Molecular Dynamics

What is molecular dynamics?

Molecular dynamics (MD) is a computer simulation technique that allows one to predict the time evolution of a system of interacting particles (atoms, molecules, granules, etc.).

The basic idea is simple.

First, for a system of interest, one has to specify:

- a set of **initial conditions** (initial positions & velocities of all particles in the system)
- interaction potential for deriving the forces among all the particles.

Second, the evolution of the system in time can be followed by solving a set of classical equations of motion for all particles in the system. Within the framework of classical mechanics, the equations that govern the motion of classical particles are the ones that correspond to the second law of classical mechanics formulated by Sir Isaac Newton over 300 years ago:

\[
    m_i \ddot{a}_i = \vec{F}_i \quad \text{or} \quad m_i \frac{d\vec{v}_i}{dt} = \vec{F}_i \quad \text{or} \quad m_i \frac{d^2\vec{r}_i}{dt^2} = \vec{F}_i \quad \text{for the } i^{th} \text{ particle}
\]
Molecular Dynamics

Solving a set of classical equations of motion for all particles in the system

\[ m_i \ddot{a}_i = \vec{F}_i \quad \text{or} \quad m_i \frac{d\vec{v}_i}{dt} = \vec{F}_i \quad \text{or} \quad m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}_i \quad \text{for the } i^{th} \text{ particle} \]

If the particles of interest are atoms, and if there are a total of \( N_{\text{at}} \) of them in the system, the force acting on the \( i^{th} \) atom at a given time can be obtained from the interatomic potential \( U(r_1, r_2, r_3, \ldots, r_{N_{\text{at}}}) \) that, in general, is a function of the positions of all the atoms:

\[ \vec{F}_i = -\nabla_i U(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_{N_{\text{at}}}) \]

Once the initial conditions and the interaction potential are defined, the equations of motion can be solved numerically. The result of the solution are the positions and velocities of all the atoms as a function of time, \( \vec{r}_i(t), \vec{v}_i(t) \)

Advantages of MD:

- the only input in the model – description of interatomic/intermolecular interaction
- no assumptions are made about the processes/mechanism to be investigated
- provides a detailed molecular/atomic-level information

Results of the “computational experiment” may lead to the discover new physics/mechanisms!
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 $t_n$:

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

Solve equations of motion for all particles in the system over a short timestep $\Delta t$.

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

$$t_{n+1} = t_n + \Delta t$$

Calculate desired physical quantities, write data to trajectory file

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

Write to the disc final atomic configuration & finish
Molecular Dynamics

Example – collision of a droplet with a substrate (by Yasushi Katsumi, UVa)

MD is a deterministic technique: given initial positions and velocities, the evolution of the system in time is, in principle, completely determined (in practice, accumulation of integration and computational errors would introduce some uncertainty into the MD output).

MD can be also used as a statistical mechanics method: it generates a set of configurations that are distributed according to statistical distribution functions. In many cases we are not interested in trajectories of individual atoms, we are interested in macroscopic properties of the material. MD information can be averaged over all the atoms in the system and over time to obtain thermodynamic parameters.

The main strengths of the MD method is the ability to study fast non-equilibrium processes with atomic-level resolution (e.g. microscopic mechanisms of damage/plastic deformation due to a shock wave propagation, dynamic fracture and crack growth, ion bombardment, cluster impact, etc.). For many of these problems, MD method does not have an alternative.
Limitations of the MD technique

1. Classical description of interatomic interaction

- Electrons are not present explicitly, they are introduced through the potential energy surface that is a function of atomic positions only (Born-Oppenheimer approximation).

- The potential energy surface, in turn, is approximated by an analytic function that gives the potential energy $U$ as a function of coordinates. Forces are obtained as the gradient of a potential energy function,

$$\vec{F}_i = -\nabla_{\vec{r}_i} U(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$$

Potential energy surfaces (solutions of electronic Schrödinger equation within the Born-Oppenheimer approximation) are not available for practically interesting systems. The choice of a potential function that approximates the actual (unknown) solution of the Schrödinger equation is a difficult task. Design of the potential function and choice of the parameters is often based on fitting to available experimental data (e.g. equilibrium geometry of stable phases, cohesive energy, elastic moduli, vibrational frequencies, temperatures of the phase transitions, etc.).

Availability of good potential functions is one of the main conditions for expansion of the area of applicability of the MD simulations to the realistic quantitative analysis of the behavior and properties of real materials.

The Born-Oppenheimer approximation and different types of the potential functions will be discussed later in the course.
Limitations of MD: Classical description of atomic motions

2. Classical description of atomic motion

- In classical MD we replace Schrödinger equation for nuclei with classical Newton equation.

One indicator of the validity of the replacement is the de Broglie wavelength $\Lambda$. Quantum effects are expected to become significant when $\Lambda$ is much larger than inter-particle distance.

For thermal motion we can use the thermal de Broglie wavelength: 
$$
\Lambda_{th} = \frac{h}{\sqrt{2\pi mk_B T}}
$$

For $T = 300 \text{ K}$ we have 
- $\Lambda_{th} = 1 \text{ Å}$ for a H atom ($m_H = 1 \text{ amu}$)
- $\Lambda_{th} = 0.19 \text{ Å}$ for a Si atom ($m_{\text{Si}} = 28 \text{ amu}$)
- $\Lambda_{th} = 0.07 \text{ Å}$ for a Au atom ($m_{\text{Au}} = 197 \text{ amu}$)

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

- All atoms, except for the lightest ones such as H, He, Ne, can be considered as “point” particles at sufficiently high temperature ($d >> \Lambda$) and classical mechanics can be used to describe their motion.
Limitations of the MD technique

- The classical approximation is rather poor for light elements (e.g. H, He) and quantum corrections are often superimposed on the classical description of motion.

Example: H$_2$O

Let’s try to use classical equipartition principle to calculate the heat capacity of water vapor.

\[ E_{th} = 3 \times \frac{1}{2}RT \text{ (transl.)} + 3 \times \frac{1}{2}RT \text{ (rotat.)} + 3 \times 2 \times \frac{1}{2}RT \text{ (vibr.)} = 6RT \rightarrow c_v = 6R \]

But experimental $c_v$ is much smaller. At T = 298 K H$_2$O gas has $c_v = 3.038R$.

*What is the reason for the large discrepancy?*

The table shows the vibrational frequencies of water along with the population of the first excited state at 600 K.

<table>
<thead>
<tr>
<th>$v$ (cm$^{-1}$)</th>
<th>$\text{Exp}(-hv/kT)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3825</td>
<td>1.0 x 10$^{-4}$</td>
</tr>
<tr>
<td>1654</td>
<td>1.9 x 10$^{-2}$</td>
</tr>
<tr>
<td>3936</td>
<td>8.0 x 10$^{-5}$</td>
</tr>
</tbody>
</table>

For the high frequency OH stretching motions, there should be essentially no molecules in the first vibrational state even at 600 K. For the lower frequency bending motion, there will be about 2% of the molecules excited. Contributions to the heat capacity can be considered classically only if $E_n \sim hv \ll k_BT$. Energy levels with $E_n \geq kT$ contribute little, if at all, to the heat capacity.

*University of Virginia, MSE 4270/6270: Introduction to Atomistic Simulations, Leonid Zhigilei*
Limitations of the MD technique

Example: \( \text{H}_2\text{O} \)

(continued)

<table>
<thead>
<tr>
<th>(\nu) (cm(^{-1}))</th>
<th>(\exp(-h\nu/kT))</th>
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</table>

OH stretch and, in a big part, OH bend remain in the ground vibrational state at any \(T\) reasonable for \(\text{H}_2\text{O}\). \(\Rightarrow\) It would be wrong to study this system classically (energy would leak into the vibrational modes and would give a wrong heat capacity and heat conduction).

Quantum “correction” in MD simulations: \(\text{H}_2\text{O}\) are usually considered to be rigid (bending and stretching motions are frozen (e.g. SHAKE/RATTLE methods)).

Quantum effects can become significant in any system as soon as \(T\) is sufficiently low (e.g. temperature dependence of the heat capacity below the Debye temperature can not be explained in classical approximation).
Examples of MD simulations of water

Substrate-assisted laser-initiated ejection of a protein molecule embedded in a water film

A small biomolecule, enkephalin (574 Da)

$\text{H}_2\text{O}$ film

Au substrate


Equations of motion are integrated using the velocity Verlet algorithm in conjunction with the RATTLE constraint method to maintain fixed O-H bond lengths and a fixed H-O-H bond angle.

Molecular mechanism of water evaporation


flexible POLY2VS and rigid SPC/E force fields for water are used, integration time step is 0.4 fs, 500 molecules are simulated for 600 ps at 331 K. Simulations are repeated 32 times.
Limitations of the MD technique

3. Time- and length-scale limitations

- The limitations on the size of the MD computational cell (number of atoms) and time of the simulation constrain the range of problems that can be addressed by the MD method.

Time-scale:

The maximum timestep of integration in MD simulation is defined by the fastest motion in the system. Vibrational frequencies in a molecular system are up to 3000 cm\(^{-1}\) which corresponds to a period of \(~10\) fs. Optical phonon frequencies are \(~10\) THz - period of \(~100\) fs. Therefore, a typical timestep in MD simulation is on the order of a **femtosecond**.

Using modern computers it is possible to calculate \(10^6 - 10^8\) timesteps. Therefore we can only simulate processes that occur within \(1 - 100\ \text{ns}\). This is a serious limitation for many problems that involve thermally-activated processes, cluster/vapor film deposition, annealing of irradiation damage, etc.

Several methods for acceleration of infrequent thermally activated events have been developed by Voter (Los Alamos), Fichthorn (Penn State), and others. The methods have been applied to study processes of surface diffusion, film deposition, evolution of point defects.
Limitations of the MD technique

Length-scale:

The size of the computational cell is limited by the number of atoms that can be included in the simulation, typically $10^4 - 10^8$. This corresponds to the size of the computational cell on the order of tens of nm. Any structural features of interest and spatial correlation lengths in the simulation should be smaller than the size of the computational cell.

To make sure that the finite size of the computational cell does not introduce any artifacts into the simulation results, one can perform simulations for systems of different size and compare the predicted properties.
Limitations of the MD technique

Due to the limitations on the size of the MD computational cell, an important aspect of any MD simulation is an adequate description of the “interaction” of atoms in the MD computational cell with surrounding “infinite” material. We have to define **boundary conditions** and apply special **methods for temperature and pressure control** in the MD cell (heat and work exchange between the MD computational cell and the surroundings). We will discuss these issues later in the course.
Limitations of MD: Small time- and length-scales

- **Number of atoms** $\sim (\text{size of the system})^3$

- **Computational cost** $\sim (\text{number of atoms})^n$
  \[ n > 1 \]

*Titan* (Oak Ridge Leadership Computing Facility)

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Direct MD simulations is nanostructured materials

(1) **MD simulations of individual structural elements** (nanofibers, nanoparticles, interfacial regions, grain boundaries, etc.) \(\rightarrow\) difficult to predict macroscopic properties of nanomaterials

(2) **Direct large-scale MD simulations** of nanomaterials. Nanocrystalline materials - system with tens of nanograins (~10⁶-10⁹ atoms) can be simulated and the effective properties can be investigated, particularly in the regime of ultrafast mechanical loading (e.g. shock wave) or heating (e.g. by short laser pulse).

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Direct MD simulations is nanostructured materials

Nucleation, growth, and coalescence of voids in dynamic failure in nanocrystalline Cu subjected to shock pulse loading.

Direct MD simulations is nanostructured materials

Bridging the gap: The need for mesoscopic models

Phani et al., Acta Mater. 59, 2172 (2011)
D. Qian et al., APL 76, 2868 (2000)
Hennrich et al., PCCP 4, 2273 (2002)
Bridging the gap: The need for mesoscopic models

Examples of mesoscopic models:

- **Dislocation Dynamics** for early stages of plastic deformation
- **Mesoscopic methods** for evolution of grain structure in polycrystalline materials (e.g. phase field models, cellular automata, kinetic Monte Carlo Potts models)
- **Coarse-grained models** for molecular and biomolecular systems
- **Mesoscopic models** for carbon nanotubes and nanofibrous materials

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First MD simulations

The first simulation using the MD method was reported in 1957 by Alder and Wainwright [Phase transition for a hard sphere system, J. Chem. Phys. 27, 1208-1209, 1957]. They investigated a solid-fluid transition in a system composed of hard spheres interacting by instantaneous collisions.

For a system of 500 particles, simulation of 500 inter-particle collisions took ~ an hour on IBM 704 computer.

solid phase  liquid phase  liquid-vapour-phase
First MD simulations

Continuous repulsive Born-Mayer interaction potential was used for the first time in MD simulation of radiation damage in a Cu target performed at Brookhaven National Lab. in 1960 [J.B. Gibson, A.N. Goland, M. Milgram, and G.H. Vineyard, *Dynamics of radiation damage*, Phys. Rev. **120**, 1229-1253, 1960]. A constant inward force was applied to each atom on the boundary of the crystallite to account for the attractive part for the interatomic interaction. This was probably the first application of the MD method in materials science.

Computational cell composed of 446 to 998 copper atoms was simulated. One integration step took about a minute on an IBM 704 computer.
First MD simulations

Aneesur Rahman in 1964 used Lennard-Jones potential to describe both attractive and repulsive interaction in a system of 864 argon atoms [Phys. Rev. 136, A405-A411, 1964]. The methods of the simulation and analysis of the MD results described in this paper are still used in many present MD simulation studies.

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 ω = 0.25(kBT/ℏ). The shape of the Van Hove function Gₐ(r,t) attains a maximum departure from a Gaussian at about t = 3.0 x 10⁻¹² sec and becomes a Gaussian again at about 10⁻¹¹ sec. The Van Hove function Gₐ(r,t) has been compared with the convolution approximation of Vineyard, showing that this approximation gives a too rapid decay of Gₐ(r,t) with time. A delayed-convolution approximation has been suggested which gives a better fit with Gₐ(r,t); this delayed convolution makes Gₐ(r,t) decay as t¹ at short times and as t at long times.

Pair correlation function, velocity autocorrelation function, and mean square displacement calculated for liquid Ar.
Control Data Corporation (CDC) 3600 at NCAR (1963-1969)

- "beautiful computer with smoked glass panels and a solid and stunning look" from http://www.cisl.ucar.edu/computers/gallery/cdc/3600.jsp
- several million dollars
Current applications of the MD simulation technique

Since the time the MD method was introduced, it has been used to investigate a wide range of problems in different research fields, e.g.

- **Chemistry and Biochemistry**: molecular structures, reactions, drug design, vibrational relaxation and energy transfer, structure of membranes, dynamics of large biomolecules, protein folding, …

- **Statistical Mechanics and Physics**: theory of liquids, correlated many-body motion, properties of statistical ensembles, structure and properties of small clusters, phase transitions.

- **Materials Science**: point, linear, and planar defects in crystals and their interactions, microscopic mechanisms of fracture, surface reconstruction, melting and faceting, film growth, friction, …

Shockwave-induced plasticity  [B.L. Holian and P.S. Lomdahl, Science 280, 2085 (1998)]

Actin filaments, simulation by W. Wriggers, University of Illinois
**MD simulation of human crowds**

Is it possible to reproduce the collective behavior of a crowd of pedestrians with a MD model?

A “social potential” can be introduced to describe interaction of humans with their neighbors in a crowd.

The interaction should be velocity-dependent: acceleration is very different for head on and parallel trajectories

empirical potential based on statistical analysis of crowd data sets:

\[ E(\tau) = k \tau^{-2} e^{-\tau/\tau_0} \]

where \( \tau \) is time to collision, i.e., time for which two pedestrians could continue walking with their current velocities before colliding

if pedestrians = discs with radii \( R_i \) and \( R_j \), \( \tau = (b - d^{1/2})/a \), where

\[ a = |v_{ij}|^2, \quad b = -x_{ij} \cdot v_{ij}, \]

\[ c = |x_{ij}|^2 - (R_i + R_j)^2, \quad \text{and} \quad d = b^2 - ac, \]

then:

\[ \vec{F}_{ij} = -\nabla_{x_{ij}} E(\tau) = -\nabla_{x_{ij}} \left( k \tau^{-2} e^{-\tau/\tau_0} \right) = -\left[ \frac{ke^{-\tau/\tau_0}}{v_{ij}^2 \tau^2} \left( \frac{2}{\tau} + \frac{1}{\tau_0} \right) \right] \vec{v}_{ij} - \frac{\vec{v}_{ij}^2 \vec{x}_{ij} - (\vec{x}_{ij} \cdot \vec{v}_{ij}) \vec{v}_{ij}}{\sqrt{\left(\vec{x}_{ij} \cdot \vec{v}_{ij}\right)^2 - \vec{v}_{ij}^2 (\vec{x}_{ij}^2 - (R_i + R_j)^2)}} \]

An additional driving force defining the desired direction of motion is also assigned to each pedestrian.

**PRL, 113, 238701, 2014**
MD: Record simulations (length-scale): **Trillions (?)** of atoms

**Trillion-atom molecular dynamics**

Germann and Kadau

2.5×2.5×2.5 μm³ cube

Simulation of a cube composed of \(10^{12}\) Lennard-Jones (LJ) atoms (\(10^4 \times 10^4 \times 10^4\) atoms, edge length of about 2.5μm) arranged into simple cubic lattice was performed in 2008 by T. C. Germann and K. Kadau ["Int. J. Mod. Phys. C" **19**, 1315 (2008)] on 212,992 processors of LLNL’s BlueGene/L cluster. The test run took \(~30\) minutes for 40 timesteps of integration.

**Ductile failure of a FCC solid under tension**

The system is a slab with 1008 atoms along the three orthogonal sides, the total number of atoms is 1,023,103,872, interaction is described by Lennard-Jones potential. The total simulation time is 200,000 timesteps. It takes 1.7 seconds per timestep for a 4096-node simulation on ASCI White computer (~four clock-days of total simulation time).

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MD: Record simulations (length-scale): Billions of atoms

MD simulation of bubble nucleation and growth

LJ potential with cutoff at $3\sigma$,
1,449,776,020 atoms

1964 864 argon atoms
[Rahman, Phys. Rev. 136, A405, 1964]

1,000,000,000,000 atoms 2014

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MD: Record simulations (time-scale): quest for milliseconds

Protein folding
The protein-folding problem is one of the major challenges of molecular biology. Functionality of proteins is directly related to their conformation - the complex folds allow proteins to latch onto other molecules and carry out its biological role. To investigate the protein folding problem in MD simulation one has to follow the evolution of a large molecule in a solution for at least microseconds.

MD simulation of the folding of the villin headpiece, one of the fastest-folding proteins

Folding@home: a distributed computing project - people from around the world download and run software to make a virtual “supercomputer,” allowing for simulations of milliseconds of folding time. http://folding.stanford.edu/