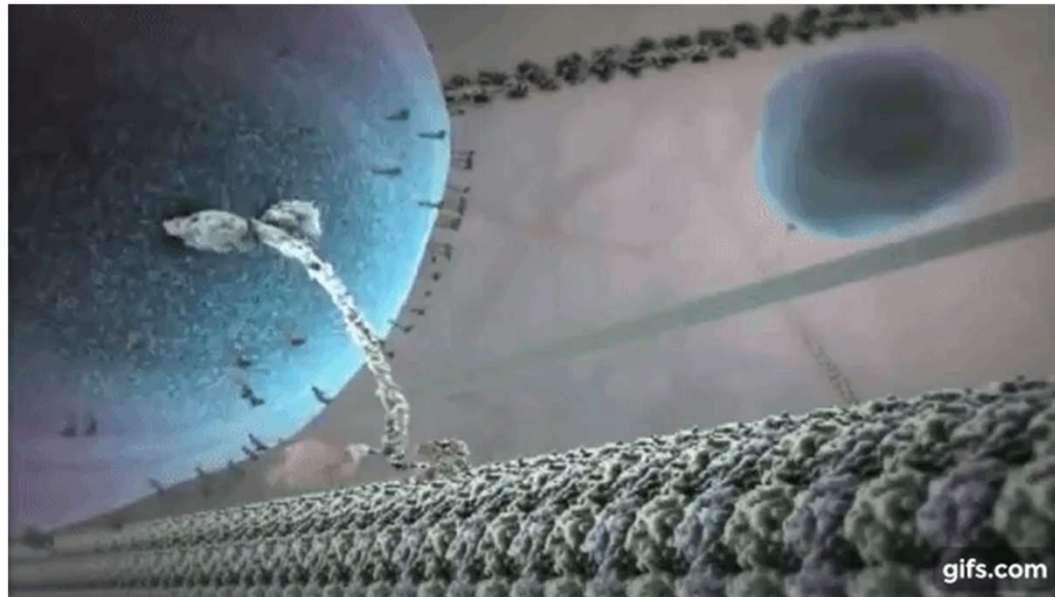# Lecture 2

Let's Learn diverse scales of Length and Time

In nature's dance, both grand and small,
It's length and time that rule it all.
From atoms' twitch to stars that roam,
Each tale unfolds in scale and tome.

Motor protein walking on the microtubule.

The Aim of Simulation Technique is to provide a microscopic description of **collective phenomena** occurring in the universe.

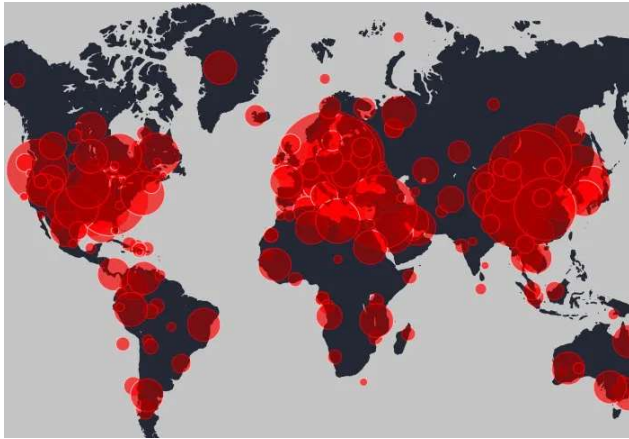

Simulation of Bacterial Swarming

Flocks of Birds: Collective Motion
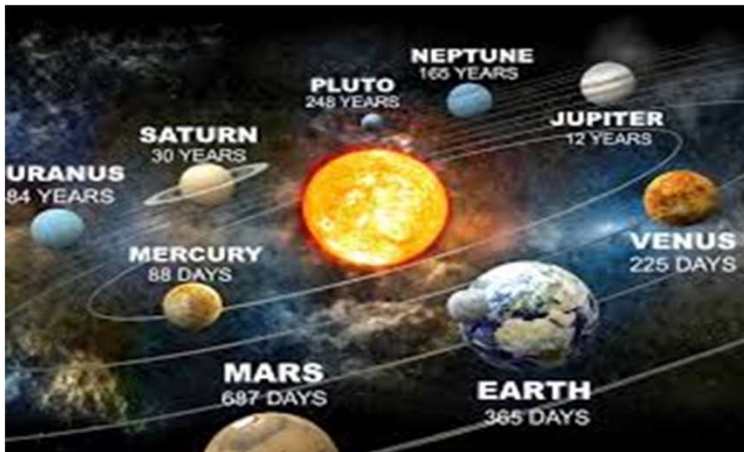→implicative to active matter physics
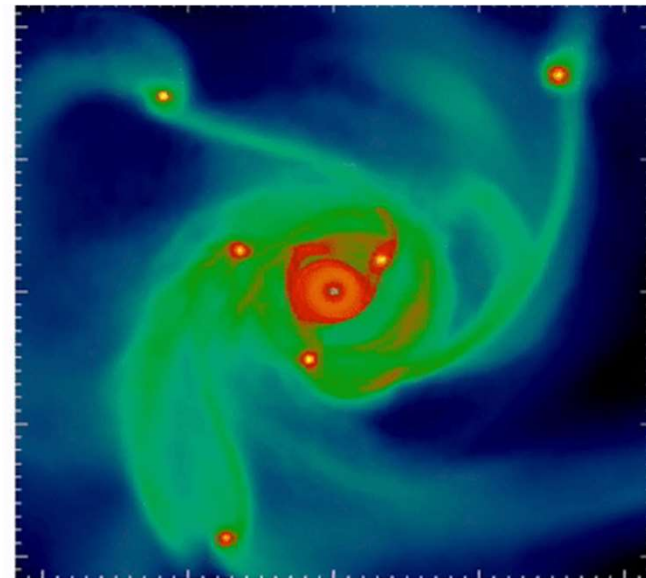
Tornedo watch

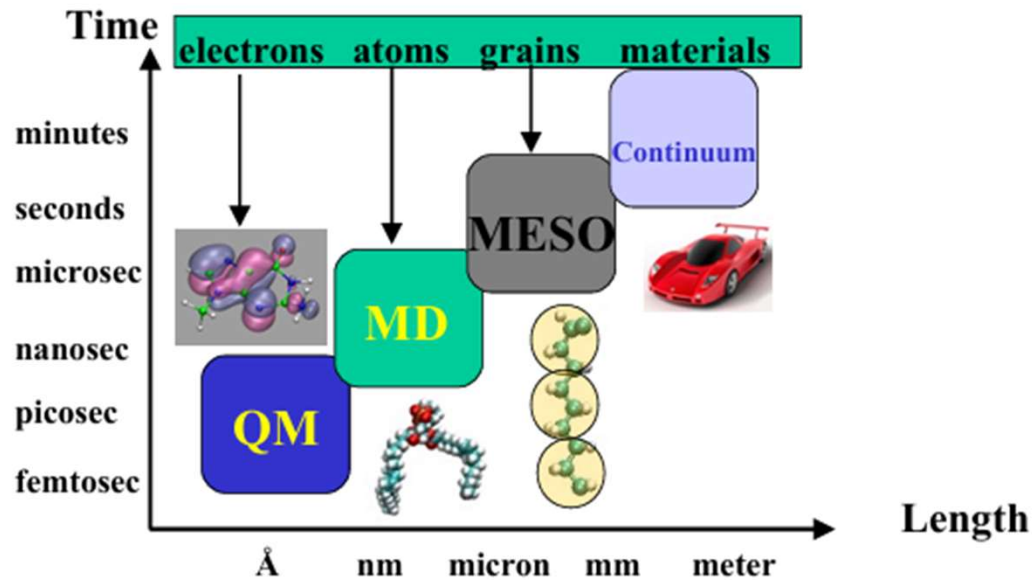Infectious disease spread simulation and prediction

Trajectory simulation of planets

Simulation of milky way-like galaxy forming

Length-scale and time scale associated with a phenomena and various multi-scale modelling approaches

High quality multi-scale simulations
➢ Quantum Mechanical calculations
➢ First Principles force fields
➢ Large scale Molecular Dyanmics (MD) simulations
➢ Mesoscopic modeling (Coarse-grained MD, DPD, BD)
➢ Macroscopic modeling (finite elements, continuum simulations, Lattice Boltzmann)

Need for Molecular simulation

➢ There are no general method for solving complex many body problems.
➢ Hamiltonian is unknown, until we solve the quantum many-body problem!
➢ In fact, in most cases not possible and requires lots of approximations.
➢ Molecular simulations provides trust-worthy solution for such complex many body systems.
➢ In many cases experiments are limited and expensive.
➢ Simulations can complement the experiment.
➢ Simulation can give molecular level understanding even at a single molecule level

"The general theory of quantum mechanics is now almost complete. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."

Dirac, 1929

Simulation Methodology

Semi-empirical

↓

Give us the phenomena and invent a model to mimic the problem.

ab initio methods

↓

Maxwell, Boltzmann and Schrödinger gave us the model. All we must do is numerically solve the mathematical problem and determine the properties.

These two approaches can be combined to make what is termed as Multi-scale modeling strategies

$$\hat{H} = \hat{T}_{\text{nuc}} + \hat{T}_{\text{el}} + \hat{V}_{\text{nuc-nuc}} + \hat{V}_{\text{el-el}} + \hat{V}_{\text{nuc-el}}$$

Expanded, this is:

$$\hat{H} = -\sum_{I} \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_{i} \frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}$$

Born-Oppenheimer Approximation:

In practice (especially in AIMD), one **separates nuclear and electronic motion**, solving the **electronic Schrödinger equation** at fixed nuclear positions:

$$\hat{H}_{\text{el}} \Psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) = E_{\text{el}}(\{\mathbf{R}_I\}) \Psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$$

The **electronic energy** $E_{\text{el}}(\{\mathbf{R}_I\})$ then becomes the **potential energy surface (PES)** on which the nuclei move.

Ref: D. Marx and J. Hutter's textbook *"Ab Initio Molecular Dynamics: Basic Theory and Advanced Methods"* (Cambridge University Press, 2009)

QM (ab initio molecular dynamics)
- Also called first-principles MD or Born-Oppenheimer MD.
- It explicitly calculates the electronic structure (orbitals, electron density, etc.) on-the-fly during the simulation using quantum mechanics.
- Examples: Car-Parrinello MD, DFT-based MD.

Feature	Description
Degrees of Freedom	Electrons and Nuclei (electrons treated with basis sets).
Scaling with system size (N)	Computational cost typically scales as N^3 or N^4 (where N = number of electrons or atoms). Some methods can achieve linear scaling, but with a very high computational cost per step.
Time step	Very small: ~0.01 fs (10^{-2} fs) because electron dynamics are very fast.
System size	Typically small, e.g., 64-256 water molecules.
Simulation duration	Short: ~100 ps is considered long.
Main limitation	Extremely expensive computationally, even with supercomputers.

Classical Atomistic Molecular Dynamics:

➤ Simulates atoms as classical particles governed by Newton's laws.
➤ Uses empirical force fields to compute interatomic forces (e.g., bond stretching, van der Waals, Coulomb).
➤ No electrons; energy is precomputed using parameter sets.

Feature	Description
Degrees of Freedom	Only atomic nuclei (atoms).
Scaling with system size	~N^2 due to pairwise interactions, but can be reduced using algorithms (e.g., cutoff radius, Ewald summation, Particle-Mesh Ewald for Coulomb).
Time step	~0.5–2 fs, depending on bond stiffness.
System size	Can simulate large systems: up to 50,000 atoms on a single CPU.
Simulation duration	Typically up to 1 ns, can go to microseconds with good parallelization.
Parallel Codes	Efficient and widely used: LAMMPS, AMBER, GROMACS, NAMD (many are open-source or freely available for academics).

What is Molecular Dynamics Simulations?
It's nothing but solving Newtonian Equation of Motion

$$F_A = \frac{dp_A}{dt} = m\frac{dv_A}{dt} = m\frac{d^2 r_A}{dt^2}$$

How can we get the force? → Calculate forces on all atoms from potential

$$F_A\left(r_A(t)\right) = -\nabla V\left(r_A(t)\right)$$

Force can be obtained as the negative gradient of the interaction potential on that atom.

By integrating Newton's equation with respect to time by using different algorithms such as verlet, leap-frog etc., we can obtain the velocity and position of particle A at any instant of time.

Inter-molecular Potential and Requirement of Statistical Mechanics

Once the inter-atomic or inter-molecular potential is determined, Statistical Mechanics can provide, in principle, all the thermodynamic functions (or, macroscopic properties) of the system.
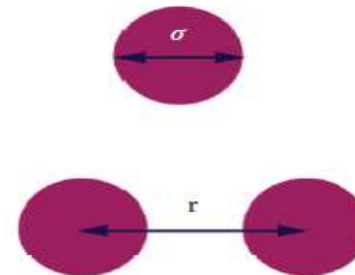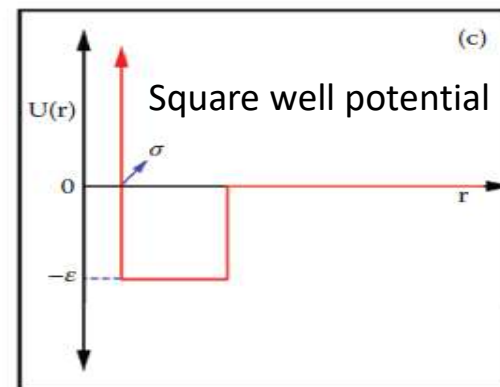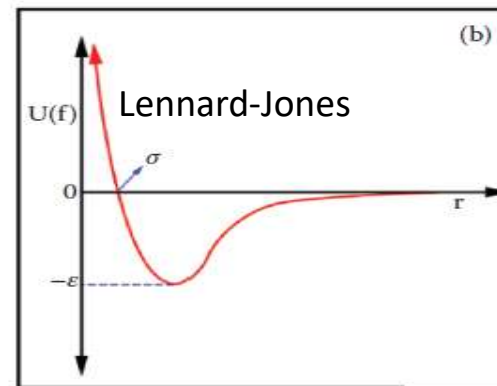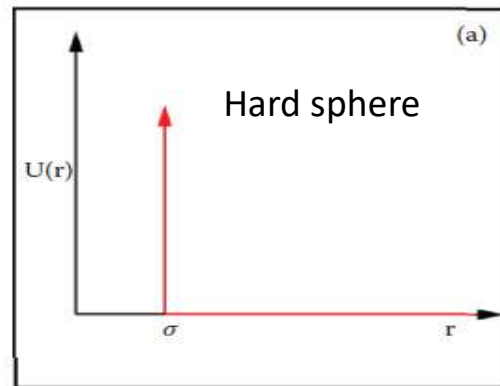
Lennard Jones Potential –A Classic Form of Non-bonded Potential
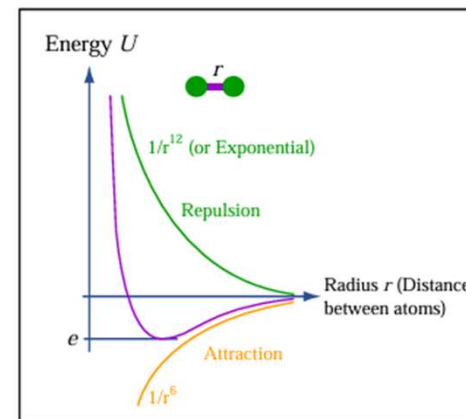
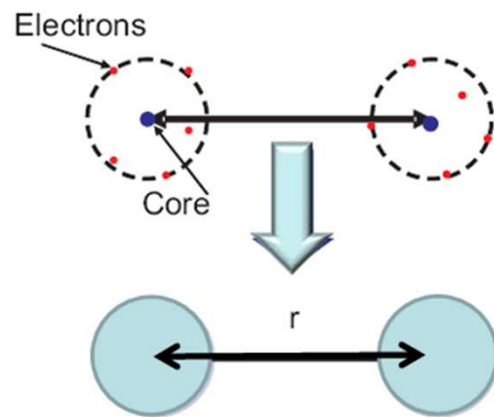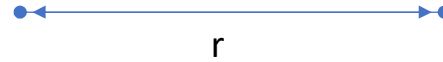- Consider energy landscape due to chemical bonds

Image by MIT OpenCourseWare.

Induced dipole-induced dipole

Attraction: Due to London dispersion forces (a type of van der Waals force)
Repulsion: Pauli exclusion (too many electrons in small volume)

$$V(r^N) = \sum_{coulomb} \frac{1}{4\pi\varepsilon_0} \frac{q_A q_B}{r_{AB}}$$

$$V(r^N) = \sum_{vdW} 4\varepsilon_{AB} \left[\left(\frac{\sigma_{AB}}{r_{AB}} \right)^{12} - \left(\frac{\sigma_{AB}}{r_{AB}} \right)^6 \right]$$

r

$$V(r^N) = \sum_{bond} V_{AB} + \sum_{angle} V_{ABC} + \sum_{dihedral} V_{ABCD} + \sum_{non-bonded} V_{AB}$$

$$= \sum_{bond} \frac{1}{2} K_{AB} \left(r_{AB} - r_{AB}^{eq} \right)^2 + \sum_{angle} \frac{1}{2} K_{ABC} \left(\theta_{ABC} - \theta_{ABC}^{eq} \right)^2$$

$$+ \sum_{improper} \frac{1}{2} K_{ABCD} \left(\phi - \phi_0 \right)^2 + \sum_{coulomb} \frac{1}{4\pi\varepsilon_0} \frac{q_A q_B}{r_{AB}} + \sum_{vdW} 4\varepsilon_{AB} \left[\left(\frac{\sigma_{AB}}{r_{AB}} \right)^{12} - \left(\frac{\sigma_{AB}}{r_{AB}} \right)^6 \right]$$

Bond stretching

Proper dihedral torsion

Angle bending

Improper dihedral torsion