History, Development and Basics of Molecular Dynamics Simulation Technique

A way to do experiments in computers
(Odourless)
Creating virtual matter and then studying them in computers

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National Workshop on Atomistic Simulation Techniques, IIT, Guahati
Dedication

• Prof. Aneesur Rahman, a gentle scientist, from Hyderabad, India
Acknowledgements

All my students:
P. Santikary (ebay, USA),
Sanjoy Bandyopadhyay (IIT, Kgp),
P. K. Padmanabhan (IIT, Guwahati),
R. Chitra (Bangalore),
A.V. Anil Kumar (NISER, Bhubhaneswar),
S.Y. Bhide (Dow Chemicals, Mumbai),
C.R. Kamala (GE, USA),
P. K. Ghorai (IISER, Kolkata),
Manju Singh (Bangalore),
B.J. Borah (private univ., Baroda),
V. Srinivas Rao (U. Queens, Australia)
Plan of the talk:

Introduction
Classical mechanics : basics
Statistical mechanics : basics
Intermolecular potentials
Numerical integration
Algorithms
Computational Tricks
Trajectory
Equilibrium and time dependent properties
Microcanonical ensemble
Other ensembles
What is molecular dynamics?

A way of solving equations of motion numerically (hence you need a computer).

Equations of motion are coupled differential equations and hence can not be solved analytically.

You can get all properties about the system being simulated (from statistical mechanical relationships)
Subjects involved in MD

• Classical mechanics
• Statistical mechanics
• Intermolecular potential
History and evolution of MD

• 1953: Metropolis Monte Carlo (MC) by Metropolis, Rosenbluth, Rosenbluth, Teller & Teller
  – simulation of a dense liquid of 2D spheres
• 1955: Fermi, Pasta, and Ulam
  – simulation of anharmonic 1D crystal
• 1956: Alder and Wainwright
  – molecular dynamics (MD) simulation of hard spheres
    (1958: First X-ray structure of a protein)
• 1960: Vineyard group
  – Simulation of damaged Cu crystal
• 1964: Rahman
  – MD simulation of liquid Ar

• 1969: Barker and Watts
  – Monte Carlo simulation of water

• 1971: Rahman and Stillinger
  – MD simulation of water

* 1972: I.R. McDonald
- NPT simulation using Monte Carlo
Correlations in the Motion of Atoms in Liquid Argon*

A. RAHMAN
Argonne National Laboratory, Argonne, Illinois
(Received 6 May 1964)

A system of 864 particles interacting with a Lennard-Jones potential and obeying classical equations of motion has been studied on a digital computer (CDC 3600) to simulate molecular dynamics in liquid argon at 94.4°K and a density of 1.374 g cm⁻³. The pair-correlation function and the constant of self-diffusion are found to agree well with experiment; the latter is 15% lower than the experimental value. The spectrum of the velocity autocorrelation function shows a broad maximum in the frequency region \( \omega = 0.25(k_BT/\hbar) \). The shape of the Van Hove function \( G_d(r,t) \) attains a maximum departure from a Gaussian at about \( t = 3.0 \times 10^{-11} \) sec and becomes a Gaussian again at about \( 10^{-11} \) sec. The Van Hove function \( G_d(r,t) \) has been compared with the convolution approximation of Vineyard, showing that this approximation gives a too rapid decay of \( G_d(r,t) \) with time. A delayed-convolution approximation has been suggested which gives a better fit with \( G_d(r,t) \); this delayed convolution makes \( G_d(r,t) \) decay as \( t^4 \) at short times and as \( t \) at long times.

Reprinted from:
THE JOURNAL OF CHEMICAL PHYSICS VOLUME 55, NUMBER 7 1 OCTOBER 1971

Molecular Dynamics Study of Liquid Water*

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AND

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(Received 6 May 1971)

A sample of water, consisting of 216 rigid molecules at mass density 1 g/cm³, has been simulated by computer using the molecular dynamics technique. The system evolves in time by the laws of classical dynamics, subject to an effective pair potential that incorporates the principal structural effects of many-body interactions in real water. Both static structural properties and the kinetic behavior have been examined in considerable detail for a dynamics “run” at nominal temperature 34.3°C. In those few cases where direct comparisons with experiment can be made, agreement is moderately good; a simple energy rescaling of the potential (using the factor 1.06) however improves the closeness of agreement considerably.

A sequence of stereoscopic pictures of the system’s intermediate configurations reinforces conclusions inferred from the various “run” averages: (a) The liquid structure consists of a highly strained random hydrogen-bond network which bears little structural resemblance to known aqueous crystals; (b) the diffusion process proceeds continuously by cooperative interaction of neighbors, rather than through a sequence of discrete hops between positions of temporary residence. A preliminary assessment of temperature variations confirms the ability of this dynamical model to represent liquid water realistically.
Unified Approach for Molecular Dynamics and Density-Functional Theory

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and

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International School for Advanced Studies, Trieste, Italy*  
(Received 5 August 1985)

We present a unified scheme that, by combining molecular dynamics and density-functional theory, profoundly extends the range of both concepts. Our approach extends molecular dynamics beyond the usual pair-potential approximation, thereby making possible the simulation of both covalently bonded and metallic systems. In addition it permits the application of density-functional theory to much larger systems than previously feasible. The new technique is demonstrated by the calculation of some static and dynamic properties of crystalline silicon within a self-consistent pseudopotential framework.

PACS numbers: 71.10.+x, 65.50.+m, 71.45.Gm

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chemical bond in a large variety of systems, but are computationally very demanding. This has so far precluded the application of DF schemes to the study of

\[
E \{ [\psi_i], \{ R_j \}, \{ \alpha_\nu \} \} = \sum_i \int_\Omega d^3r \psi_i^*(r) \left[ -\left( \hbar^2/2m \right) \nabla^2 \right] \psi_i(r) + U [n(r), \{ R_j \}, \{ \alpha_\nu \}].
\]

Here \( \{ R_j \} \) indicate the nuclear coordinates and \( \{ \alpha_\nu \} \) are all the possible external constraints imposed on the system. like the volume \( \Omega \), the strain \( \epsilon \), etc. The

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normal orbitals: \( n(r) = \sum_i |\psi_i(r)|^2 \). A point of the BO potential energy surface is given by the minimum with respect to the \( \psi_i(r) \) of the energy functional,

\[
L = \sum_i \frac{1}{2} \mu_i \int_\Omega d^3r |\dot{\psi}_i|^2 + \sum_j \frac{1}{2} \mathbf{M}_j \dot{\mathbf{R}}^2 + \sum_\nu \frac{1}{2} \mu_\nu \dot{\alpha}_\nu^2 - E \{ [\psi_i], \{ R_j \}, \{ \alpha_\nu \} \}.
\]

where the \( \psi_i \) are subject to the holonomic constraints

\[
\int_\Omega d^3r \psi_i^*(r,t) \psi_j(r,t) = \delta_{ij}.
\]

---

In our method we consider the parameters \( \{ \psi_i \}, \{ R_j \}, \{ \alpha_\nu \} \) in the energy-functional [Eq. (1)] to be dependent on time and introduce the Lagrangean

---

laxation, and volume and strain relaxation are achieved simultaneously. The amount of classical
Aneesur Rahman in his younger days
Post 1980 developments: the extended Hamiltonian methods

- 1980: H. C. Andersen
  - MD method for NPH, NVT, NPT ensembles
- 1980: M. Parrinello and A. Rahman
  - Parrinello-Rahman method for study of crystal structure transformation with corrections from S. Yashonath
- 1986: R. Car and M. Parrinello
  - Ab initio MD (includes electronic degrees of freedom)
A chart of development of simulation methods

1. Metropolis et al
   Monte Carlo 1953

2. Fermi, Pasta, Ulam
   1D crystal 1955

3. Alder & Wainright
   Hard sphere 1956

4. Simulation of damaged Cu crystal
   Vineyard 1960

5. Rahman
   MD of argon 1964

6. Barker and Watts
   MC of water 1969

7. Rahman and Stillinger
   MD simulation of water, 1971

8. NPT of argon
   McDonald 1972
Feynman vs. Einstein

• “...everything that is living can be understood in terms of jiggling and wiggling of atoms.” R. Feynman.

• Everything Should Be Made as Simple as Possible, But Not Simpler : A. Einstein
MD jargon: Terms often used

- Monatomic: single atom or molecule with single atom
- Polyatomic: molecule with multiple atoms
- Euler angles and quaternions
- Images
- Simulation cell, parallelopiped
- Cut-off radius, long-range and short-range interactions
Simple microcanonical ensemble MD

\[ a_i = F_i / m_i \]

How does one get force \( F_i \)? From the intermolecular potential:

\[ F_i = \text{grad of potential} \]

We need: \( F_i \) or potential \( \phi_i \).
A knowledge of intermolecular interaction potential is therefore central to molecular dynamics. Without it, you can not perform a MD simulation.

Before we go into the various potential functions, we need to understand the origin of the intermolecular interaction. What are these and how they originate?
Molecular Dynamics : the nitty gritty details !

through the slides of Prof. P. K. Padmanabhan
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
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Department of Chemical Engineering,
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University of Amsterdam
Amsterdam, The Netherlands

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Department of Chemical Engineering
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Three Atoms

\[ F_{ij} = -\nabla U_{ij} \]

Newton's II\textsuperscript{nd} Law:

\[ a_i = \frac{F_i}{m_i} \]
Progress in time...

\[ r(t) \rightarrow r(t + \Delta t) \]
\[ x(t) \rightarrow x(t + \Delta t) \]
\[ y(t) \rightarrow y(t + \Delta t) \]
\[ z(t) \rightarrow z(t + \Delta t) \]

\[ \Delta t \sim 1-5 \text{ fs (}10^{-15}\text{ sec)} \]

Advance positions & velocities of each atom:

**Taylor Expansion:**

\[ \mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \Delta t \frac{f(t)}{m} \]

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

too crude to use it as such!!
A good Integrator

...for example!

**Verlet Scheme:**

\[
\begin{align*}
    r(t + \Delta t) &= r(t) + v(t)\Delta t + \frac{f(t)}{2m} \Delta t^2 + \frac{\Delta t^3}{3!} \dddot r + O(\Delta t^4) \\
    r(t - \Delta t) &= r(t) - v(t)\Delta t + \frac{f(t)}{2m} \Delta t^2 - \frac{\Delta t^3}{3!} \dddot r + O(\Delta t^4)
\end{align*}
\]

Newton’s equations are time reversible,

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 advanced our atoms to time \( t + \Delta t \)!!

Velocity of the atoms:

\[
    v(t) = \frac{r(t + \Delta t) - r(t - \Delta t)}{2\Delta t}
\]
...Atoms move forward in time!

$\Delta t \sim 1-5 \text{ fs (}10^{-15}\text{sec)}$

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… \textbf{Forces?}

\textbf{Force is the gradient of potential:}

\[ f_x(r) = -\frac{\partial u(r)}{\partial x} \]

\textbf{Gravitational Potential:}

\[ U = \frac{-Gm_1m_2}{r} \]

too weak, Neglect it!!

\textbf{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

1. Lennard-Jones Potential:

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

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

Instantaneous dipoles

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

For Ar:

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

Should be known apriori.

\[ \frac{\epsilon}{k_B} = 119.8 \text{ K}, \quad \sigma = 3.405 \text{Å} \]

Pauli's repulsion

"dispersion" interaction

\[ F_{ij} = -\nabla U_{ij} \]

\[ F_{ij}^x = -\frac{\partial U}{\partial x_i} = -\frac{\partial U}{\partial r_i} \frac{\partial r_i}{\partial x_i} \]

\[ F_{ij}^x = 4\epsilon \left( \frac{12\sigma^{12}}{r_i^{14}} - \frac{6\sigma^6}{r_i^8} \right)(x_i - x_j) \]
**Length and Times of MD simulation**

Typical experiment sample contains $\sim 10^{23}$ atoms!

Typical MD simulations (on a single CPU)

  a) Can include 1000 – 10,000 atoms ($\sim$20-40 Å in size)!
  b) run length $\sim 1$ –10 ns ($10^{-9}$ seconds)!

**Consequence of system size:**

Larger fraction of atoms are on the surface, 

$$
\frac{N_s}{N} = \frac{4 \pi r^2 \, dr \, \rho / m}{\frac{4}{3} \pi r^3 \, \rho / m} = 3 \frac{dr}{r}
$$

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

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

**Surface atoms have different environment than bulk atoms!**
**The Simulation Cell**

Insert the atoms in a perfectly **porous** box – simulation super-cell. If crystal structure/unit cell parameters are **unknown** (e.g., liquids) The length of the box is determined as, \( L^3 = \frac{M}{D_{\text{exp}}} = \frac{N \cdot m}{D_{\text{exp}}} \)

\[ D_{\text{exp}} = \text{Expt. density}; \quad m = \text{At. mass}; \quad N = \text{No. of atoms}; \]

Assign positions and velocities(=0) for each atom.
Periodic Boundary Condition

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

Image coordinates:

\[ x' = x + n_1 L \]
\[ y' = y + n_2 L \]
\[ z' = z + n_3 L \]

\( n_1, n_2, n_3 \in -1,0,1, \)

Now, there are no surface atoms!
Minimum Image Convention

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

$R_c$ is chosen such that $U(R_c) \sim 0$

A large enough system (ie, bigger sim.-cell) is chosen such that $R_c \leq L/2$.

Thus particle $i$ interact either with particle $j$ or one of its images, but not both!
As Time Progress...

Force between \( i \) & \( j \):

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

How to find the image of \( j \) that is nearest to \( i \)?
folding

If you have coordinates which are anywhere between (-infinity,infinity), and if you want to bring the coordinates between (0,L) then this procedure is called folding. Assuming L is 10, we see that:

(234,-546) → (4,-6) → (4,4). If we have L = 10, we get the same answer. However, if L = 12, 12 x 19 = 228 and 12 x 45 = 540. Therefore, you get (234-228, -546+540) → (6,-6) → (6,6).
Unfolding

• If you have coordinates between (0,L) at many time steps then can you unfold it? That is, can you map it to the range (-infinity, infinity)?

• Timestep 1 : (4,3), 2: (3.5,3.4), 3: (3.3,3.6), 4:(3.09,3.9), 5:(2.2,4.2), 6: (1.4,4.3), 7: (0.3, 5.0), 8: (9.4, 6.6)

• Noting that coordinates between step 7 and 8 have large difference (of the order of L), then we can guess that they have been folded. Then we can see that the unfolded coordinates at step 8 are (-0.6,6.6)
The three lines of code...

Define,

\[
dx = x(j) - x(i) \\
dy = y(j) - y(i) \\
dz = z(j) - z(i)
\]

\[
dx = dx - L \times \text{ANINT}(dx/L) \\
dy = dy - L \times \text{ANINT}(dy/L) \\
dz = dz - L \times \text{ANINT}(dz/L)
\]

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

\[
rij_2 = (dx^{**2} + dy^{**2} + dz^{**2})
\]

\[
rij_8 = rij_2^{**4} \quad rij_{14} = rij_2^{**7}
\]
\[ dx = dx - L \text{AINT}(dx/L) \]
\[ dy = dy - L \text{AINT}(dy/L) \]

\[ xi-xj = (2-19)-10 \text{AINT}(2-19)/10 = -17 - (-10\times2) = 3 \]

\[ yi-yj = (8+4)-10 \text{AINT}(12/10) = 12 - (10\times1) = 2 \]
\[ u_{lj}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \]

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

Should be known \textit{apriori}.

\[ F_{ij} = -\nabla U_{ij} \]

\[ F_{ij}^x = -\frac{\partial U}{\partial x_i} = -\frac{\partial U}{\partial r} \frac{\partial r}{\partial x_i} \]

\[ F_{ij}^x = 4\epsilon \left( \frac{12\sigma^{12}}{r^{14}} - \frac{6\sigma^6}{r^8} \right)(x_i - x_j) \]
The structure of a simple MD code

program md

  call init
  t=0
  do while (t.lt.tmax)
    call force(f,en)
    call integrate(f,en)
    t=t+delt
    call sample
  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 – throughout our simulation!

\[
E = K + U
\]

\[
K = \frac{1}{2} \sum_{i=1}^{N} m_i v_i^2
\]

\[
U = \frac{1}{2} \sum_{i=1}^{N} U_i
\]

(fluctuates)

remain const.

(fluctuates)

**Transient phase**

**Equilibrated state**
Calculating Temperature

**Equipartition** theorem: \[ \frac{3}{2} N k T(t) = \frac{1}{2} \sum_i^N m_i v_i^2 \]

**Instantaneous** temperature: \[ T(t) = \frac{1}{3Nk} \sum_i^N m_i v_i^2 \]

Average temperature: \[ < T > = \frac{1}{M} \sum_{m=1}^M T(t_m) \]

\( M \) – 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 outside the fluctuation window around \( T_r \):  

\[ T_r - \Delta T < T < T_r + \Delta T \]

Then *scale* all velocities:

\[ v_r = \left( \frac{T_r}{T} \right)^2 v \]

This instantly bring the \( T = T_r \)!

---

However to sustain the temp. around \( T_r \) we will need to do this procedure several times at intervals.

---

This phase of the simulation **should not** be used for averaging!
Calculating thermodynamic quantities

Average Energy,

\[ <U> = \frac{1}{M} \sum_{i=1}^{M} U_i \]

Average Pressure,

\[ \langle \mathcal{P} \rangle = \frac{N k_B T}{V} + \frac{1}{3V} \sum_{i=1}^{N} \langle \vec{r}_i \cdot \vec{f}_i \rangle \]

Heat Capacity, \( C_v \):

\[ \frac{\langle T^2 \rangle - \langle T \rangle^2}{\langle T \rangle^2} = \frac{2}{3N} \left( 1 - \frac{3k_B}{2C_v} \right) \]
Remarks on Energy Conservation

• Energy conservation, \( \frac{\Delta E}{E} \sim 10^{-6} / \text{ps} \) -good check on your code!
  
  -time integrator!
  
  -on time step (\( \Delta t \)) 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!
Structural Characterization

Radial Distribution Function (rdf)

\[ g(r) = \frac{V}{4\pi r^2 \Delta r N^2} \sum_{i}^{N} n_i(r, \Delta r) \]

Running Coordination Numbers:

\[ n_c = 4\pi \rho \int_{0}^{r_c} dr \ r^2 g(r) \]

Rdf of fcc-solid
**Dynamical Properties: Diffusion Coefficient**

Fick’s Law:

\[ \vec{j}(\vec{r}, t) = -D \nabla \rho(\vec{r}, t) \]

Continuity Eq.:

\[ \frac{\partial \rho(\vec{r}, t)}{\partial t} + \nabla \cdot \vec{j}(\vec{r}, t) = 0 \]

Diffusion Eq.:

\[ \frac{\partial \rho(\vec{r}, t)}{\partial t} = D \nabla^2 \rho(\vec{r}, t) \]

Einstein’s relation:

\[ D = \lim_{t \to \infty} \frac{1}{6t} \langle |r(t) - r(0)|^2 \rangle \]

Nernst-Einstein’s relation:

\[ \sigma = Nq^2 D / f k_B T \]
...Diffusion Coefficient: CaF$_2$

\[ \sigma = Nq^2D / f k_B T \]

...Dynamical Properties: Vibrational Spectrum

Velocity Autocorrelation Spectrum,

\[ C_{VV}(\tau) = \langle \mathbf{v}_i(\tau) \mathbf{v}_i(0) \rangle \]

Power Spectrum,

\[ C_{VV}(\omega) = \int_{-\infty}^{\infty} d\tau \ e^{-i\omega\tau} c_{uv}(\tau) \]

Helps interpreting IR spectrum.

Water @ 300 K
...Structural Properties: Site Occupancies

\( \alpha \text{-AgI} \quad T > 420 \text{ K} \)

- \( I^- \) or \( \text{Se}^{2-} \)
- Tetrahedral interstitial sites
- Trigonal interstitial sites
- Octahedral interstitial sites

PRL 97, 166401 (2006)
Ion Channel’s In NASICON’s

$\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$

Supriya Roy and P.P. Kumar, PCCP (2014).
Simulation of Live-Virus!!

Charge distribution around the virus