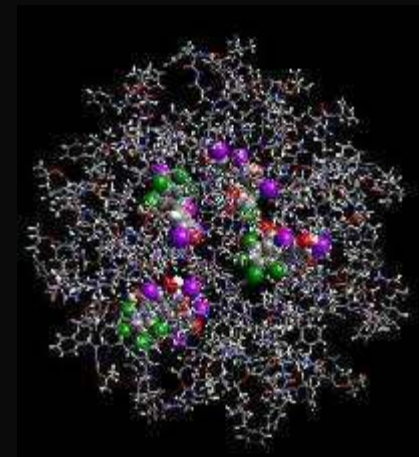


Multiscale modelling, Molecular Dynamics(MD)
&
Density Functional Theory(DFT):
An introduction

Material and Mechanical Science and Engineering

March 2013



Collaborators

USM



Dr. TL Yoon



Prof SK Lai,
National Central University,
Taiwan



JJ



Wei Chun



Prof Nazarov,
Institute of Physics of Moldova

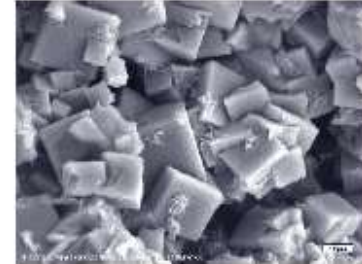
Examples of Crystals



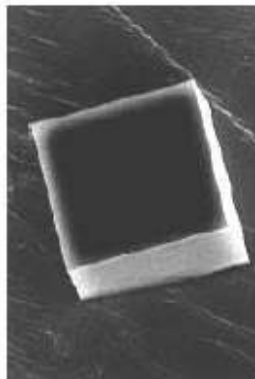
Snow



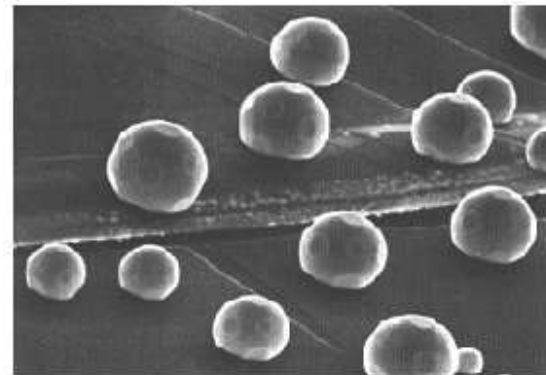
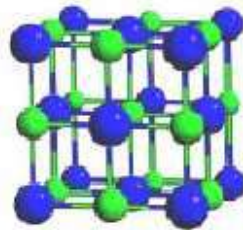
Quartz



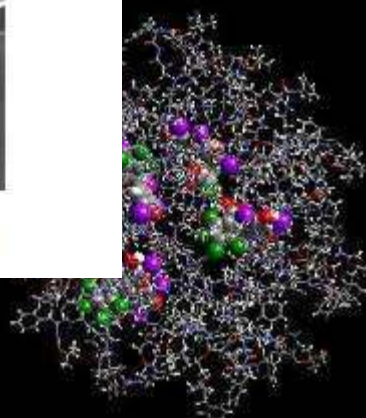
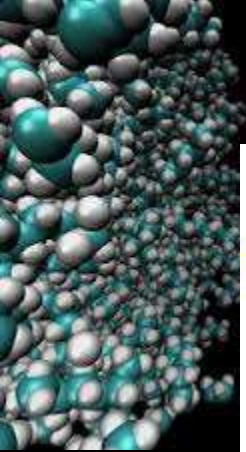
Copper oxide



Salt (NaCl) crystal



Gold (Au) crystals at 1000 C



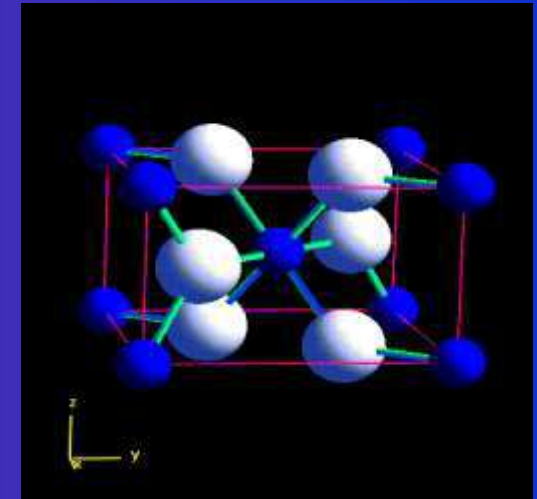
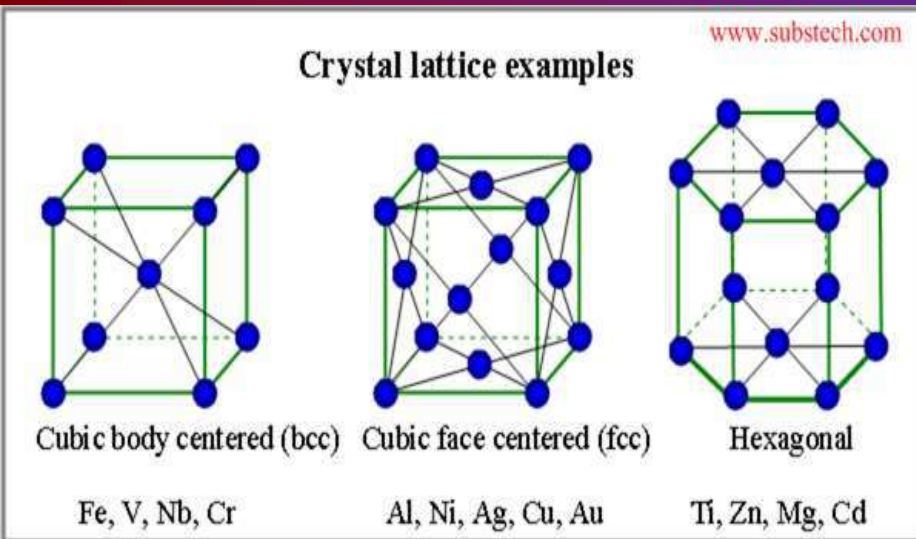
Keyword

Modeling – systems or process, often in mathematical terms, devised to facilitate calculations and predictions

Molecular modeling – ways to mimic the behavior of molecules and molecular system

-- one way is through computational techniques

Crystal structure



TiO₂, Rutile

Space group: P42/mnm

Number: 136

Unit cell dimensions:

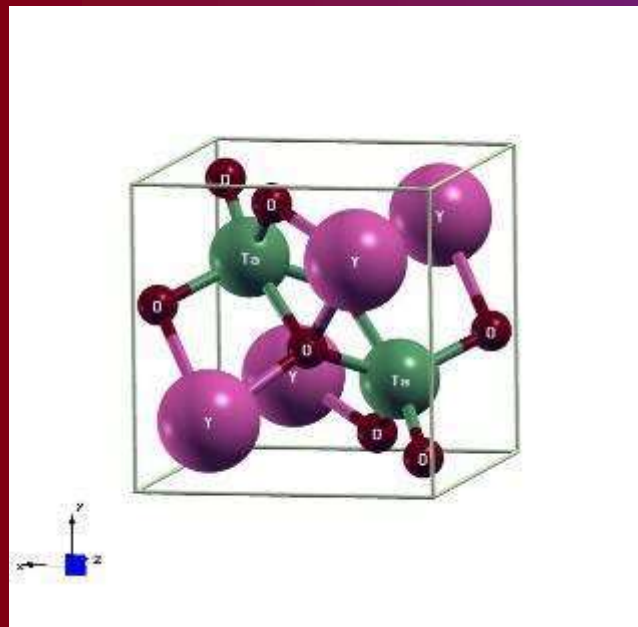
a = 4.594 Å, c = 2.958 Å

Atomic positions:

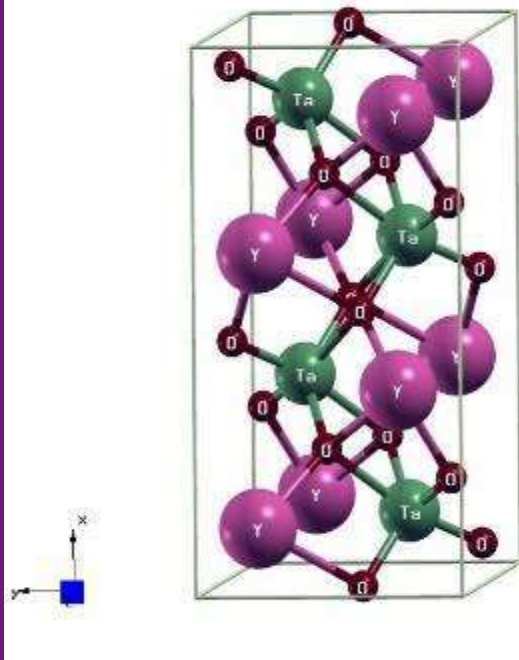
Ti at (0, 0, 0)

O at (0.3053, 0.3053, 0)

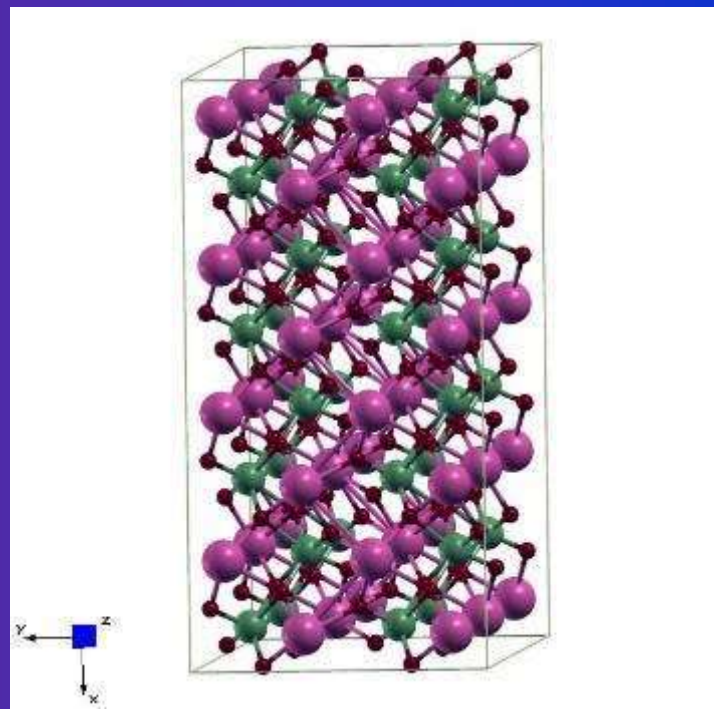
Unit cell and supercell



Unitcell
1x1x1

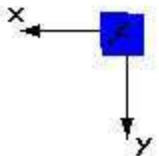
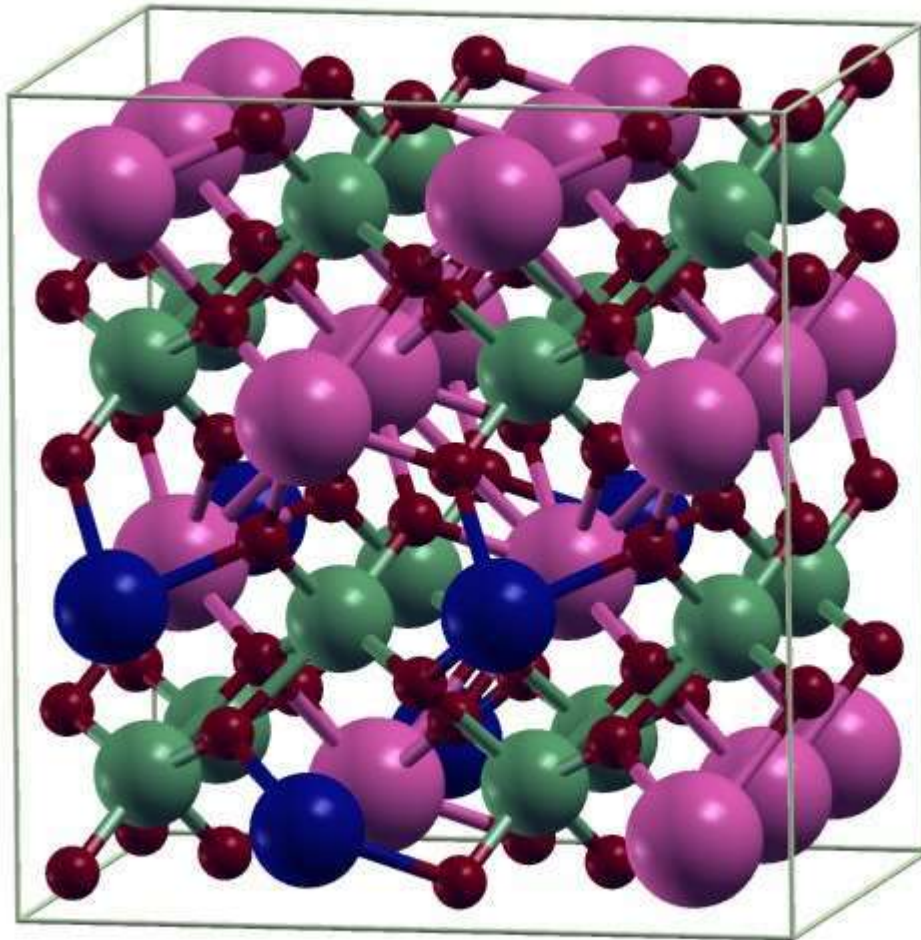


Supercell
2x1x1



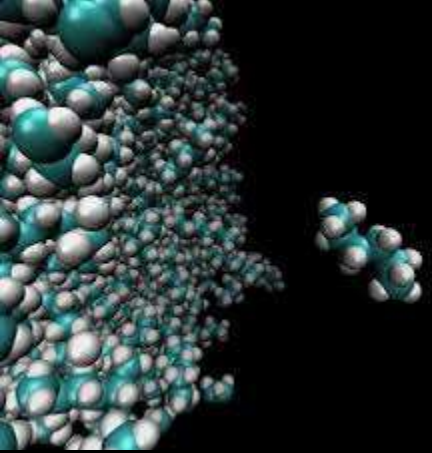
Supercell
2x2x2

Impurities
through supercell



Replace 3 atoms
of Y with Eu

Multiscale modeling

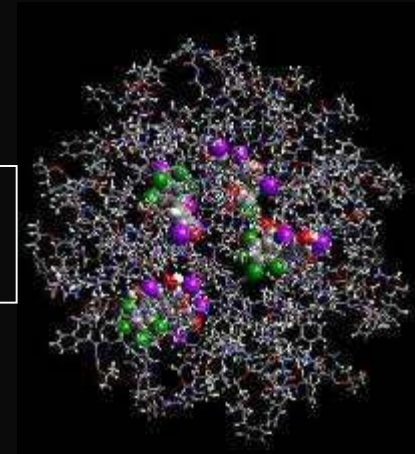


Material Science
Experimental Methods

Multiscale Modeling

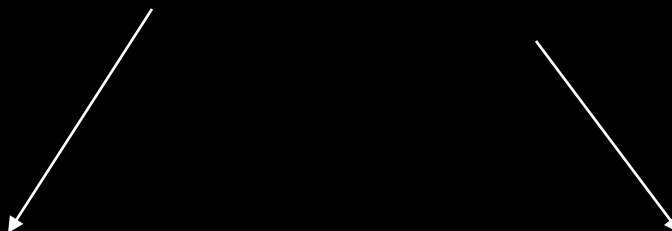
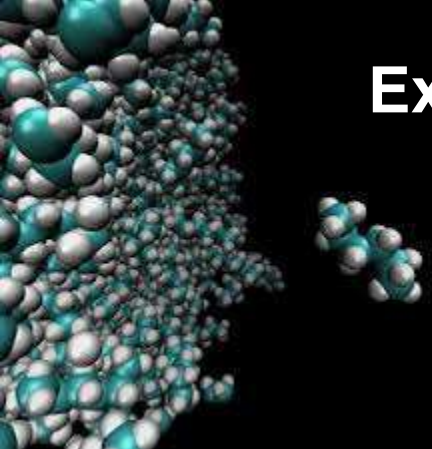
Solid State Physics
Computational - Theoretical

Mechanical Engineering
Modeling - Continuum



Experiment vs Ab initio

Computational Material Science & Engineering



Using empirical or experimentally derived quantities

Empirical or semiempirical

- Interpolate and extrapolate from known materials

Not using any of these

Ab initio/first principle methods

- Predicting trends across the materials
- Predicting new materials
- Theoretical results is used for initial calibration of the experimental setup



Ab initio



“First principle” means things that cannot be deduced from any other

Ab initio : “From the beginning”

the only input information in “First Principle”
calculation

TiO₂, Rutile

Space group: P42/mnm

Number: 136

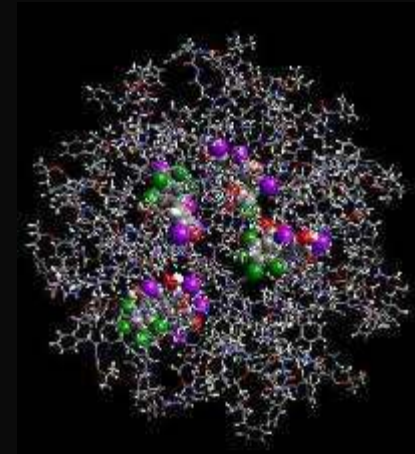
Unit cell dimensions:

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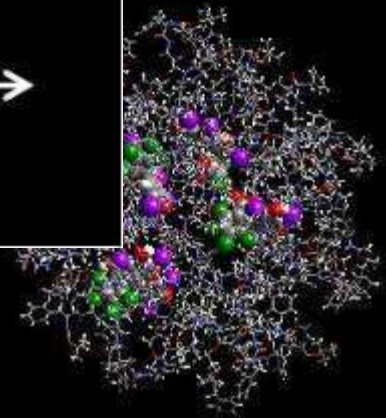
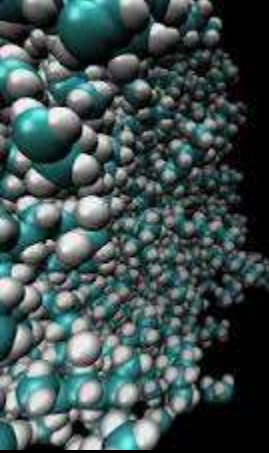
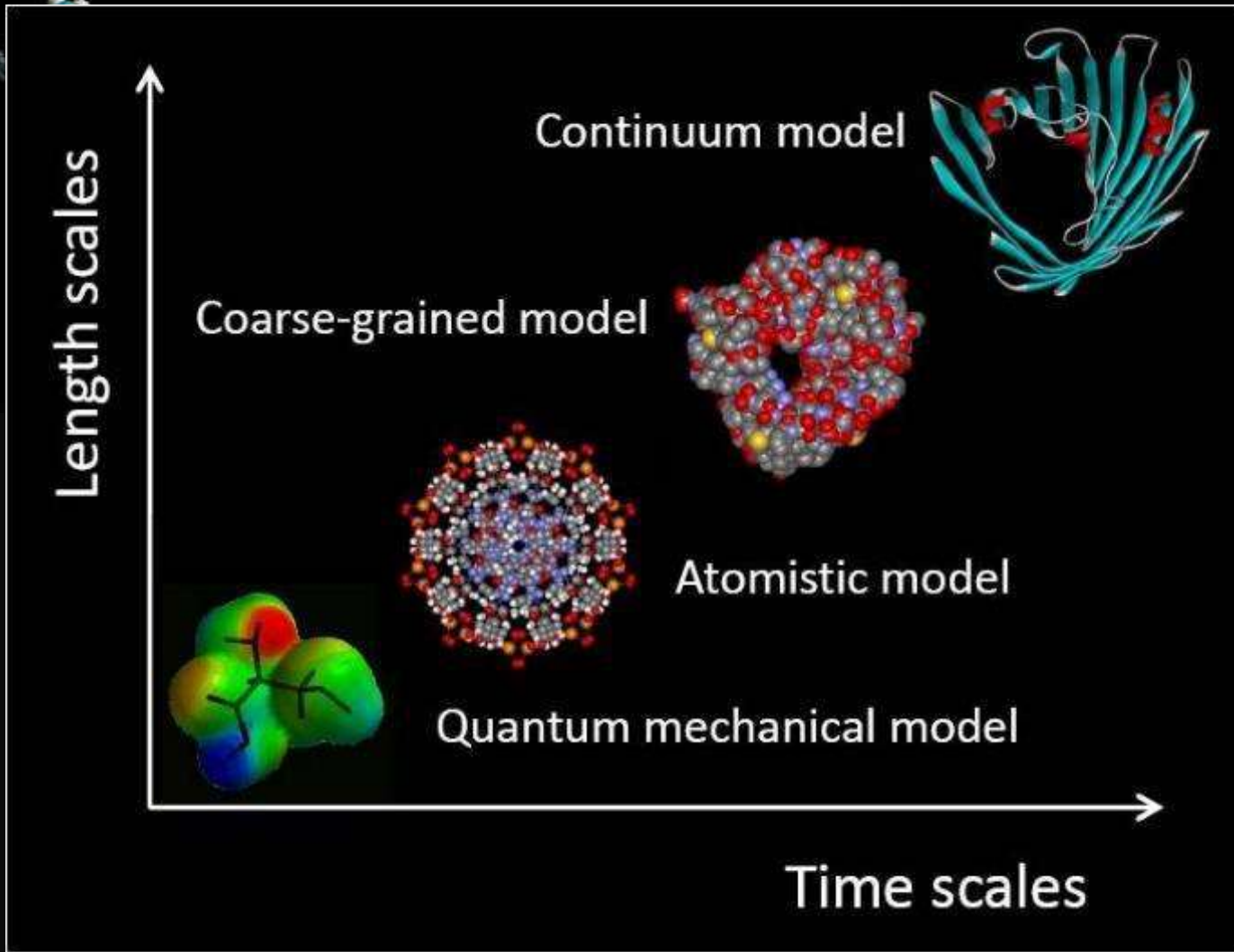
Atomic positions:

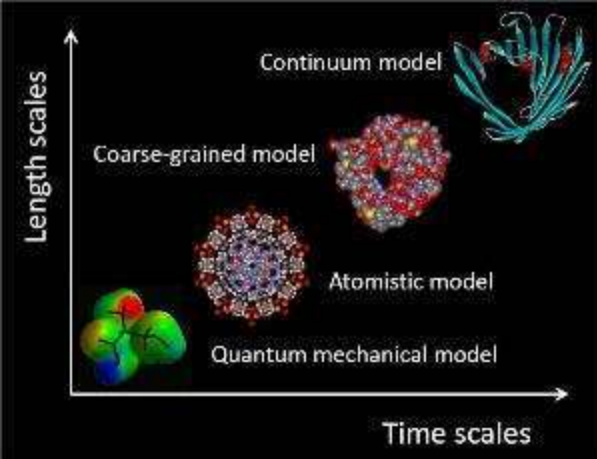
Ti at (0, 0, 0)

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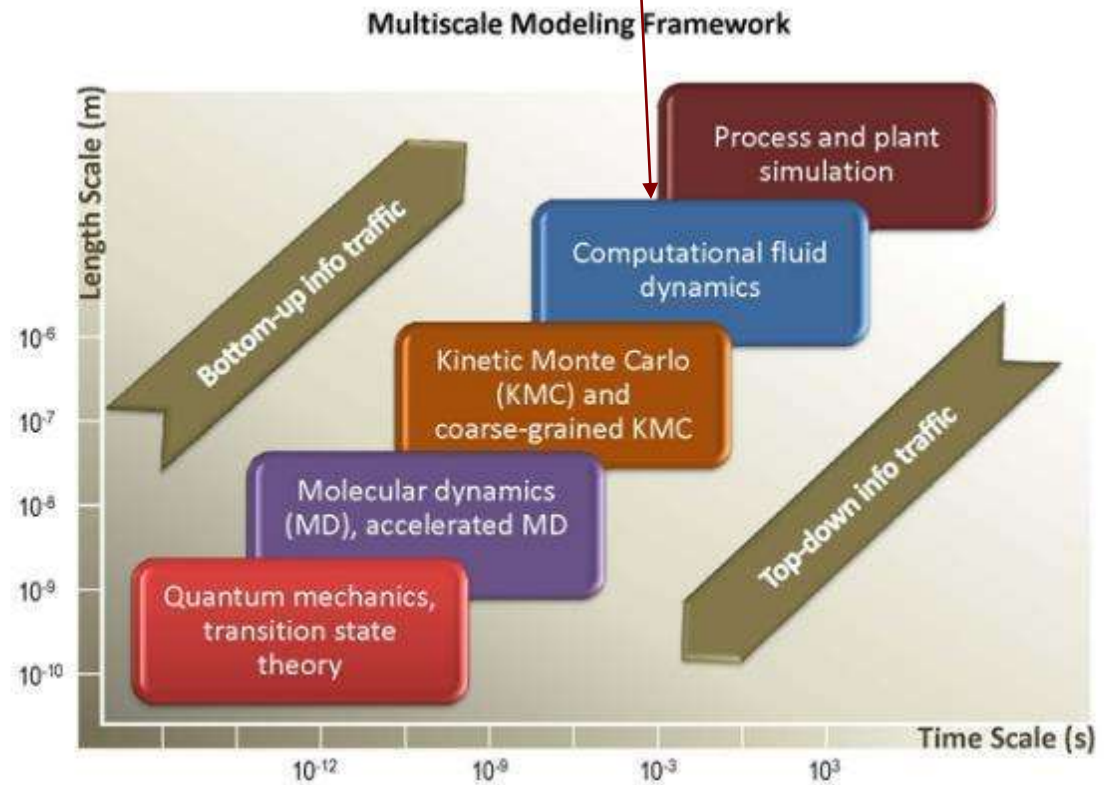


Multiscale modeling

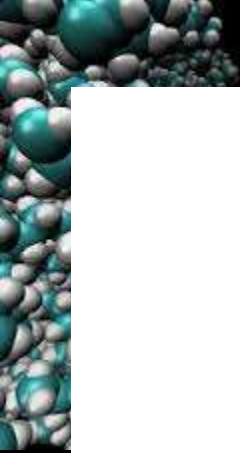
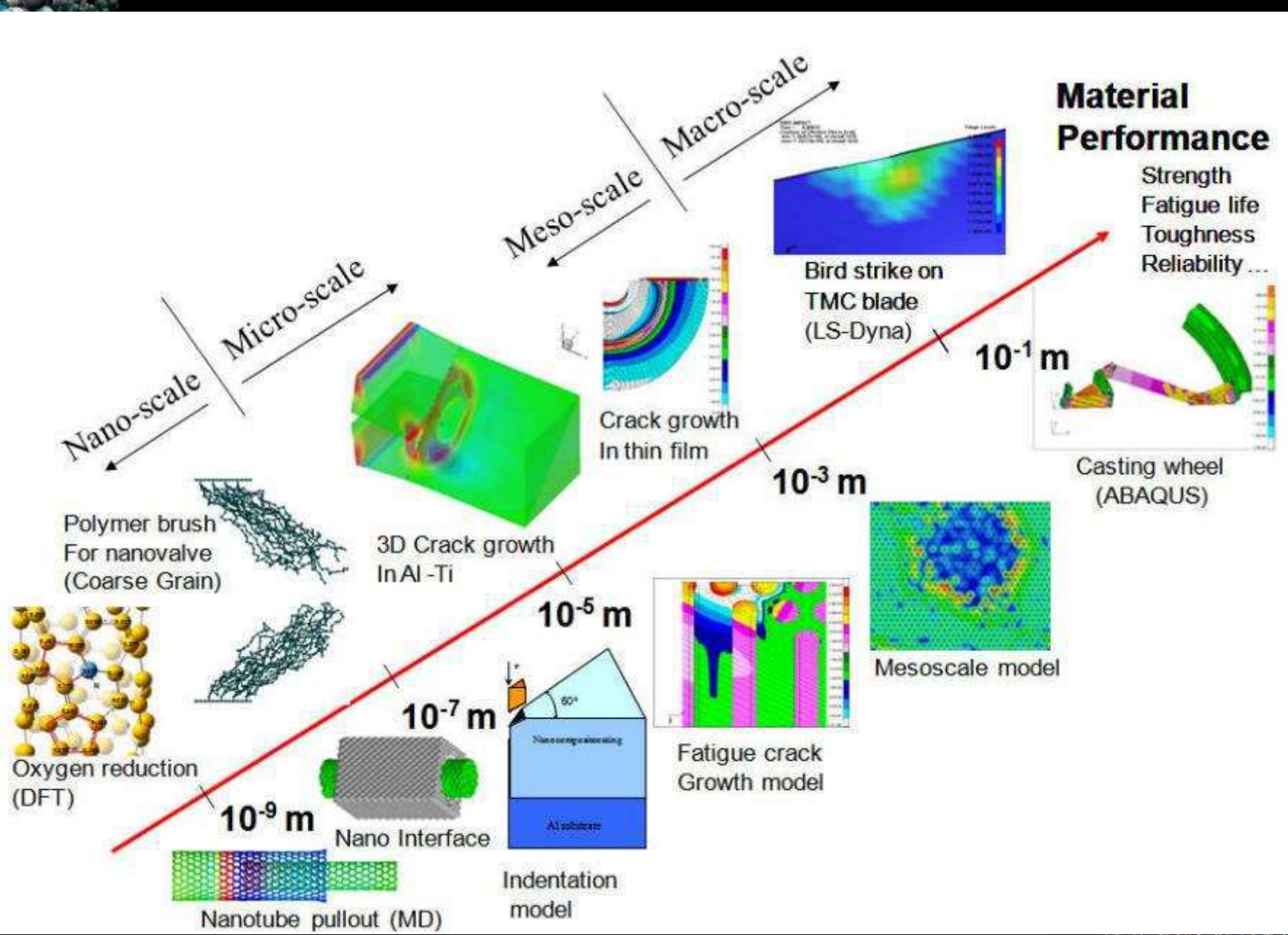




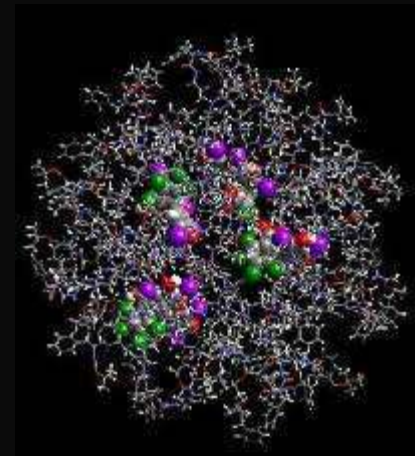
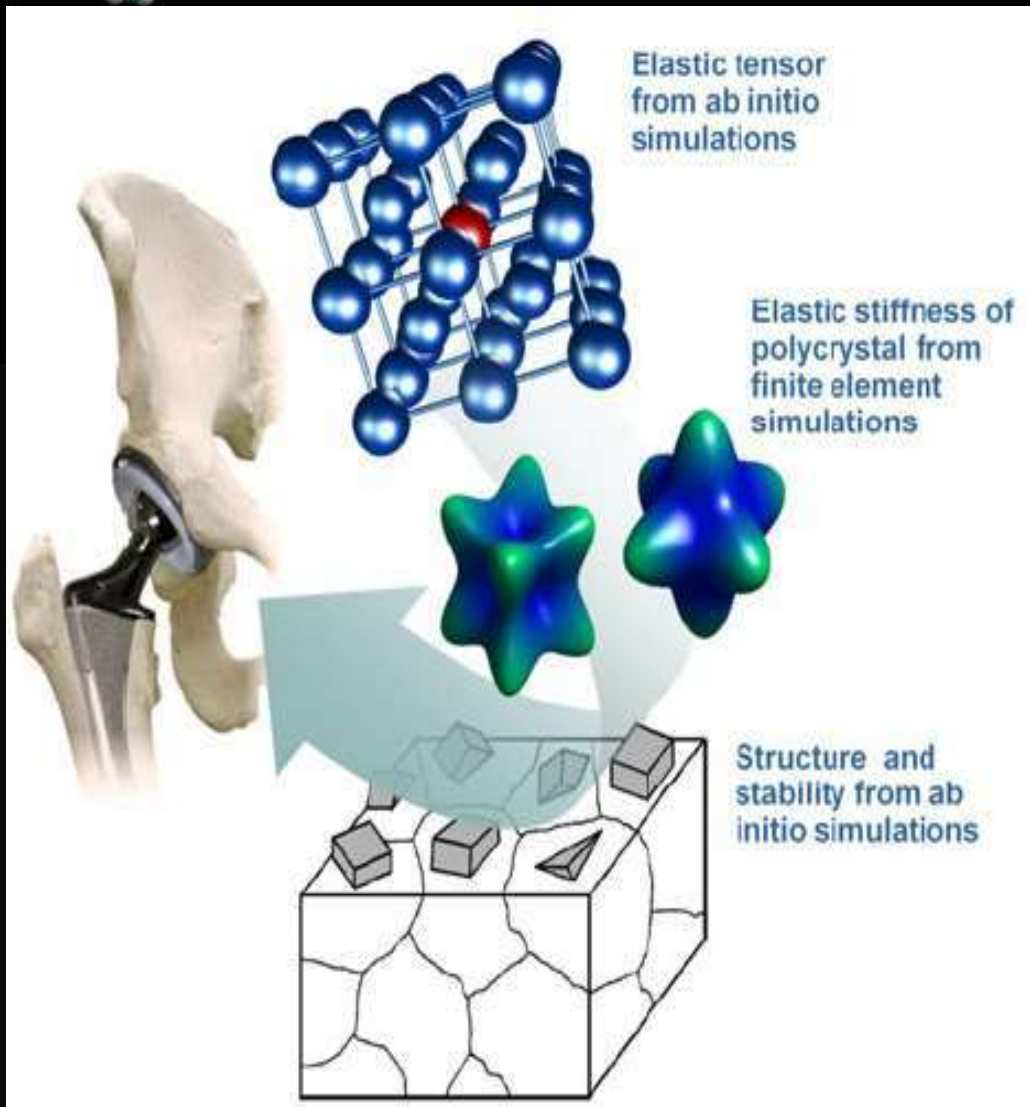
CFD



Multiscale modeling framework for catalytic processes that exhibit strong coupling between scales.
Adapted from Vlachos, *Adv. Chem. Eng.* 30, 1-61 (2005)



Ab initio guided alloy and product design: Development of new implant biomaterials



Advanced High Strength Steel Project

Materials Design of Steel Alloys

Researchers: Seong-Gon Kim, Hongjoo Rhee, Sungho Kim, Mark F. Horstemeyer

Goal: Design a new high-strength steel alloy with improved strength and ductility for automotive applications.

Objectives: (1) Identify the **fundamental mechanisms** at quantum mechanical and micromechanical level that determine overall strength and ductility of steel alloys. (2) Investigate the **interaction among different phases** of high-strength steel alloys. (3) Investigate the **effect of micro-alloying elements** to the material properties of high-strength steel alloys. (4) Investigate the **effect of various strengthening mechanisms** to the material properties of high-strength steel alloys.

Approach:

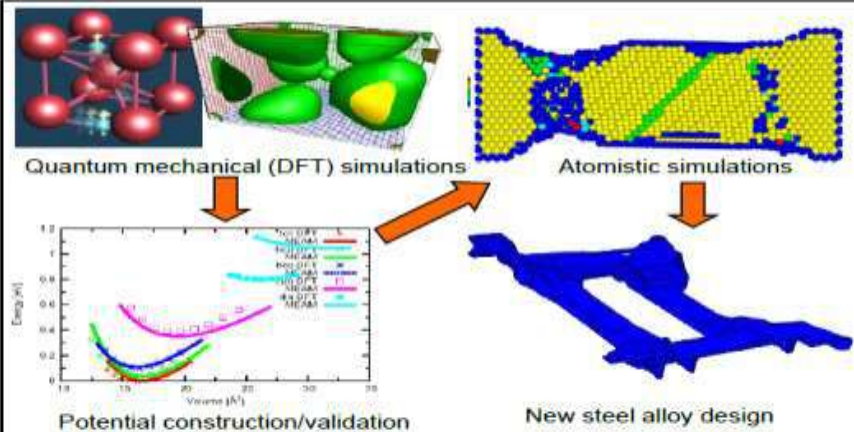
-Use a **hierarchical multi-scale methodology** to investigate the effect of precipitates and additives to the overall **strength** and **ductility** in steel alloy design for automotive applications.

-Critical issues being addressed include: selection of key micro-alloying elements, interaction of precipitate and matrix phases, and ultimately composition-structure-property relationship.

-**Quantum mechanical first-principles simulations** based on **Density Functional Theory (DFT)** will be performed.

-Accurate atomistic simulations will be performed using **Modified Embedded Atom Method (MEAM)** and **force-matching-embedded-atom-method (FMEAM)** potentials.

-**Large scale atomistic simulations** will be conducted to study the effect that size, shape, and volume fraction of different inclusion particles have on the material properties of steel alloys.



- **Subtask 6.1** -- Construct and validate reliable inter-atomic potentials to model various phases of high-strength steel alloys
- **Subtask 6.2** -- Perform electronic and atomistic simulations to obtain the electronic, structural and mechanical properties of the **main phases** of steel alloys.
- **Subtask 6.3** -- Perform electronic and atomistic simulations to investigate the **interactions between main phases** of high-strength steel alloys.
- **Subtask 6.4** -- Perform electronic and atomistic simulations to investigate the effect of **microalloying** of high-strength steel alloys.
- **Subtask 6.5** -- Perform experiments to investigate the effect of various **strengthening mechanisms** to the material properties of high-strength steel alloys.

Density Functional Theory (DFT)

= Quantum Mechanics modeling used in physics and chemistry to investigate electronic structure (especially the ground state) of many body systems (atoms, molecules, crystals, and etc)

DFT

= 2 Hohenberg-Kohn theorems (involving quantum mechanics)
+ computer simulation

Choosing a simulation package

Package-License-Language-Basis-Periodic?-DFT?

Wien2k – Commercial – Fortran/C – FP+(L)APW+lo – 3d – Yes

VASP – Commercial/Education – Fortran – PW – Any - Yes

Density functional theory

Time-independent Schrodinger Equation

$$\hat{H} = -\sum_{k=1}^M \frac{\hbar^2}{2M_k} \nabla_{\vec{R}_k}^2 - \sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_{\vec{r}_i}^2 + \frac{1}{2} \sum_{k_1 \neq k_2=1}^M \frac{1}{4\pi\epsilon_o} \frac{Z_{k_1} Z_{k_2} e^2}{|\vec{R}_{k_1} - \vec{R}_{k_2}|}$$

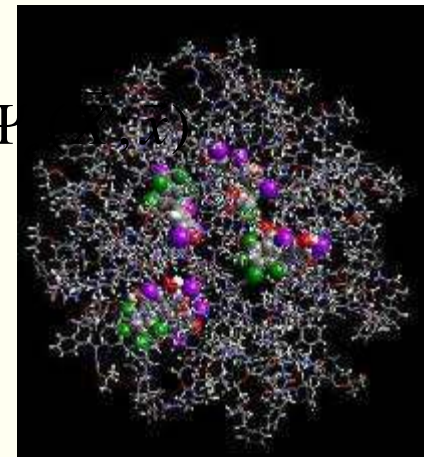
$$+ \frac{1}{2} \sum_{i_1 \neq i_2=1}^N \frac{1}{4\pi\epsilon_o} \frac{e^2}{|\vec{r}_{i_1} - \vec{r}_{i_2}|} - \sum_{k=1}^M \sum_{i=1}^N \frac{1}{4\pi\epsilon_o} \frac{Z_k e^2}{|\vec{R}_k - \vec{r}_i|}$$

Within the Born-Oppenheimer Approximation

$$+ \frac{1}{2} \sum_{i_1 \neq i_2=1}^N \frac{1}{4\pi\epsilon_o} \frac{e^2}{|\vec{r}_{i_1} - \vec{r}_{i_2}|} - \sum_{k=1}^M \sum_{i=1}^N \frac{1}{4\pi\epsilon_o} \frac{Z_k e^2}{|\vec{R}_k - \vec{r}_i|}] \Psi$$

$$= E_e(\vec{X}) \Psi_e(\vec{X}; \vec{x})$$

Nuclei are treated classically
They go in the external potential



Using atomic unit

$$\left[-\sum_{i=1}^N \frac{1}{2} \nabla_{\vec{r}_i}^2 + \frac{1}{2} \sum_{i_1 \neq i_2=1}^N \frac{1}{|\vec{r}_{i_1} - \vec{r}_{i_2}|} - \sum_{k=1}^M \sum_{i=1}^N \frac{Z_k}{|\vec{R}_k - \vec{r}_i|} \right] \Psi_e(\vec{X}; \vec{x}) = E_e(\vec{X}) \Psi_e(\vec{X}; \vec{x})$$

A molecule of CO₂ needs 66-dimensional function

Nanocluster of 100 Pt atoms, 23,000 dimensions

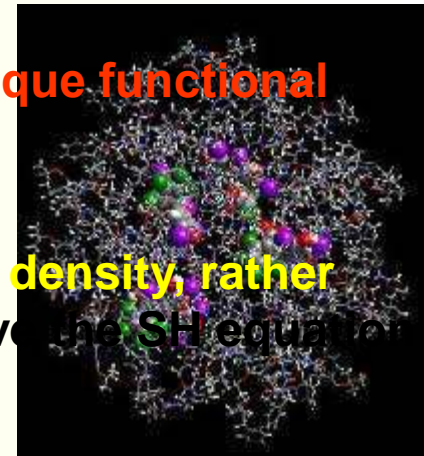
What dft can do?

Mapping *any* interacting many-body system exactly to a much easier-to-solve non-interacting problem

Kohn-Sham theorem

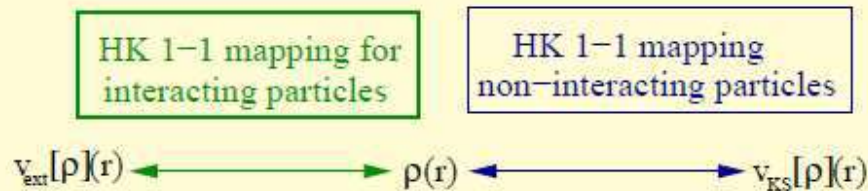
The ground-state energy from Scrodinger's equation is a unique functional of the electron density,

=> Finding a function of three spatial variables, the **electron density**, rather than a function of 3N variables of the wavefunction, will solve the SH equation



Functional vs. Function

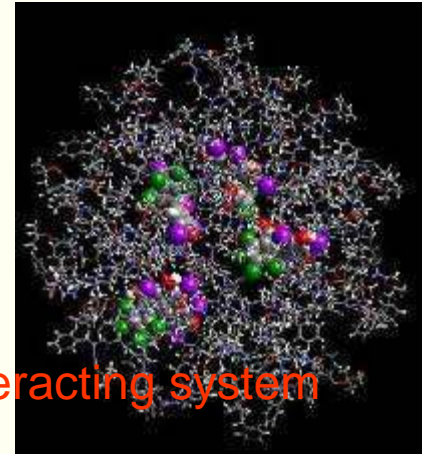
- Function maps a variable to a result
 - For example: $g(x) \rightarrow y$
- Functional maps a function to a result
 - For example: $f[n(r)] \rightarrow y$



Essence

The density of a system of interacting particles can be calculated exactly as the density of an auxiliary system of **non-interacting** particles

⇒ Reformulation in terms of **single-particle orbitals!**



A non-interacting system should have the same ground state as interacting system

2. The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the SH equation

So we say that, the wavefunction is a single-electron wavefunction,

and the energy functional is written as

the original proof is valid for local, spin-independent external potential, non-degenerate ground state there exist extensions to degenerate ground states, spin-dependent, magnetic systems, etc.

$$\begin{aligned}
 E[\{\psi_i\}] = & 2 \sum_i \int \psi_i \left(-\frac{\hbar^2}{2m} \right) \nabla^2 \psi_i d^3 r && \text{Kinetic energy of the electron} \\
 & + \int V_{ion}(r) n(r) d^3 r && \text{Coulomb interaction between e- and ions} \\
 & + \frac{e^2}{2} \int \frac{n(r)n(r')}{|r-r'|} d^3 r d^3 r' && \text{Coulomb interaction between electrons} \\
 & + E_{ion}(\{R_I\}) && \text{Static Coulomb interaction between ions} \\
 & + E_{xc}[n(r)]
 \end{aligned}$$

Kohn-Sham eq

$$\left[\frac{\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{XC}(r) \right] \psi_i(r) = \varepsilon_i \psi_i$$

$$V_H(r) = e^2 \int \frac{n(r')}{|r-r'|} d^3 r'$$

Hartree potential which includes a Coulomb Interaction between electron and itself

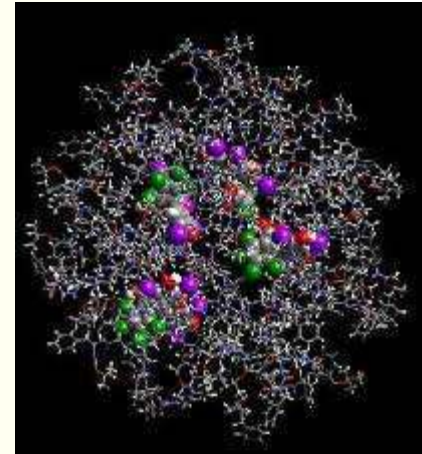
 V_{XC}

Exchange correlation functional that contains:

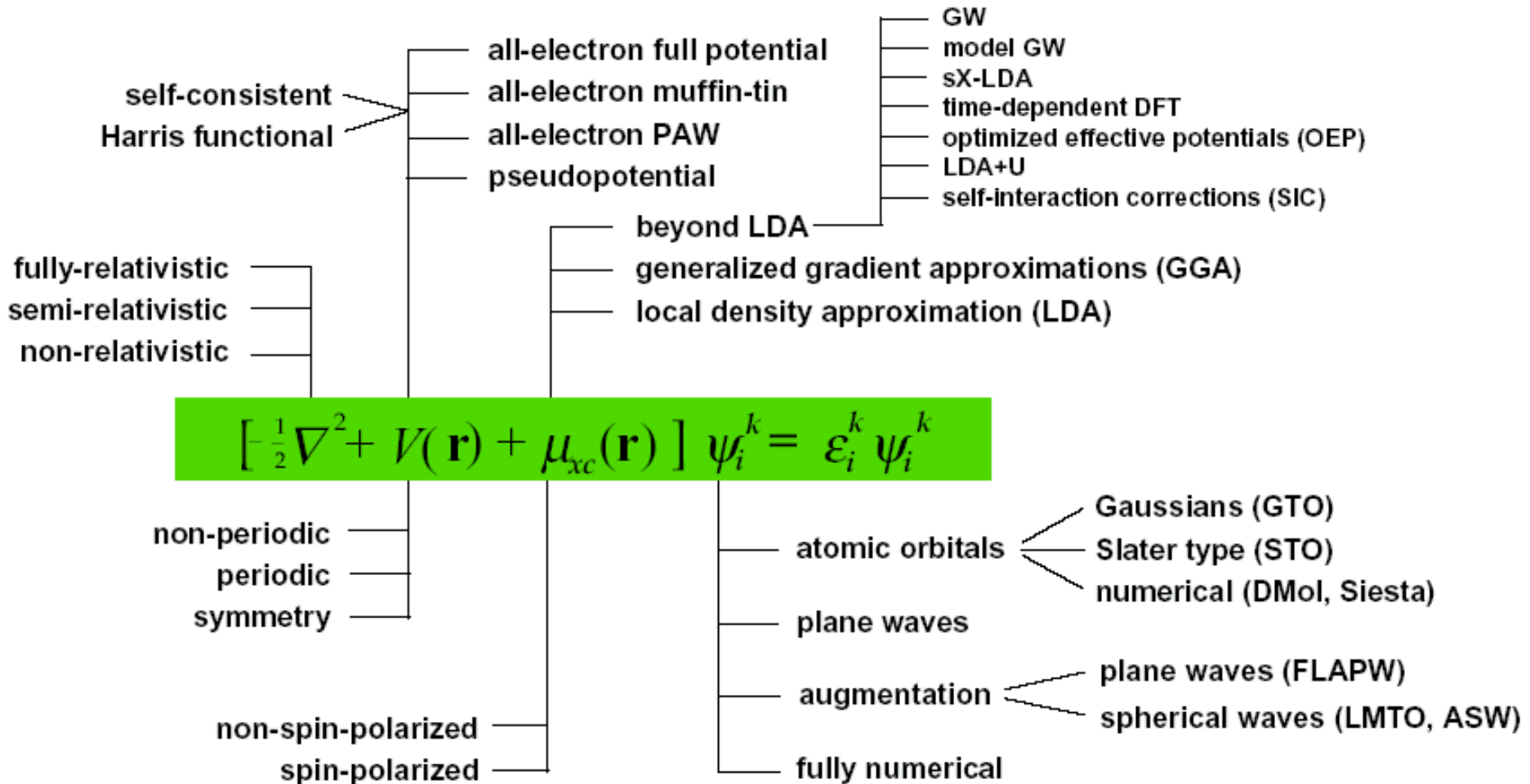
- Exchange
- Correlation

account for the Pauli exclusion and spin effects

- Interacting part of K.E.
- But exact form is never known



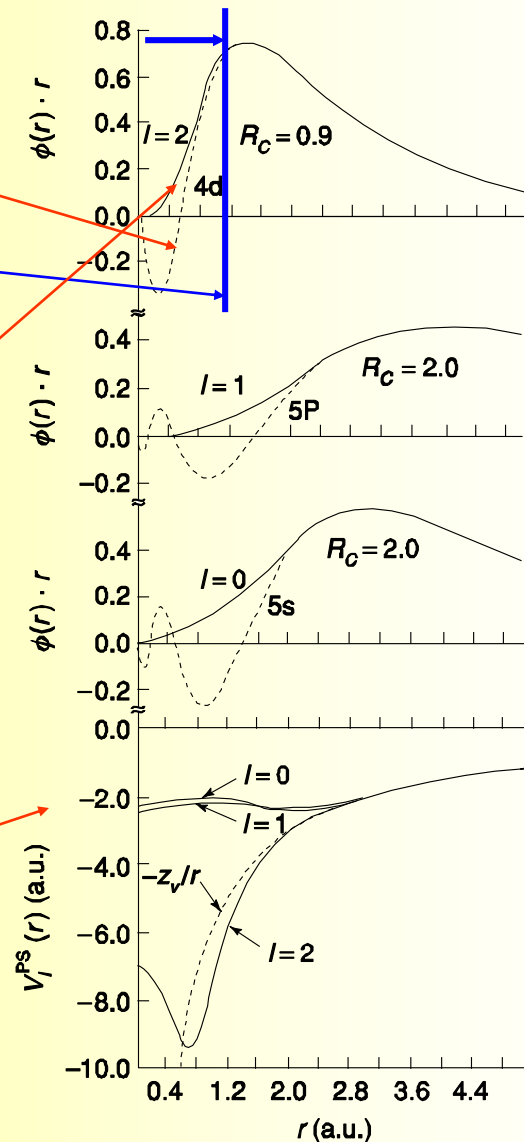
DFT Implementations



Plane Waves

DFT

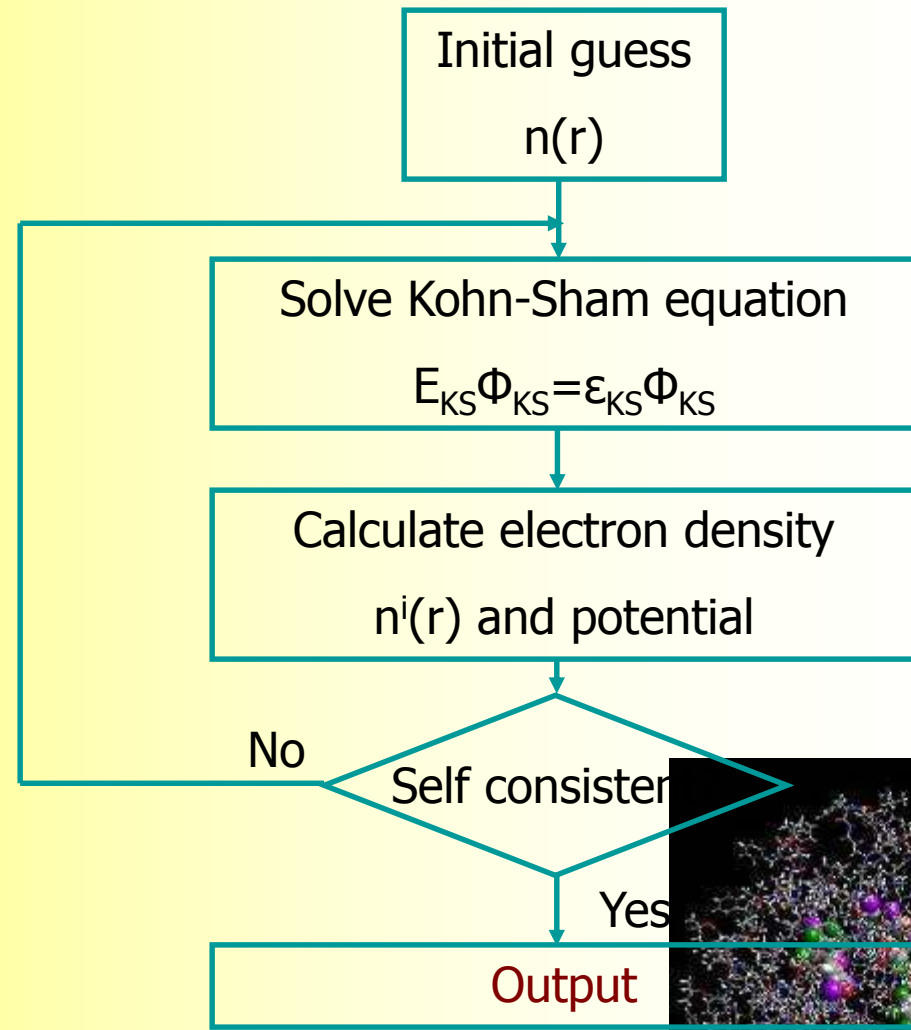
- **APW**
Match all-electron wave function at sphere boundary
- **PAW**
Smooth function plus added function only inside sphere
- **Pseudopotential**
Cast theory in terms of only the smooth functions that are solutions of pseudopotential equations



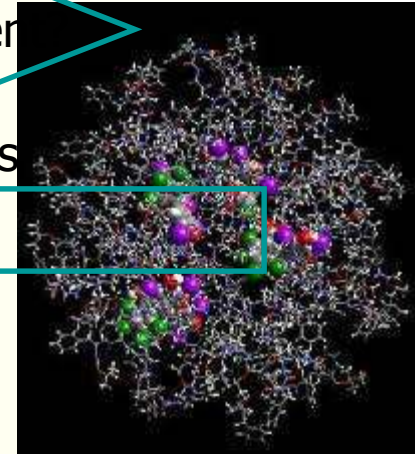
Solving KS self-consistently

- Solving an interacting many-body electrons system is equivalent to minimizing the Kohn-Sham functional with respect to electron density.

Structure, types of atoms

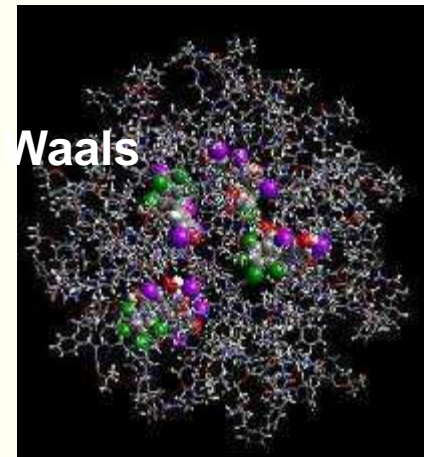


Total energy, force, stress, ...
Eigenvalues

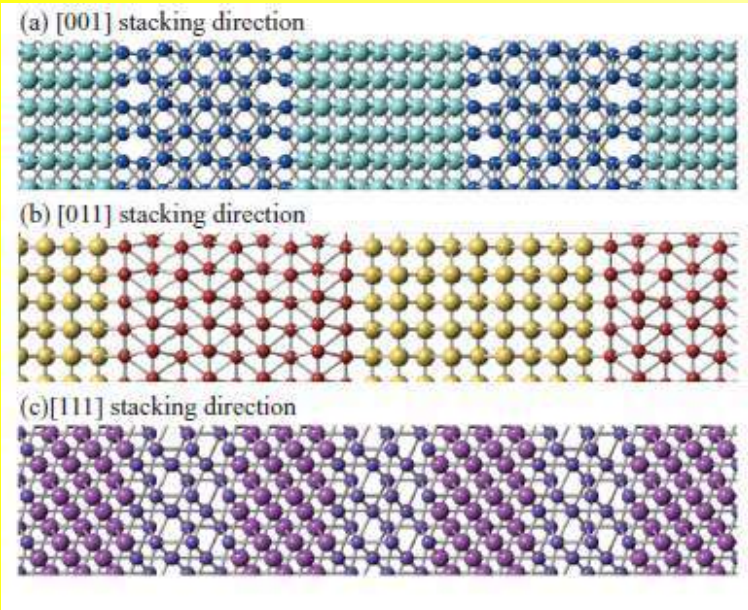


Limitations of current techniques

- Solving the KS Eqs., solution by diagonalization scales as $(N_{\text{electron}})^3$ – (Improved methods $\sim N^2$, Order-N – “Linear Scaling”
Allows calcs. for large systems – integration with classical methods for multiscale analysis
- Size restrictions. Max ~ 1000 atoms
- Excited states properties, e.g., optical band gap. Excitations are not well described by LDA or GGA within DFT. The Kohn-Sham orbitals are only exact for the ground states.
- Strong or intermediate correlated systems, e.g., transition-metal oxides
- Soft bond between molecules and layers, e.g., Van de Waals interaction



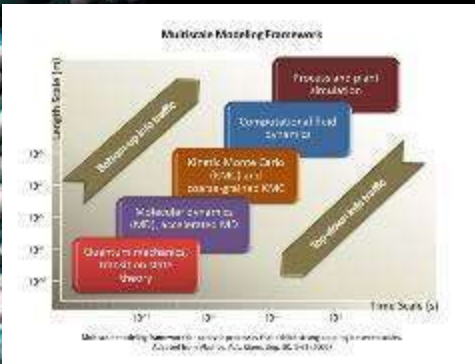
Phys. Rev. B 86, 184104 (2012) Density functional theory investigation of titanium-tungsten superlattices: Structure and mechanical properties



The calculated tensile properties of Ti/W superlattices show no improvement over those calculated for the elemental phases. At best, Ti/W superlattices allow a tuning of the material properties by selecting stacking direction and layer thickness.

Molecular Dynamics Simulation

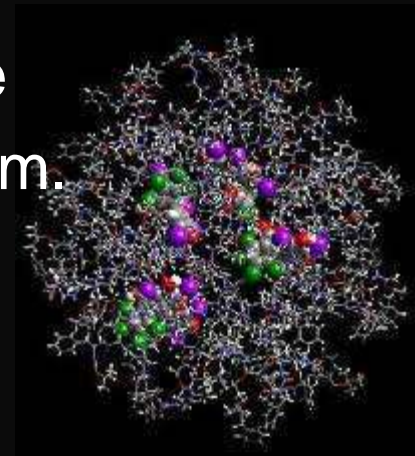
Why Not Quantum Mechanics?



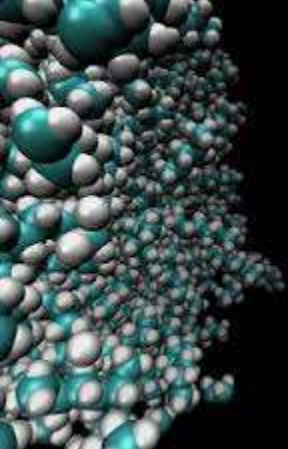
- Modeling the motion of a complex molecule by solving the wave functions of the various subatomic particles would be accurate.....but

$$\frac{-\hbar^2}{2m} \nabla^2 \Psi + U(x, y, z) \Psi(x, y, z) = E \Psi(x, y, z)$$

- Instead of using Quantum mechanics, we can use classical Newtonian mechanics to model our system.



Molecular Dynamics Simulation



**Quantum Statistics + Quantum Mechanics
+ computer simulations
= Ab initio Molecular Dynamics**

**Quantum Statistics + Classical Mechanics
+ computer simulations
= Classical Molecular Dynamics**

Choosing appropriate software

LAMMPS –

License(Free), GPU(Yes)

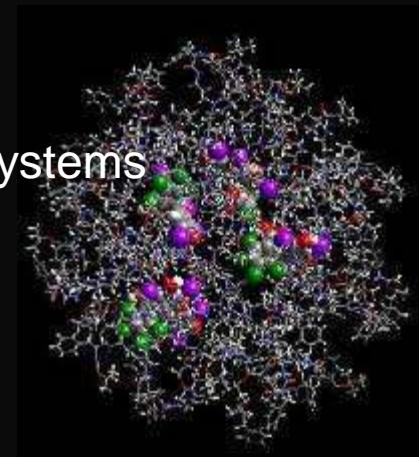
Monte Carlo, Molecular Dynamics, Optimization

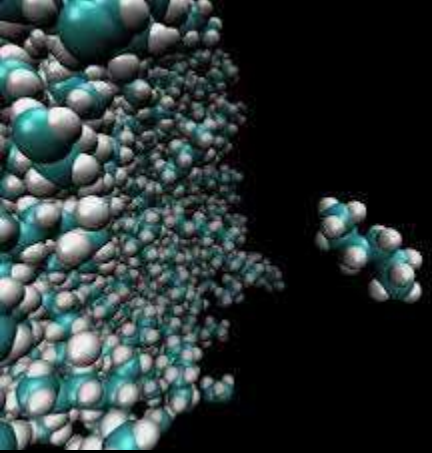
Has potentials for soft and solid-state materials and coarse-grain systems

GULP –

License(Free)

Molecular Dynamics

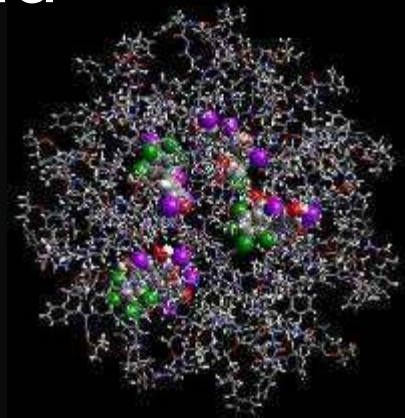




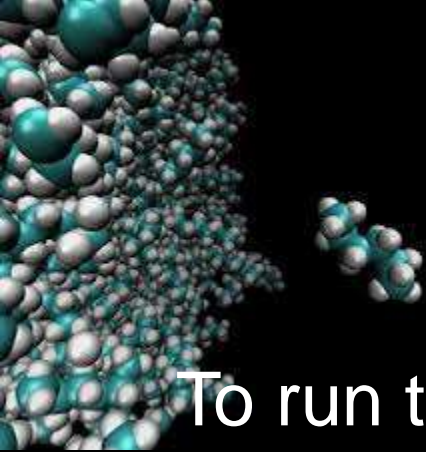
Molecular Modeling

For each atom in every molecule, we need:

- Position (r)
- Momentum ($m + v$)
- Charge (q)
- Bond information (which atoms, bond angles, etc.)



Molecular Dynamics Simulation



To run the simulation, we need the force on each particle.

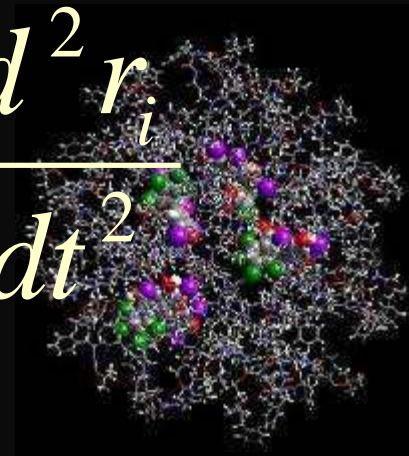
$$F_i = m_i a_i$$

We use the gradient of the potential energy function.

$$F_i = -\nabla_i V$$

Now we can find the acceleration.

$$-\frac{dV}{dr_i} = m_i \frac{d^2 r_i}{dt^2}$$

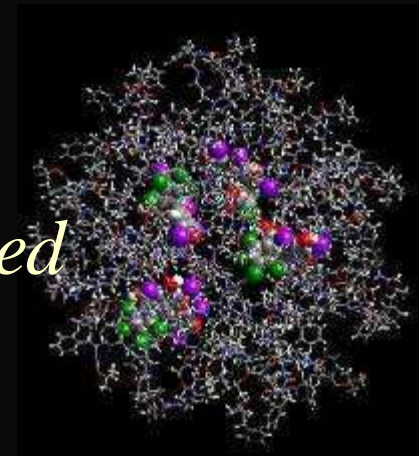


What is the Potential?

A single atom will be affected by the potential energy functions of every atom in the system:

- Bonded Neighbors
- Non-Bonded Atoms (either other atoms in the same molecule, or atoms from different molecules)

$$V(R) = E_{\text{bonded}} + E_{\text{non-bonded}}$$

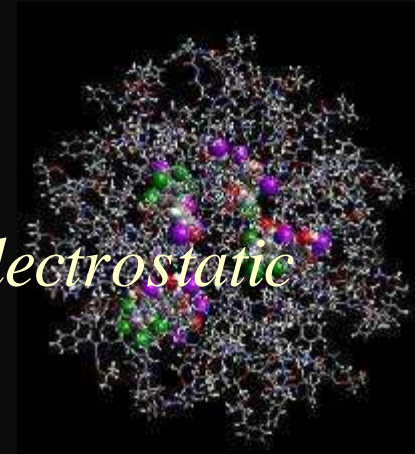


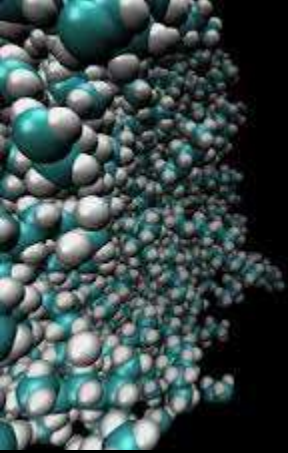
Non-Bonded Atoms

There are two potential functions we need to be concerned about between non-bonded atoms:

- van der Waals Potential
- Electrostatic Potential

$$E_{non-bonded} = E_{van-der-Waals} + E_{electrostatic}$$

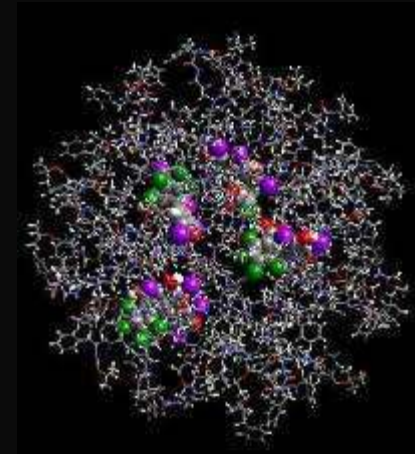




The van der Waals Potential

$$E_{Lennard-Jones} = \sum_{\substack{\text{nonbonded} \\ \text{pairs}}} \left(\frac{A_{ik}}{r_{ik}^{12}} - \frac{C_{ik}}{r_{ik}^6} \right)$$

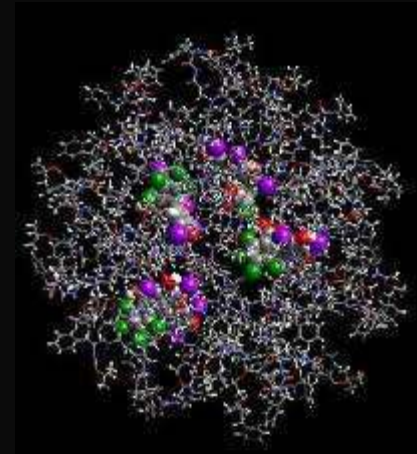
The Constants A and C depend on the atom types, and are derived from experimental data.



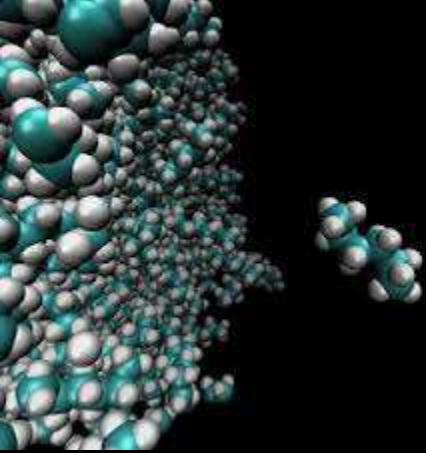
The Electrostatic Potential

- Opposite Charges Attract
- Like Charges Repel
- The force of the attraction is inversely proportional to the square of the distance

$$E_{electrostatic} = \sum_{\substack{\text{nonbonded} \\ \text{pairs}}} \frac{q_i q_k}{Dr_{ik}}$$



Molecular Dynamics Simulation



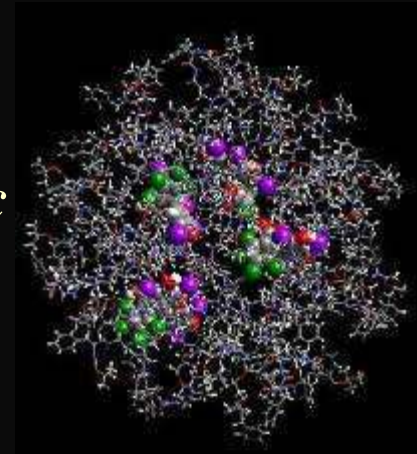
Coulomb's
Law

$$F = \frac{q_1 q_2}{4\pi\epsilon_0 r^2}$$

The Non-Bonded Potential

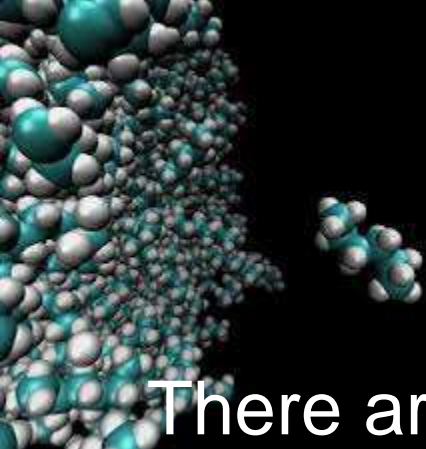
Combine the LJ and Electrostatic
Potentials

$$E_{non-bonded} = E_{van-der-Waals} + E_{electrostatic}$$



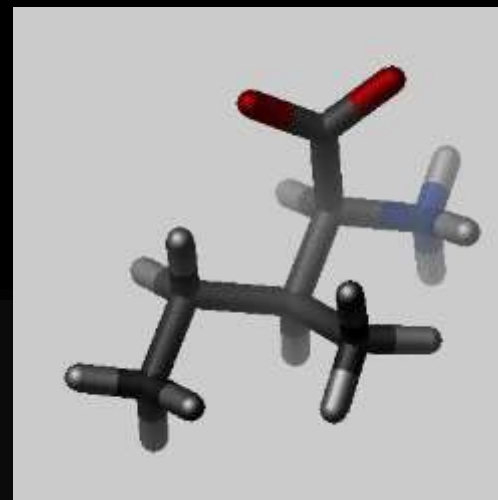
Molecular Dynamics Simulation

Bonded Atoms



There are three types of interaction between bonded atoms:

- Stretching along the bond
- Bending between bonds
- Rotating around bonds

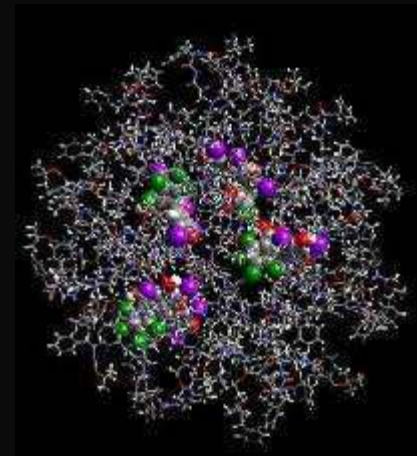


$$E_{bonded} = E_{bond-stretch} + E_{angle-bend} + E_{rotate-along-bond}$$

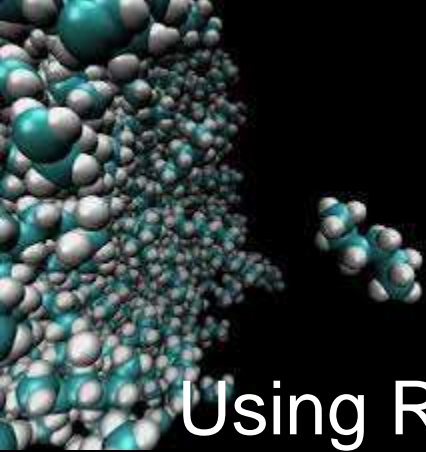


Integration Algorithms

- Forces like the LJ potential have powers of 12, which would make Euler horribly unstable (even worse than usual)
- RK and Midpoint algorithms would seem to help
- However, force calculations are extremely expensive, and RK and Midpoint require multiple force calculations per timestep



Molecular Dynamics Simulation



Using RK is justifiable in other circumstances, because it allows you to take larger timesteps (two force calculations allowing you to more than double the timestep)

- This is normally not achievable in MD simulations, because the forces are very rapidly changing non-linear functions.
- We need an algorithm with the stability benefits of RK without the cost of extra force calculations!



Molecular Dynamics Simulation

Verlet Algorithm

- First, take a third-order Taylor step:

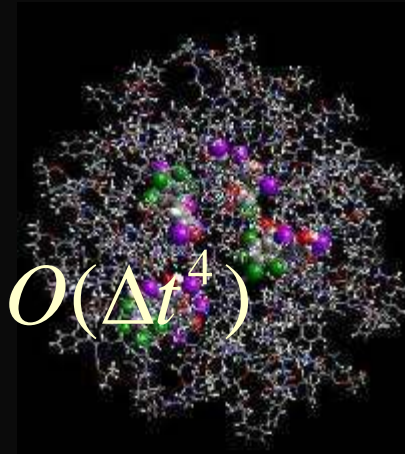
$$r(t + \Delta t) =$$

$$r(t) + v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2 + \frac{1}{3!}r(t)\Delta t^3 + O(\Delta t^4)$$

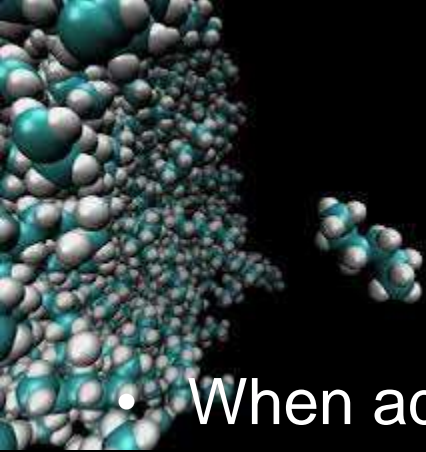
- Now take a step backward:

$$r(t - \Delta t) =$$

$$r(t) - v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2 - \frac{1}{3!}r(t)\Delta t^3 + O(\Delta t^4)$$



Molecular Dynamics Simulation

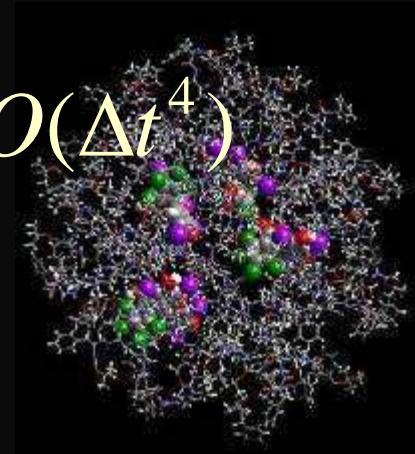


- When adding the two formulas, the first and third derivatives cancel out:

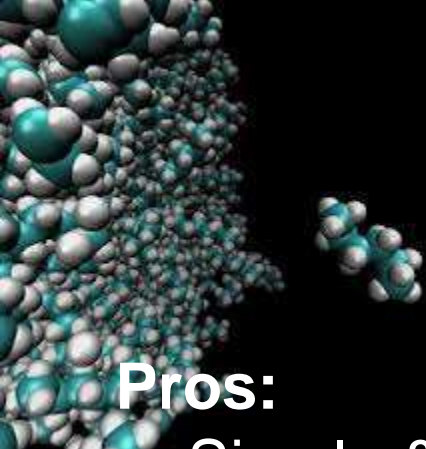
$$r(t + \Delta t) + r(t - \Delta t) = 2r(t) + a(t)\Delta t^2 + O(\Delta t^4)$$

- And we can express the next timestep in terms of the previous position and the current acceleration:

$$r(t + \Delta t) = 2r(t) - r(t - \Delta t) + a(t)\Delta t^2 + O(\Delta t^4)$$



Molecular Dynamics Simulation

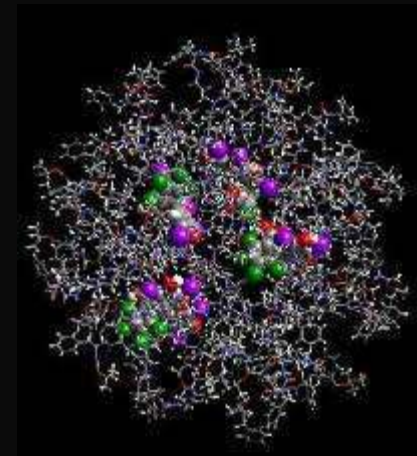


Pros:

- Simple & Effective
- Low Memory & CPU Requirements (don't need to store velocities or perform multiple force calculations)
- Time Reversible
- Very stable even with large numbers of interacting particles

Cons:

- Not as accurate as RK
- We never calculate velocities!
(when would we need them?)

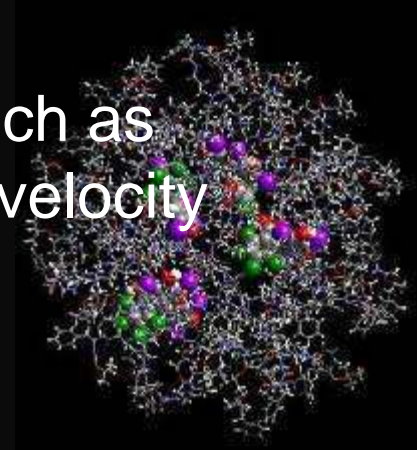


Obtaining Velocities

- We can estimate the velocities using a finite difference:

$$v(t) = \frac{1}{2\Delta t} [r(t + \Delta t) - r(t - \Delta t)] + O(\Delta t^2)$$

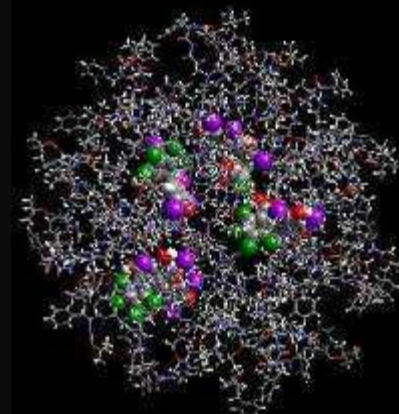
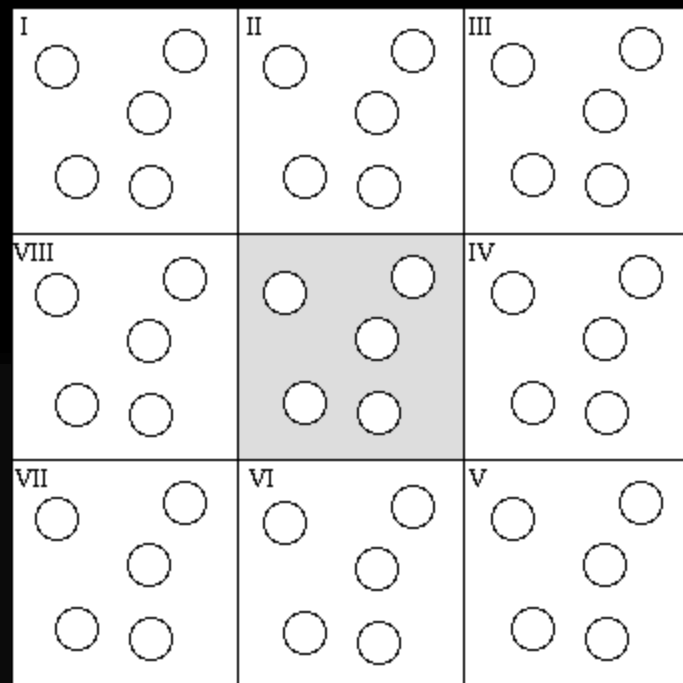
- This has a second order error, while our algorithm has a fourth order error
- There are variations of the Verlet algorithm, such as the leapfrog algorithm, which seek to improve velocity estimations.



Molecular Dynamics Simulation

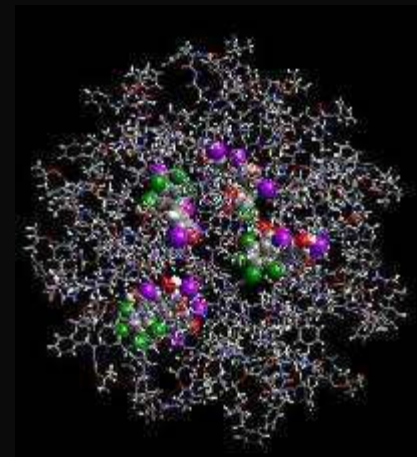
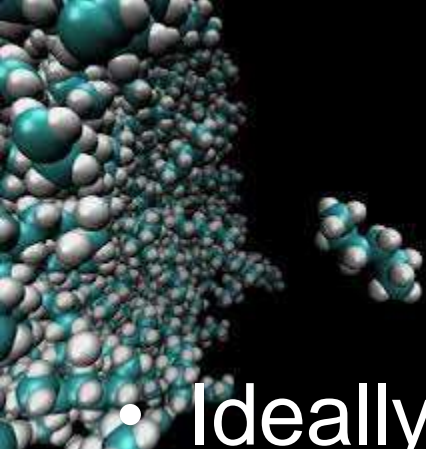
Periodic Boundary Conditions

- Simulate a segment of molecules in a larger solution by having repeatable regions
- Potential calculations are run only on each atom's closest counterpart in the 27 cubes
- When an atom moves off the edge, it reappears on the other side (like in asteroids)



Cutoff Methods

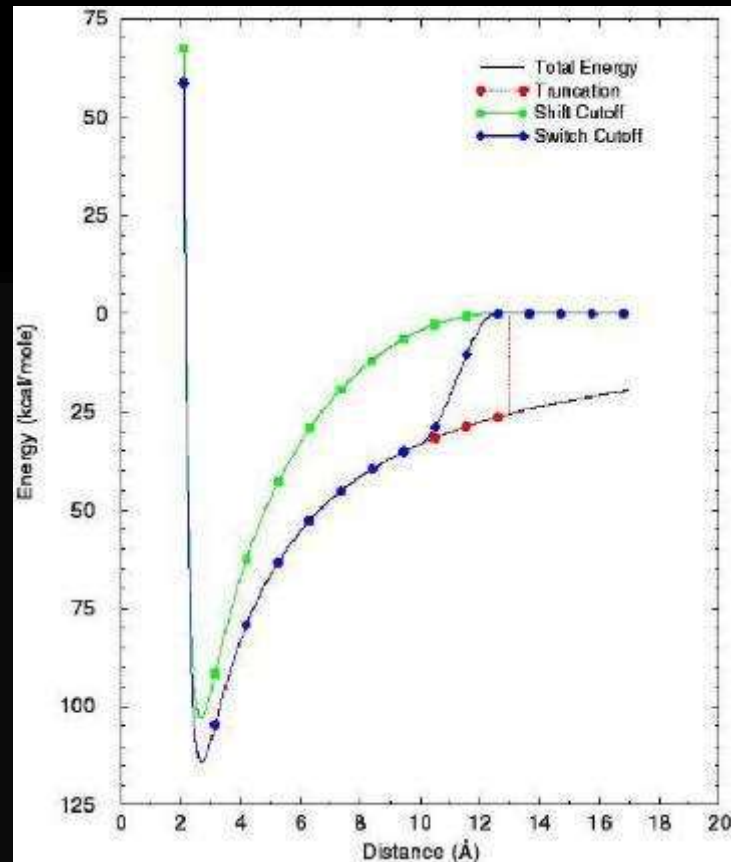
- Ideally, every atom should interact with every other atom
- This creates a force calculation algorithm of quadratic order
- We may be able to ignore atoms at large distances from each other without suffering too much loss of accuracy



Molecular Dynamics Simulation

Cutoff Methods

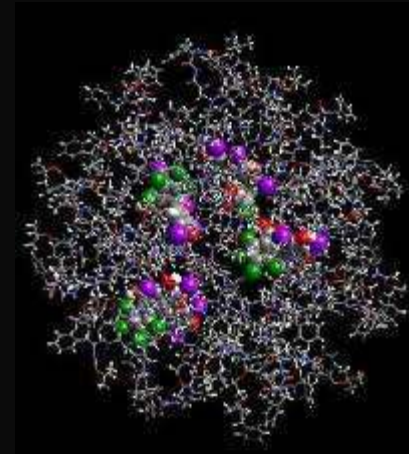
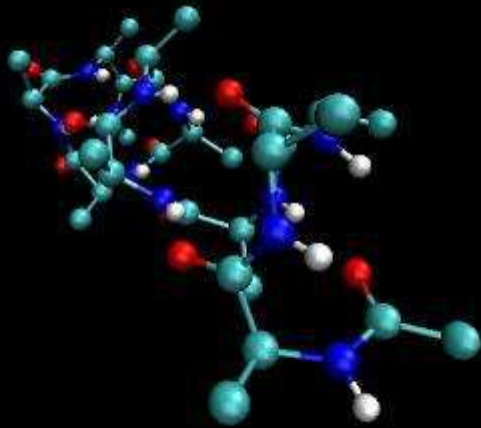
- Truncation – cuts off calculation at a predefined distance
- Shift – alters the entire function as to be zero at the cutoff distance
- Switch – begins tapering to zero as the function approaches the cutoff distance



Molecular Dynamics Simulation

Visualization

VMD (Visual Molecular Dynamics)



Molecular Dynamics Simulation

Multi-scale Modeling and Simulations of Tribological Processes: *Molecular dynamic studies of mechano-chemical properties of lubricating systems*

Ugur Mart¹; Georges Limbert^{1,2}; Robert J.K. Wood¹

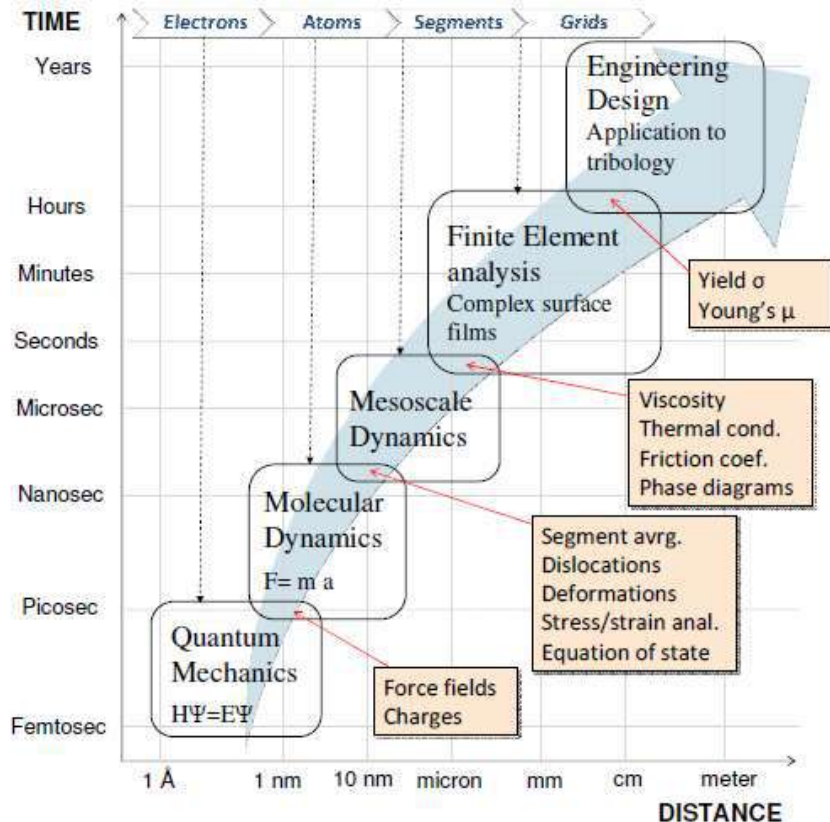
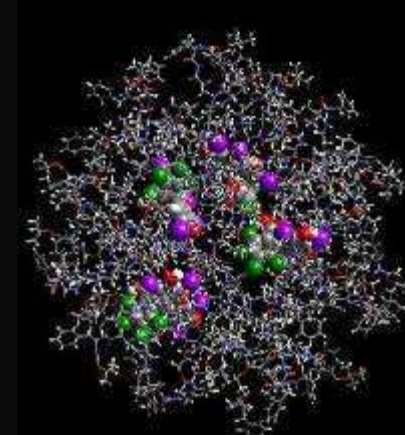


Figure 1. Multiscale modelling hierarchy for tribology researches.



MD of lubricants under shear condition

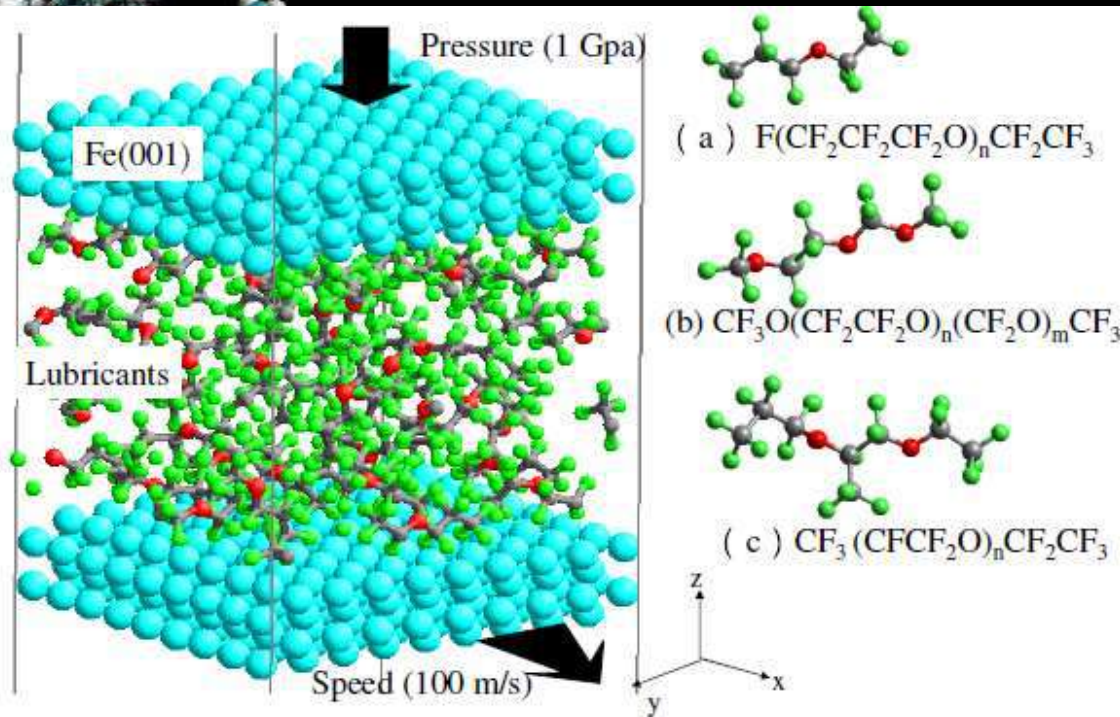


Figure 2. Model of the MD simulation of lubricants (PFPE) under shear condition.

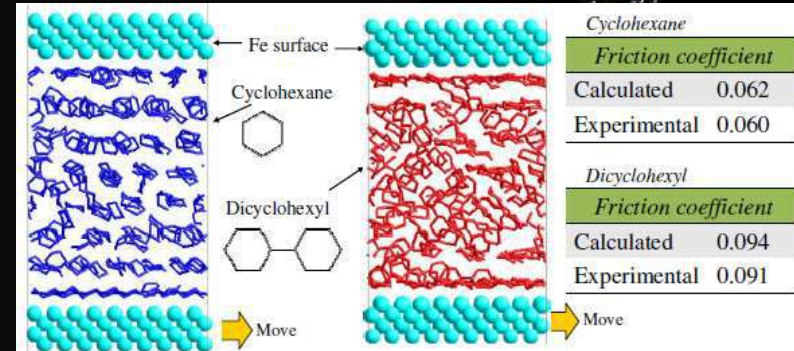
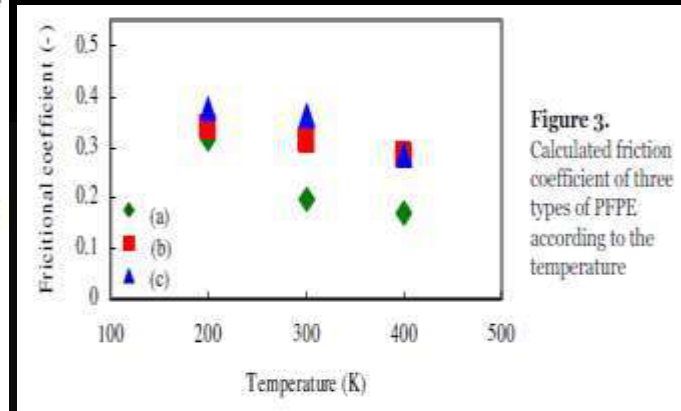


Figure 4. MD simulation of friction process and properties of lubricants



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Mesoscopic simulation of fluid flow in periodically grooved microchannels



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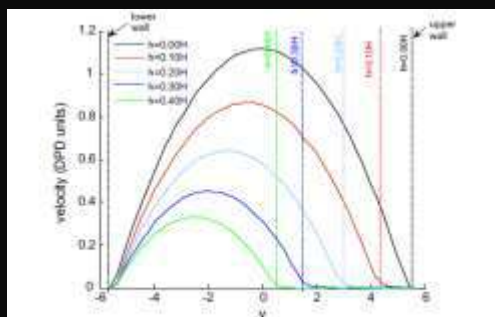
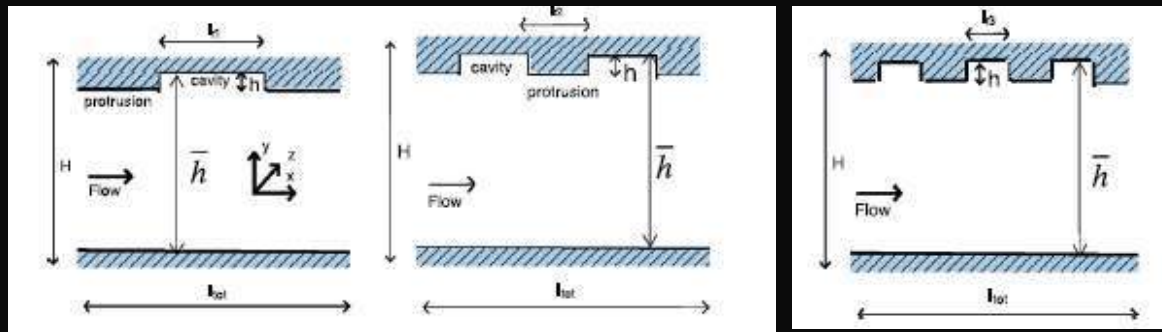


Fig. 5. Bin-averaged velocity profiles over the whole channel region for $l_p = 0.167l_{tot}$ and $l_c = 0.02l_{tot}$ (microchannel).

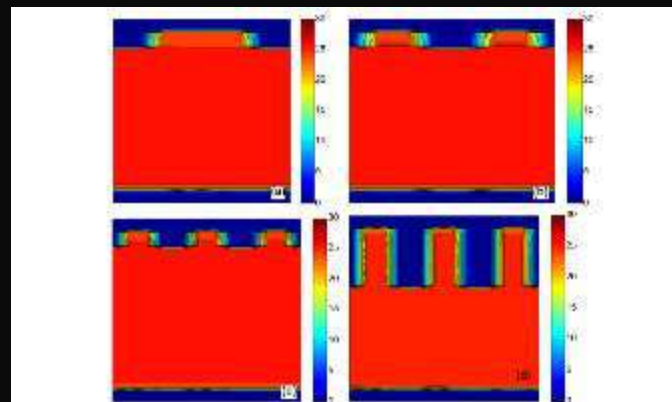
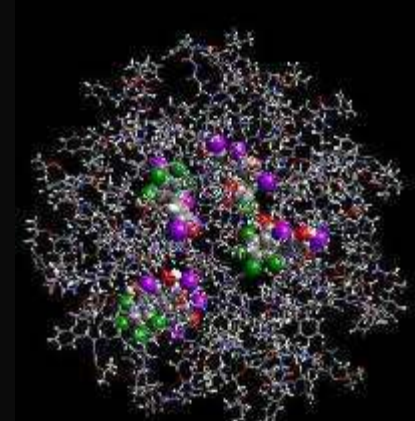
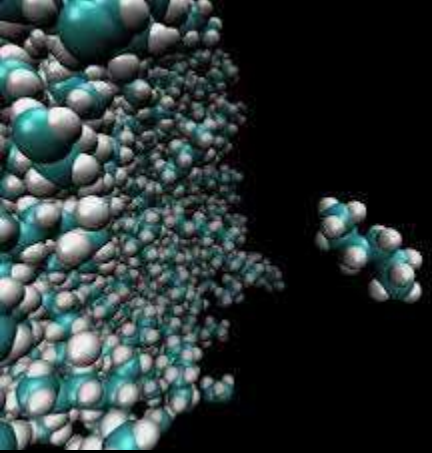


Fig. 6. Velocity contours with $l_p = 0.167l_{tot}$ and $l_c = 0.02l_{tot}$ (a) $h = 0.125l_{tot}$; (b) $h = 0.25l_{tot}$; (c) $h = 0.375l_{tot}$; (d) $h = 0.50l_{tot}$ (microchannel).





Thank you for your attention.



Molecular Dynamics Simulation

