}{d\vec{x}_i} \right]$$

So the general idea is that we loop over the atoms in orde to construct the potential and we distribute the forces

Fortran 95

- language is the **Fortran 95** (http://en.wikipedia.org/wiki/Fortran_95_language_features
- tested by gfortran compiler (version GCC 4.6.0) (GCC is the GNU compiler collection)
- For fortran beginners learn by trying program **first.f90**
- **Modules** are also briefly reviewed
- A simple makefile is described



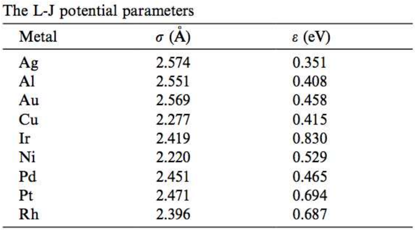
```
.SUFFIXES: .f .f90 .o .mod  .F
#
#include make.include
F90C=gfortran -fbounds-check


NAME = mdlj.x
VPATH = #./MODULES  #SUBROUTINE

objectsMod= \
module_system.o \
module_utilities.o \
module_force_model.o \
module_time_evolution.o

objectMain= md.o
```

Figure: Makefile

Exercise on force model

Exercise 1: Use the codo.0 to calculate the forces for a dimer of Pt atoms

- step0



The L-J potential parameters

Metal	σ (Å)	ε (eV)
Ag	2.574	0.351
Al	2.551	0.408
Au	2.569	0.458
Cu	2.277	0.415
Ir	2.419	0.830
Ni	2.220	0.529
Pd	2.451	0.465
Pt	2.471	0.694
Rh	2.396	0.687

Figure: Parameters taken from P. M. Agrawal, Surface Science 515 (2002) 21–35

Time evolution (trajectories)

Analytical trajectory for one particle 1D problem.

$$t = \int_0^{x(t)} \frac{dx}{\sqrt{2m(E - 4\epsilon\left[\left(\frac{\sigma}{x}\right)^{12} - \left(\frac{\sigma}{x}\right)^{6}\right])}}$$

The simplest approach is to discretize the first and the second derivative

$$\dot{x}(t) = \frac{x(t+dt)-x(t)}{dt}$$

$$\ddot{x}(t) = \frac{\frac{x(t+dt)-x(t)}{dt} - \frac{x(t)-x(t-dt)}{dt}}{dt} = \frac{x(t+dt)-2x(t)+x(t-dt)}{dt^2}$$

and to impose the Newton equation law on acceleration

$$m\ddot{x} = F(x)$$

.

Time evolution (II)

It is easily obtained an expression that make possible to evolve positions from the knowledge of accelerations

$$x(t+dt) = 2x(t) - x(t-dt) + dt^2\, F(x(t))/m$$

The trajectories can be calculated (error dt^4) without the need of velocities; these latter are calculated apart

$$v(t) = \frac{x(t+dt)-x(t-dt)}{dt}$$

The overall algorithm was adopted by Verlet(1967).

Time evolution (II)

By using Taylor expansion, and relation $a = F/m$

$$x(t + dt) = x(t) + dt\, v(t) + dt^2\, F(x(t))/m$$

$$v(t) = v(t) + dt\, F(x(t))/m)$$

Time evolution (III)

Integrate equations of motion

Velocity-Verlet algorithm

VV algorithm is probably the most attractive proposed to date because of its numerically stability, convenience and simplicity:

$$x(t+dt) = x(t) + v(t)dt + \frac{1}{2}dt^2 F(x(t))/m$$

$$v(t+dt) = v(t) + \frac{1}{2}dt\,[F(x(t))/m + F(x(t+dt)/m)]$$

Time evolution (IV)

Integrate equations of motion

Velocity-Verlet algorithm

VV algorithm is probably the most attractive proposed to date because of its numerically stability, convenience and simplicity:

$$v(t+\tfrac{dt}{2}) = v(t) + \tfrac{1}{2} dt\, F(x(t))/m$$

$$x(t+dt) = x(t) + dt\, v(t+\tfrac{dt}{2})$$

$$v(t+dt) = v(t+\tfrac{dt}{2}) + \tfrac{1}{2} dt\, F(x(t+dt)/m)$$

First order formulation

The Newton equation of motion $\ddot{x}(t) = F(x)$ is equivalent to:

$$\begin{cases} \dot{x} = p/m \\ \dot{p} = F(x) \end{cases}$$

By naming $\Gamma(t) = (x, p)$ the point of the phase space representing the system, its time evolution can be written as

$$\dot{\Gamma} = iL\Gamma$$

where

$$iL = \dot{x}\frac{\partial}{\partial x} + \dot{p}\frac{\partial}{\partial p}$$

The solution is formally obtained by applying the exponential operator $e^{i\Gamma t}$ to the point at initial time

$$\Gamma(t) = e^{iLt}\Gamma(0)$$

Time propagation

The Trotter-Suzuki decomposition makes possible to approximate the exponential operator:

$$e^{A+B} = \lim_{n\to\infty}(e^{\frac{A}{n}}e^{B}e^{\frac{A}{n}})^n \sim e^{\frac{A}{2}}e^{B}e^{\frac{A}{2}}$$

It can be applied to the Liouville operator

$$e^{iLdt} = e^{dt\,\dot{x}\frac{\partial}{\partial x}+dt\,\dot{p}\frac{\partial}{\partial p}} = e^{dt\dot{x}\frac{\partial}{\partial x}+dtF(x)\frac{\partial}{\partial p}} \sim e^{\frac{dt}{2}\,F(x)\frac{\partial}{\partial p}}e^{dt\,\dot{x}\frac{\partial}{\partial x}}e^{\frac{dt}{2}\,F(x)\frac{\partial}{\partial p}}$$

The action of the exponential of the derivative can be calculated

$$e^{\alpha\frac{\partial}{\partial x}}f(x,p) = f(x+\alpha,p)$$

and the Velocity Verlet in the simpletic form is obtained; for integrating thermostat and barostat a further action can be usefule$e^{\alpha x\frac{\partial}{\partial x}}f(x,p) = f(xe^{\alpha},p)$

Choice of the timestep

The timestep of molecular dynamics must be smaller than the timescale of the the molecular phenomena. A simple estimate is obtained by considering that $[t] = \left[EM^{-1}L^{-2}\right]$ where the energies of interatomic interactions are of the order of $eV = 1.6 \cdot 10^{-19}J$, atomic masses are $10^{-3}/N_{Avogadro} = 1/6.02 \cdot 10^{-26}Kg$ and distances ∼ Å.

$$[t] \sim 1.014 \cdot 10^{-14} \sim 10\ fs$$

		S.I
$[E]$	$1eV/atom$	$1.602 \cdot 10^{-19}J$
$[M]$	$1a.m.u$	$1.66{\times}10^{-27}Kg$
$[L]$	1	$10^{-10}m$
$[T]$	$1 \cdot 10^{-14}s$	

		S.I
$[E]$	$kcal/mol$	$4.18kJ/mol$
$[M]$	$1a.m.u$	$1.66{\times}10^{-27}Kg$
$[L]$	1	$10^{-10}m$
$[T]$	$1 \cdot 10^{-14}s$	

Exercise

Exercise dynamics

Implement the Velocity Verlet algorithm see step1-step2

Damping and optimization

*Damping*is a physical effect that reduces the amplitude of oscillations in an oscillatory system. During damping the system moves towards the minimum (*minimizing optimizing relaxing*). Within molecular dynamics there are two simple methods for damp

Zero-velocity dynamics

Set all the velocities to zero at each step.

$$v = 0 \quad \mathit{always}$$

The system evolves “slowly” untill the forces are zero (minimum); the system goes towards the minimum but it cannot accelerate.

Damped dynamics:

Set the velocities to zero if moving against the the force

$$v(\alpha, i) = 0 \;\; \mathit{if} \quad F(\alpha, i) \cdot \mathit{vel}(\alpha, i) < 0$$

The system evolves untill the forces are zero; the system is allowed to accelerate when moving towards the minimum.

Exercise

Exercise damping 3

Implement zero velocity method for dissipating kinetic energy and reach the minimum energy configuration; use the damped dynamics method

Exercise

putting atoms at random positions

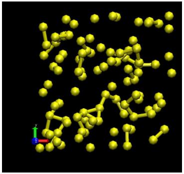


Figure: initial random positions

cluster of Pt atoms obtained by damping or by dynamics

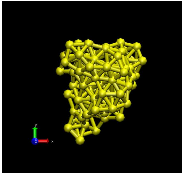


Figure: relaxed structure

Computational workload

Calculate the workload as a function of the number of particles of the system

$$T \sim \alpha N^2$$

The N^2 scaling si associated to double loops over atoms

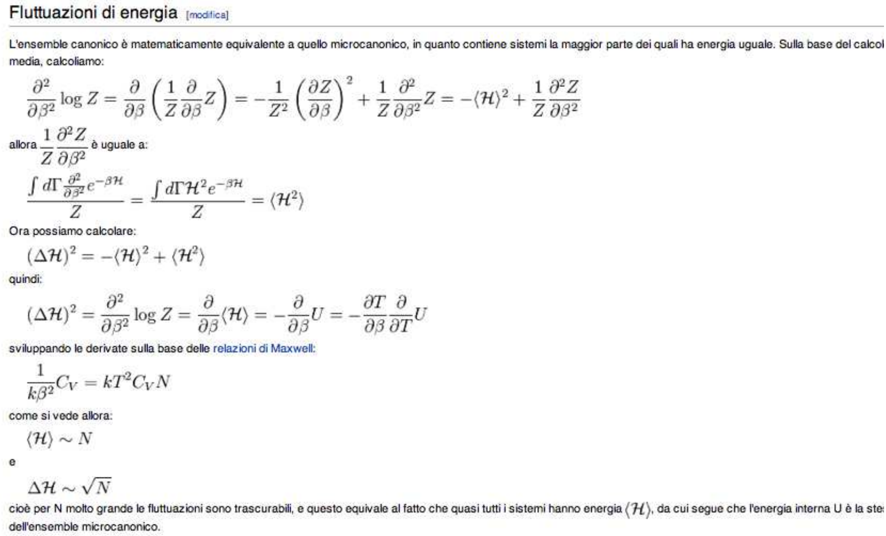
$$\Sigma_{i=1,num\_atoms} dr_{ij} = pos(:,i) - pos(:,j)$$

Verlet list method consists in store the list of neighboring atoms instead of calculating at each step. In order to do this it is necessary to store the list of atoms in sphere larger than the physical cutoff $R_V \sim 1.1 cutoff$ and to reduce the num

$$T \sim \frac{1}{\Delta t_V} N^2 + (\Delta T_V - 1)(N_V - N_{neigh}) \sim \frac{\alpha}{T}$$

Fluctuations

Fluctuations



Fluttuazioni di energia [modifica]

L'ensemble canonico è matematicamente equivalente a quello microcanonico, in quanto contiene sistemi la maggior parte dei quali ha energia uguale. Sulla base del calcol media, calcoliamo:

$$\frac{\partial^2}{\partial\beta^2}\log Z = \frac{\partial}{\partial\beta}\left(\frac{1}{Z}\frac{\partial}{\partial\beta}Z\right) = -\frac{1}{Z^2}\left(\frac{\partial Z}{\partial\beta}\right)^2 + \frac{1}{Z}\frac{\partial^2}{\partial\beta^2}Z = -\langle\mathcal{H}\rangle^2 + \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2}$$

allora $\frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2}$ è uguale a:

$$\frac{\int d\Gamma \frac{\partial^2}{\partial\beta^2} e^{-\beta\mathcal{H}}}{Z} = \frac{\int d\Gamma \mathcal{H}^2 e^{-\beta\mathcal{H}}}{Z} = \langle\mathcal{H}^2\rangle$$

Ora possiamo calcolare:

$$(\Delta\mathcal{H})^2 = -\langle\mathcal{H}\rangle^2 + \langle\mathcal{H}^2\rangle$$

quindi:

$$(\Delta\mathcal{H})^2 = \frac{\partial^2}{\partial\beta^2}\log Z = \frac{\partial}{\partial\beta}\langle\mathcal{H}\rangle = -\frac{\partial}{\partial\beta}U = -\frac{\partial T}{\partial\beta}\frac{\partial}{\partial T}U$$

sviluppando le derivate sulla base delle relazioni di Maxwell:

$$\frac{1}{k\beta^2}C_V = kT^2 C_V N$$

come si vede allora:

$$\langle\mathcal{H}\rangle \sim N$$

e

$$\Delta\mathcal{H} \sim \sqrt{N}$$

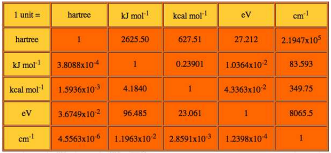
cioè per N molto grande le fluttuazioni sono trascurabili, e questo equivale al fatto che quasi tutti i sistemi hanno energia $\langle\mathcal{H}\rangle$, da cui segue che l'energia interna U è la ste dell'ensemble microcanonico.

Short-range interactions and truncation

Let us consider an homogenerous system where the density is constant everywhere $\rho = \frac{dn}{dV}$. If the particle-particle forces (potential) go to zero faster than $F \sim r^{-3}$ $(U \sim r^{-2})$, than the total sum on a particle falls to zero as r increases. In this case $F_{ij}(r) \sim \frac{1}{r^{3+\delta}}$ $(U_{ij} \sim \frac{1}{r^{2+\delta}})$ and the total force acting on a particle i is

$$|F_i| < \sum_{r_{ij}<R} |F_{ij}| \sim \int_0^R dr' r'^2 F(r') \sim R^{-\delta}$$

that tends to zero when $\delta > 0$. This is the case of Van der Waals interactions $U_{VdW} \sim r^{-6}$ (as well as Buckingham potential, Morse and many others). This is not the case of charge-charge $U \sim r^{-1}$ and charge-dipole $U \sim r^{-2}$ Coulombic interactions.



1 unit =	hartree	kJ mol^{-1}	kcal mol^{-1}	eV	cm^{-1}
hartree	1	2625.50	627.51	27.212	2.1947×10^{5}
kJ mol^{-1}	3.8088×10^{-4}	1	0.23901	1.0364×10^{-2}	83.593
kcal mol^{-1}	1.5936×10^{-3}	4.1840	1	4.3363×10^{-2}	349.75
eV	3.6749×10^{-2}	96.485	23.061	1	8065.5
cm^{-1}	4.5563×10^{-6}	1.1963×10^{-2}	2.8591×10^{-3}	1.2398×10^{-4}	1

Figure: