Molecular Dynamics
Preliminaries

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A Brief History of MD

✓1957, 59 **Alder-Wainwright,** introduction of basic MD

- Of hard sphere particles.

✓1964 **Rahman**, study of liquid Ar (NVE-MD)

- First quantitative study reported.

✓1980, 81 **Andersen, Parrinello-Rahman**

- Constant Pressure (NPT) MD.

✓1984, 86 **Nose, Hoover**

- Constant Temperature (NVT) MD.

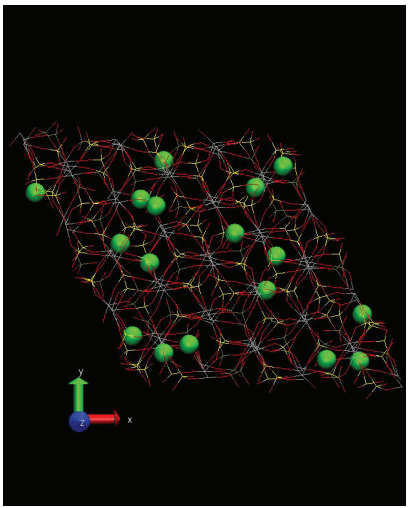
✓1985 **Car-Parrinello**, *ab initio* MD

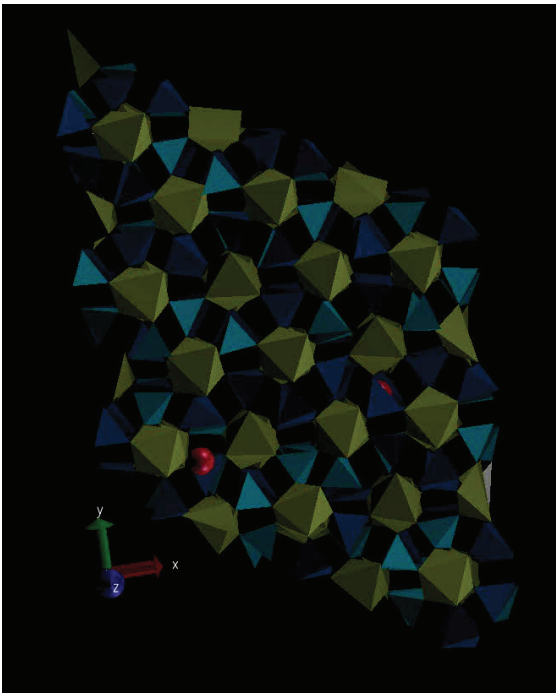
- Based on Density Functional Theory (1960s)
  - **Hohenbrg-Sham**
  - **Kohn-Sham**

A movie

System:

$Na_3Zr_2Si_2PO_{12}$





Two excellent Books

Computer Simulation of Liquids

M. P. ALLEN
H. H. Wills Physics Laboratory
University of Bristol

and

D. J. TILDESLEY
Department of Chemistry
The University, Southampton

Understanding Molecular Simulation

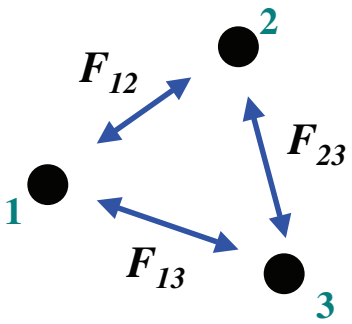
From Algorithms to Applications

Daan Frenkel
FOM Institute for Atomic and Molecular Physics,
Amsterdam, The Netherlands

Department of Chemical Engineering,
Faculty of Sciences
University of Amsterdam
Amsterdam, The Netherlands

Berend Smit
Department of Chemical Engineering
Faculty of Sciences
University of Amsterdam
Amsterdam, The Netherlands

Three Atoms



$$F_i = \sum_{j \neq i} F_{ij}$$

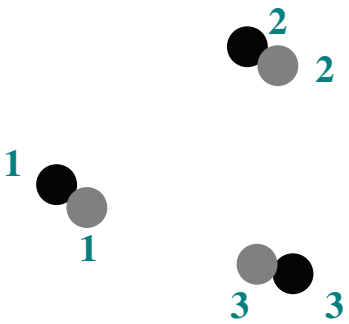
$$F_1 = F_{12} + F_{13}$$

$$F_2 = F_{21} + F_{23}$$

$$F_3 = F_{31} + F_{32}$$

Newton's IInd Law: $a_i = F_i / m_i$

As Time Progress…



$x(t) \rightarrow x(t+\Delta t)$

$y(t) \rightarrow y(t+\Delta t)$

$z(t) \rightarrow z(t+\Delta t)$

Δt ~ 1-5 fs (10^{-15}sec)

Taylor Expansion:

$$v(t+\Delta t) = v(t) + \Delta t \frac{f(t)}{m}$$

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2$$

too crude to use it as such!!

A good Integrator

Verlet Scheme:

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 + \frac{\Delta t^3}{3!}\dddot{r} + \mathcal{O}(\Delta t^4)$$

Newton's equations are time reversible,

$$r(t-\Delta t) = r(t) - v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 - \frac{\Delta t^3}{3!}\dddot{r} + \mathcal{O}(\Delta t^4)$$

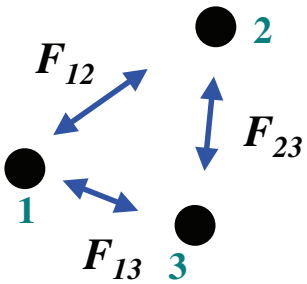
Summing the two equations,

$$r(t+\Delta t) \approx 2r(t) - r(t-\Delta t) + \frac{f(t)}{m}\Delta t^2$$

Now we have to advanced our atoms to time t+Δt !!

Velocity of the atoms: $v(t) = \dfrac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t}$

…Atoms move forward in time!

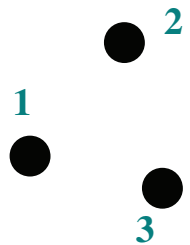


t+Δt

2nd MD Step

1. Calculate $f(t + \Delta t)$
2. Update $v(t + 2\Delta t)$
3. Update $r(t + 2\Delta t)$

Δt ~ 1-5 fs (10^{-15}sec)



t+2Δt

3rd MD Step

Continue this procedure for several lakhs of Steps.
Or as much as you can afford!

The main O/P of MD is the **trajectory**.

The missing ingredient… *Forces?*

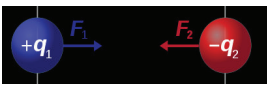
Force is the gradient of potential: $f_x(r) = -\frac{\partial u(r)}{\partial x}$

Gravitational Potential: $U = \frac{-Gm_1m_2}{r}$

too weak, Neglect it!!

The predominant inter-atomic forces are Coulombic in *origin*!

$$U = \frac{1}{4\pi\varepsilon_0}\frac{q_1q_2}{r}$$



However, this pure monopole interaction need not be present**!**

Interatomic forces for simple systems

(non-bonded interactions)

1. Lennard-Jones Potential:

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

Gives an accurate description of ***inert gases***
(Ar, Xe, Kr etc.)

2. Born-Mayer (Tosi-Fumi) Potential:

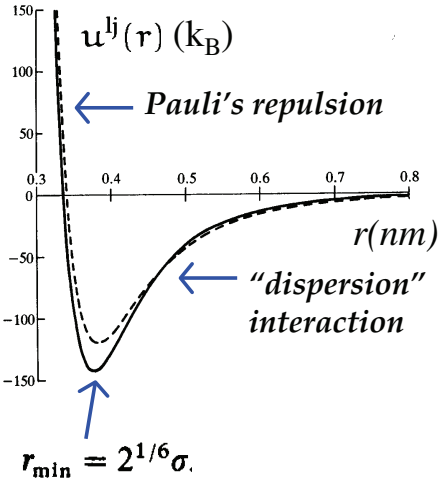
$$\mathcal{U}(r_{ij}) = \frac{q_i\, q_j}{r_{ij}} + A_{ij}\, exp(-r_{ij}/\rho_{ij}) - \frac{C_{ij}}{r_{ij}^6}$$

Faithful in describing ***pure*** ionic solids
(NaCl, KCl, NaBr etc.)

The Lennard-Jones Potential

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

for Ar : $\epsilon/k_B = 119.8\ \mathrm{K}$, $\sigma = 3.405\ \text{Å}$



$$F_{ij} = -\nabla U_{ij}$$

$$F_{ij}^{x} = -\frac{\partial U}{\partial x_i} = -\frac{\partial U}{\partial r_i}\frac{\partial r}{\partial x_i}$$

$$F_{ij}^{x} = 4\varepsilon\left(\frac{12\sigma^{12}}{r^{14}} - \frac{6\sigma^{6}}{r^{8}}\right)(x_i - x_j)$$

Length and Times of MD simulation

Typical experiment sample contains **~ 10^{23}** atoms!

Typical MD simulations (on a single CPU)

a) Can include 1000 – 10,000 atoms (~20-40 Å in size)!

b) run length ~ 1 –10 *ns* (10^{-9} seconds)!

Consequence of system size:

Larger fraction of atoms are on the surface, $\frac{Ns}{N} = \frac{4\pi r^2 dr\rho / m}{\frac{4}{3}\pi r^3 \rho / m} = 3\frac{dr}{r}$

$$\frac{Ns}{N}(Expt.) \sim 3\frac{(3\text{A})}{10^8\,\text{A}} \sim 10^{-7}$$

$$\frac{Ns}{N}(MD) \sim 3\frac{(3\text{A})}{20\text{A}} \sim 0.45$$

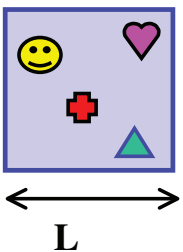
Surface atoms have different environment than bulk atoms!

The Simulation Cell

Insert the atoms in a perfectly **porous** box – simulation super-cell.

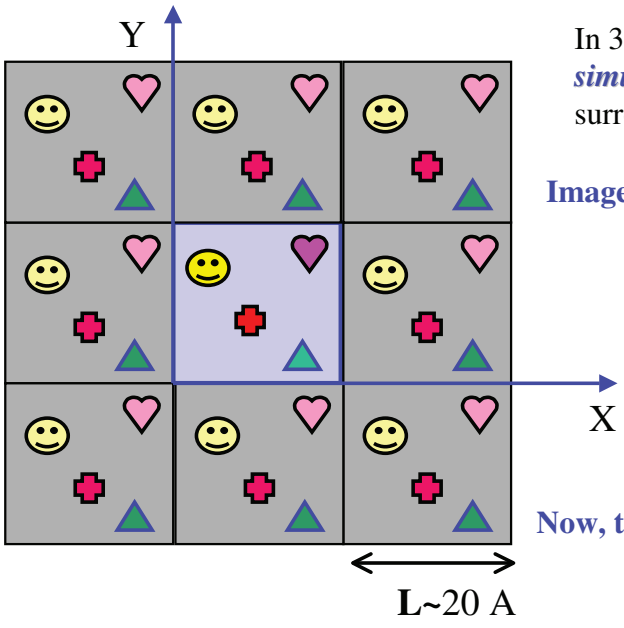
The length of the box is determined as, $\mathbf{L^3 = M/D_{exp} = N*m/D_{exp}}$

$\mathbf{D_{exp}}$ = Expt. density; **m** = At. mass; **N**= No. of atoms;



Periodic Boundary Condition

Construct Periodic Images:



In 3-D the simulation ***simulation-super-cell*** is surrounded by 26 **image cells!**

Image coordinates:

$$x' = x + \mathbf{n}_1 L$$

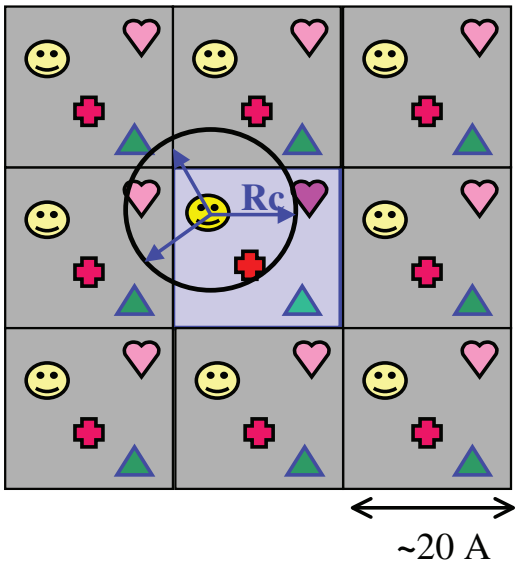
$$y' = y + \mathbf{n}_2 L$$

$$z' = z + \mathbf{n}_3 L$$

$\mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3 \in$ **0, 1, -1!**

Now, there are no surface atoms!

Minimum Image Convention



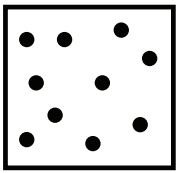
Interactions between atoms separated by a chosen cut-off distance (**Rc**) or larger (ie, $r_{ij} > Rc$) are neglected.

Rc is chosen such that U(**Rc**) ~ 0

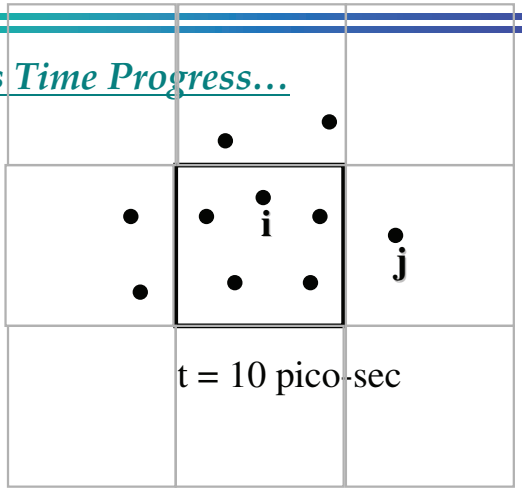
A large enough system (ie, bigger ***sim.-cell***) is chosen such that **Rc ≤ L/2.**

Thus particle **i** interact either with particle **j** or one of its images, **but not both**!

As Time Progress…



t = 0



t = 10 pico-sec

Force between **i** & **j** : $F_{ij}^{x} = 4\varepsilon(\frac{12\sigma^{12}}{r_{ij}^{14}} - \frac{6\sigma^{6}}{r_{ij}^{8}})(x_i - x_j)$

How to find the image of **j** that is nearest to **i ?**

The three lines of code…

Define,

dx = x(j) – x(i)

dy = y(j) – y(i)

dz = z(j) – z(i)

```
dx = dx – boxl*ANINT(dx/boxl)
dy = dy – boxl*ANINT(dy/boxl)
dz = dz – boxl*ANINT(dz/boxl)
```

rij_2 = (dx**2 + dy**2 + dz**2)

rij_8 = rij**8

rij_14 = rij**14

boxl ≡ L

ANINT(3.49) = 3

ANINT(1.2) = 1

ANINT(3.51) = 4

ANINT(-11.50) = -11

$$F_{ij}^{x} = 4\varepsilon\left(\frac{12\sigma^{12}}{r_{ij}^{14}} - \frac{6\sigma^{6}}{r_{ij}^{8}}\right)(x_i - x_j)$$

The structure of a simple MD code

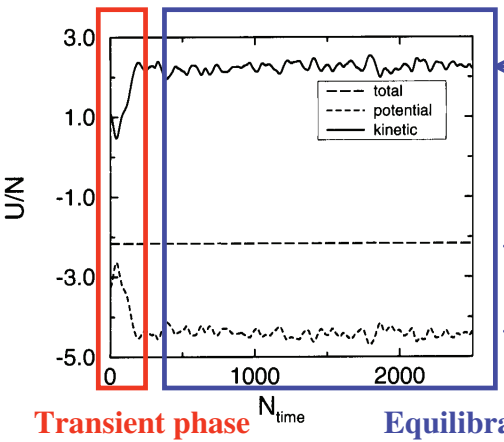
```
program md                          simple MD program

call init                          initialization
t=0
do while (t.lt.tmax)               MD loop
   call force(f,en)                determine the forces
   call integrate(f,en)            integrate equations of motion
   t=t+delt
   call sample                     sample averages
enddo
stop
end
```

Remarks on Statistical Ensemble

There is no energy coming in Or going out of our system of atoms: **micro-canonical (NVT)** ensemble.

Thus the **total energy (E)** and total linear momentum of the system should be conserved – through out our simulation!



$K = \sum_{i=1}^{N} m_i v_i^2$ **(fluctuates)**

$E = K + U$ ***remain const.***

$U = \frac{1}{2}\sum_{i=1}^{N} U_i$ **(fluctuates)**

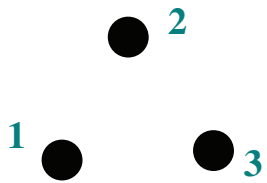
Calculating Temperature

Equipartition theorem: $\frac{3}{2}NkT(t) = \frac{1}{2}\sum_{i}^{N} m_i v_i^2$

Instantaneous temperature: $T(t) = \frac{1}{3Nk}\sum_{i}^{N} m_i v_i^2$

Average temperature : $< T >= \frac{1}{M}\sum_{m=1}^{M} T_m$

M – no. of MD steps performed



Even if we start with $v_i = 0$, the system picks up non-zero v (hence **some T**) as time progress!

This **some T(!)** need not be what we want!

So how do we **control T**?

Controlling the Temperature ?

Velocity rescaling:

Actual temp. at some instant. $$T = \frac{1}{3Nk}\sum_{i}^{N} m_i v_i^2$$

If T is out side the fluctuation window around T_r: $T_r - \Delta T < T > T_r + \Delta T$

Then **scale** all velocities: $$v_r = \left(\frac{T_r}{T}\right)^{\frac{1}{2}} v$$

This instantly bring the $T = T_r$!

However to sustain the temp. around Tr we will need to do this procedure several times at intervals.

Note: This phase of the simulation is should not used for averaging!

Calculating thermodynamic quantities

Average Energy, $$< U >= \frac{1}{M} \sum_{i=1}^{M} U_i$$

Average Pressure, $$\langle P \rangle = \frac{N k_B T}{V} + \frac{1}{3V} \sum_{i=1}^{N} \left\langle \vec{r}_i \cdot \vec{f}_i \right\rangle$$

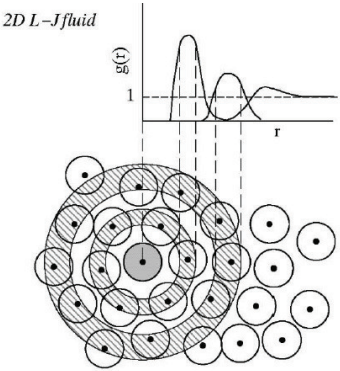
Heat Capacity, Cv: $$\frac{[\langle T^2 \rangle - \langle T \rangle^2]}{\langle T \rangle^2} = \frac{2}{3N} \left(1 - \frac{3k_B}{2C_v} \right)$$

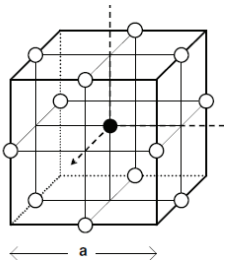
Structural Characterization

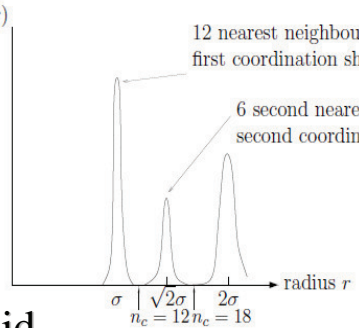
Radial Distribution Function (rdf)

$$g(r) = \frac{V}{4\pi r^2 \Delta r N^2} \sum_i^N n_i\,(r, \Delta r)$$

$$n_c = 4\pi\rho \int_0^{r_c} dr\, r^2 g(r)$$



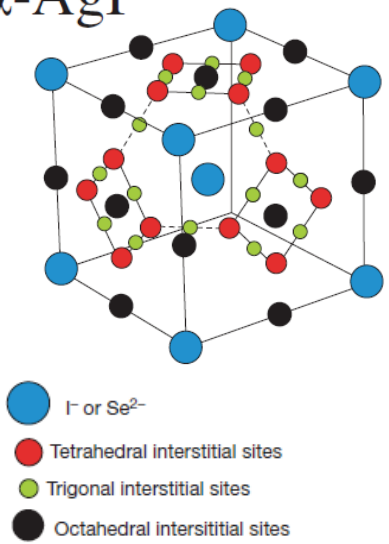


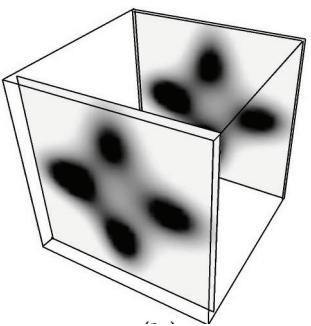


Rdf of fcc-solid

…Structural Properties: Site Occupancies

α-AgI $T > 420$ K





PRL **97, 166401 (2006)**

Dynamical Properties: Diffusion Coefficient

Fick's Law: $\vec{j}(\vec{r},t) = -D\nabla\rho(\vec{r},t)$

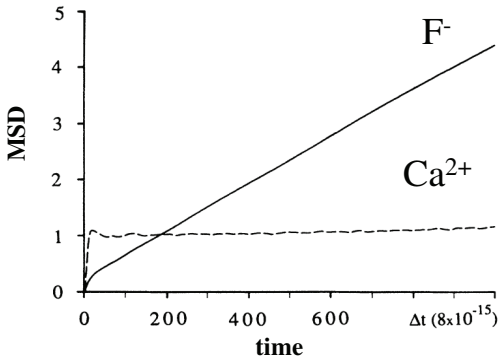
Continuity Eq.: $\partial\rho(\vec{r},t)/\partial t + \nabla\cdot\vec{j}(\vec{r},t) = 0$

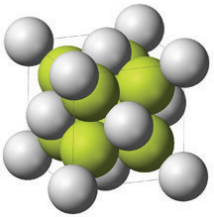
Diffusion Eq.: $\partial\rho(\vec{r},t)/\partial t = D\nabla^2\rho(\vec{r},t)$

Einstein's relation: $D = \lim_{t\to\infty}\frac{1}{6t}\langle|\mathbf{r}(t)-\mathbf{r}(0)|^2\rangle$ ⟸ *Nr.* MSD

Nernst-Einstein's relation: $\sigma = Nq^2D\,/\,fk_BT$

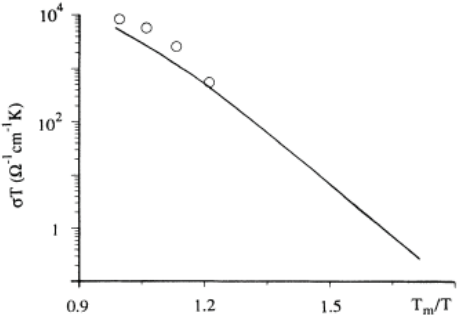
…Diffusion Coefficient: CaF2





CaF2

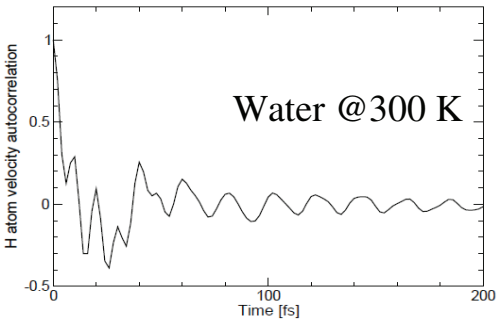
$$\sigma = Nq^2 D / fk_B T$$



…Dynamical Properties: Vibrational Spectrum

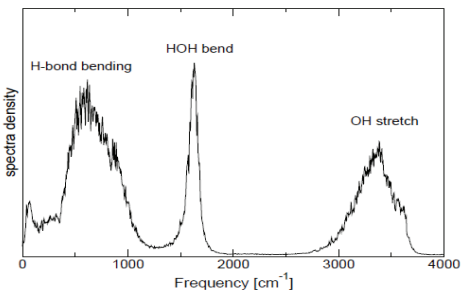
Velocity Autocorrelation Spectrum,

$$c_{vv}(\tau) = \langle \mathbf{v}_i(\tau)\mathbf{v}_i(0)\rangle$$



Power Spectrum,

$$\text{Spectrum} = \int_{-\infty}^{\infty} d\tau\, e^{-i\omega\tau} c_{vv}(\tau)$$



Remarks on Energy

- Energy conservation, $\frac{\Delta E}{E} \sim 10^{-6}$ -good check on your code!
  -time integrator!
  -on time step (Δt) used!

- Start from the expt. crystal structure if available.

- Else? Start from good guess! (like, in bio-systems, polymers, liquids)

  - And, perform an energy minimization!

    (Routines available in standard packages.

    Or, do an MD with constant velocity scaling.)

  - Reaching a well equilibrated structure can be very very costly!

- Fluctuation of U(t) about a mean helps to identify equilibrated system.

Remarks on Interatomic Forces

- Development of good force fields (FF) can be a tough task!

  FF's are developed by empirical methods or ab-initio calculations.

- FF assume that electronic clouds around the nucleus of atoms is intact irrespective of the environment around the atom!

  This can be a poor assumption for highly polarizable atoms/ions!

  Solution?

  Develop a shell model of atoms/ions!

  Or DFT-based *ab-initio* (Car-Parrinello) MD calculations !

Comments on Classical MD

Very powerful in studying a variety of physical phenomena and under several external conditions (T & P).

Extensively employed to understand Physical processes at atomic resolution

Phase Transitions,

Diffusion and transport properties,

Local structural and short-time relaxation of

- ✓ crystalline and amorphous solids
- ✓ liquids
- ✓ solid-fluid interfaces
- ✓ nano-clusters

And, serves a very useful bridge between experiment and theory!

Not useful in the study of electronic properties!

Not powerful enough to describe chemical reactions!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Indian Institute of Technology Guwahati

Thank you!