Introduction to Molecular Dynamics

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Overview

- Applications
- Methodology
- Discussion on Force Fields
- Computational Considerations

What is Molecular Dynamics?

- A computational tool that applies Newton's equations of motion to **predict trajectories** and **resolve material properties** of a finite number of atoms in a simulation domain.
- Applications
  - Material science
  - Biochemistry
  - Condensed-phase chemistry
  - And many other engineering applications…

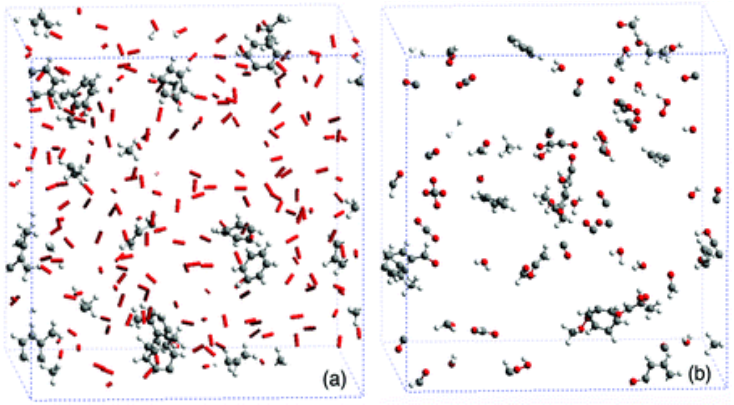


Figure 4. Oxidation of a mixture of hydrocarbon molecules [4]

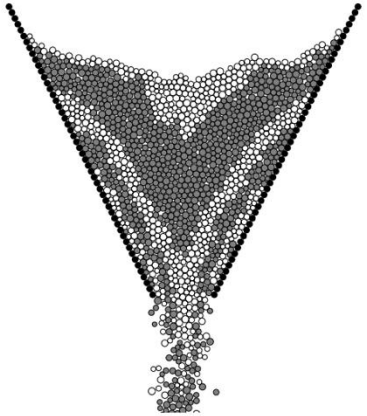


Figure 1. Rigid, spherical particles flowing out of a conical hopper [1]

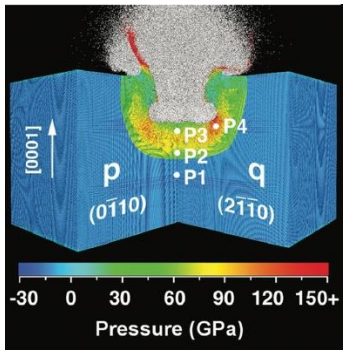


Figure 2. Deformation mechanisms of α-aluminum from hypervelocity impact [2]

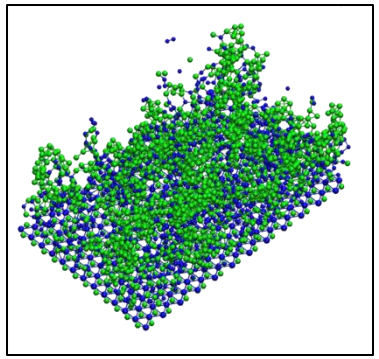


Figure 3. Ion bombardment on hexagonal Boron Nitride surface for Hall thruster channel wall erosion evaluation [3]

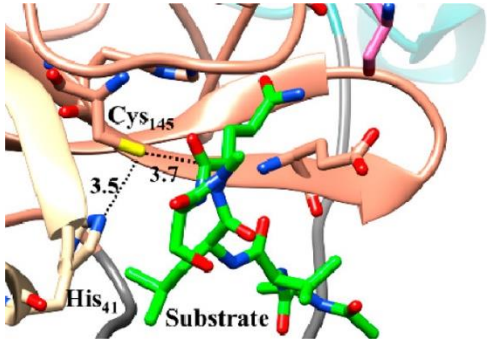
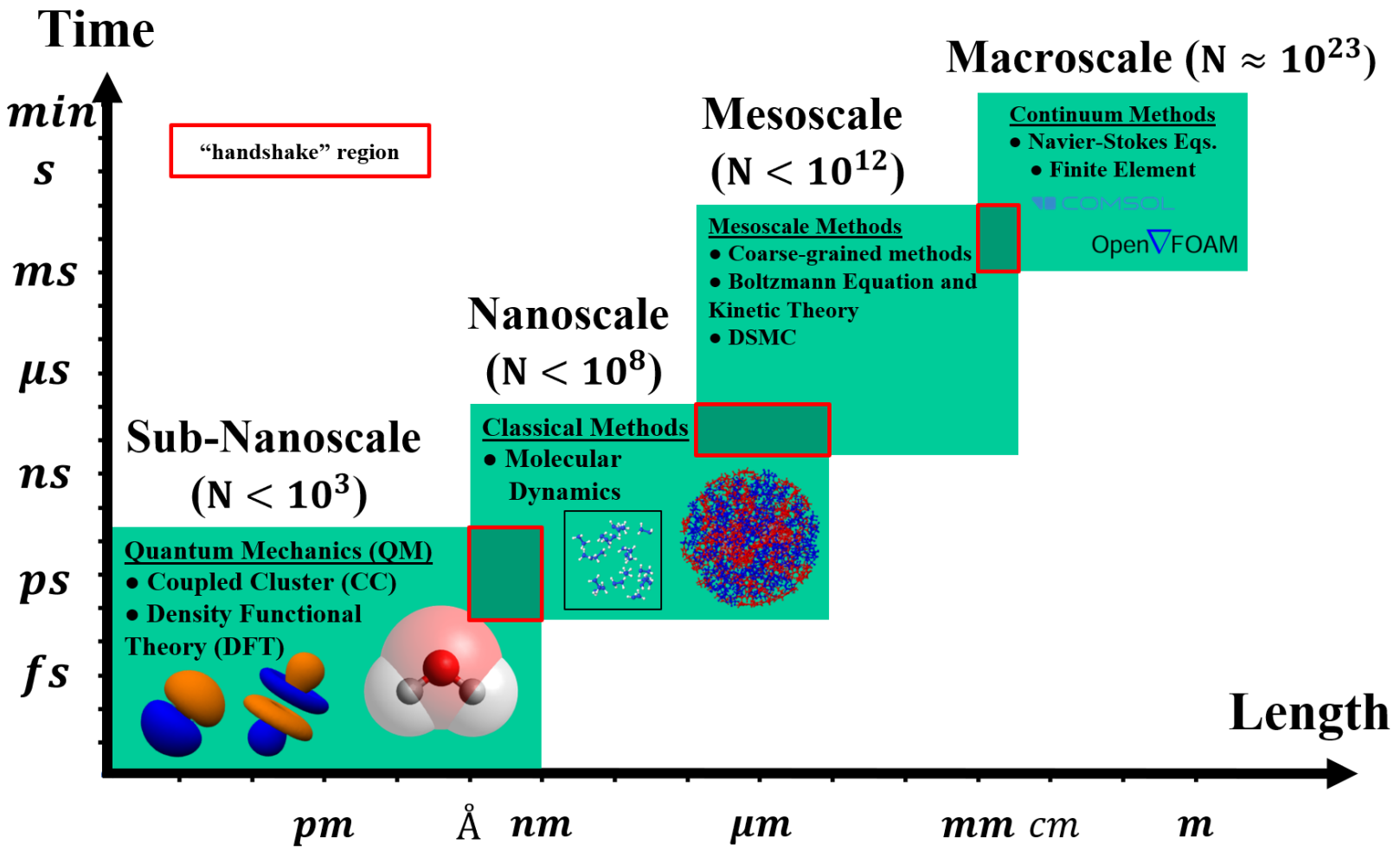


Figure 5. Study of structural properties and flexibility SARS-CoV-2 protease (an enzyme that breaks down proteins) [5]

[1] T. Pöschel and T. Schwager, Computational Granular Dynamics: Models and Algorithms. Springer Berlin Heidelberg, 2005.
[2] C. Zhang, R. K. Kalia, A. Nakano, P. Vashishta, and P. S. Branicio, "Deformation mechanisms and damage in α-alumina under hypervelocity impact loading," J. Appl. Phys., vol. 103, no. 8, p. 83508, Apr. 2008, doi: 10.1063/1.2891797.
[3] Y. Choi, J. Loverich, S. Mahalingam, and P. Messmer, "Towards Hall Thruster Erosion Prediction Using a Kinetic Plasma Model and a Molecular Dynamics Simulation," in 48th AIAA Aerospace Sciences Meeting Including the New Horizons Forum and Aerospace Exposition, American Institute of Aeronautics and Astronautics, 2010.
[4] K. Chenoweth, A. C. T. van Duin, and W. A. Goddard, "ReaxFF Reactive Force Field for Molecular Dynamics Simulations of Hydrocarbon Oxidation," J. Phys. Chem. A, vol. 112, no. 5, pp. 1040–1053, Feb. 2008, doi: 10.1021/jp709896w.
[5] D. Suárez and N. Díaz, "SARS-CoV-2 Main Protease: A Molecular Dynamics Study," J. Chem. Inf. Model., Jul. 2020, doi: 10.1021/acs.jcim.0c00575.

When to use MD?

- Molecular dynamics is primarily used in the **nanoscale** domain
- MD takes an average for the electronic structures whereas QM methods explicitly solve for the electronic structure
- "Handshake" regions have pushed the boundaries of MD
  - *Ab initio* molecular dynamics (AIMD) and ReaxFF further bridge the gap between sub-nanoscale and nanoscale domains
  - Coarse graining aims to reduce number of terms needed to solve for the potential energy and effectively reduce computational complexity



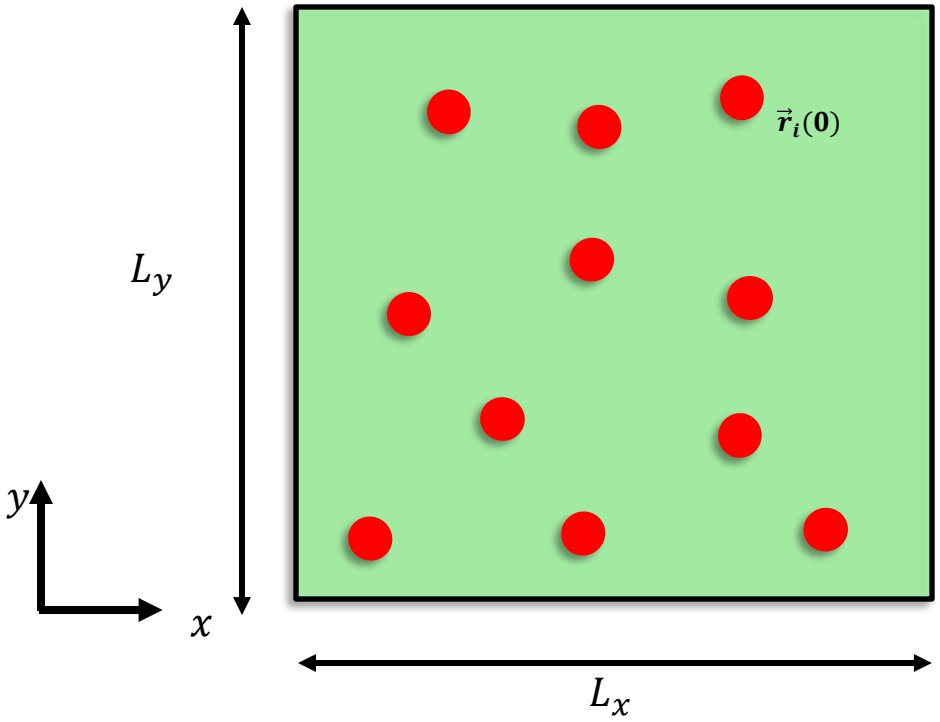
Adapted from Jaramillo-Botero et al. [1]

[1] A. Jaramillo-Botero, R. Abrol, and A. C. T. van Duin, "Multiscale-Multiparadigm Modeling and Simulation of Nanometer Scale Systems and Processes for Nanomedical Applications," in Nanomedicine: A Systems Engineering Approach, 1st ed., New York: Jenny Stanford Publishing, 2009, pp. 245–300.

How does MD work?

Initialization

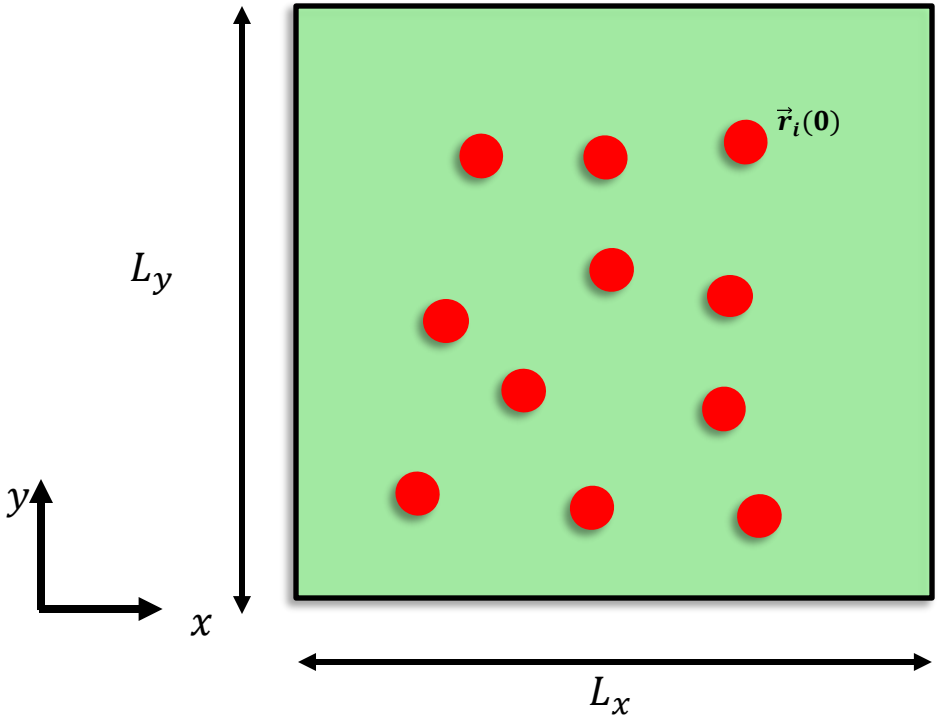
- Assign positions $\vec{r}_i$

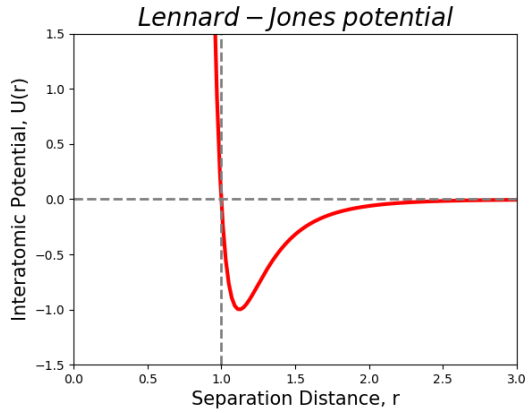


How does MD work?

Initialization

- Assign positions $\vec{r}_i$
- Minimization





2D Potential Energy Surface (PES)

3D PES

Need to use minimization algorithm (e.g. steepest descent method, conjugate gradient method, etc.)

How does MD work?

Initialization

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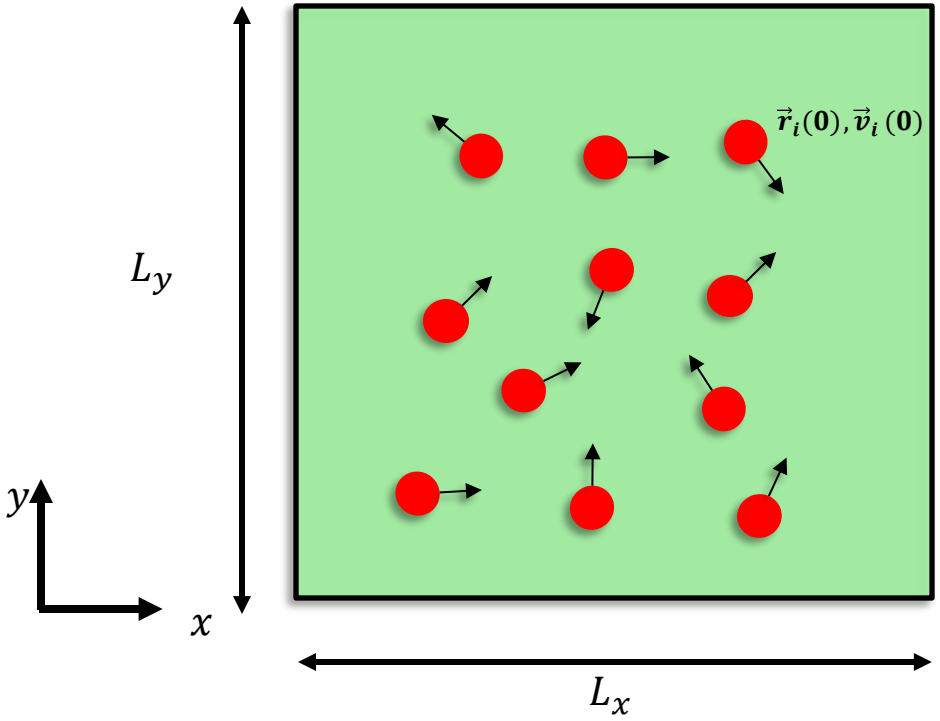
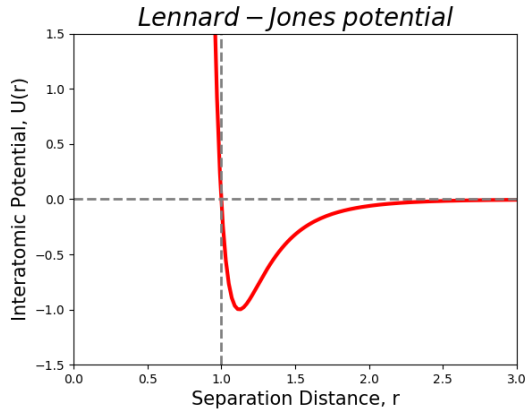
- Minimization
- Assign velocities $\vec{v}_i$





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- Assign velocities $\vec{v}_i$
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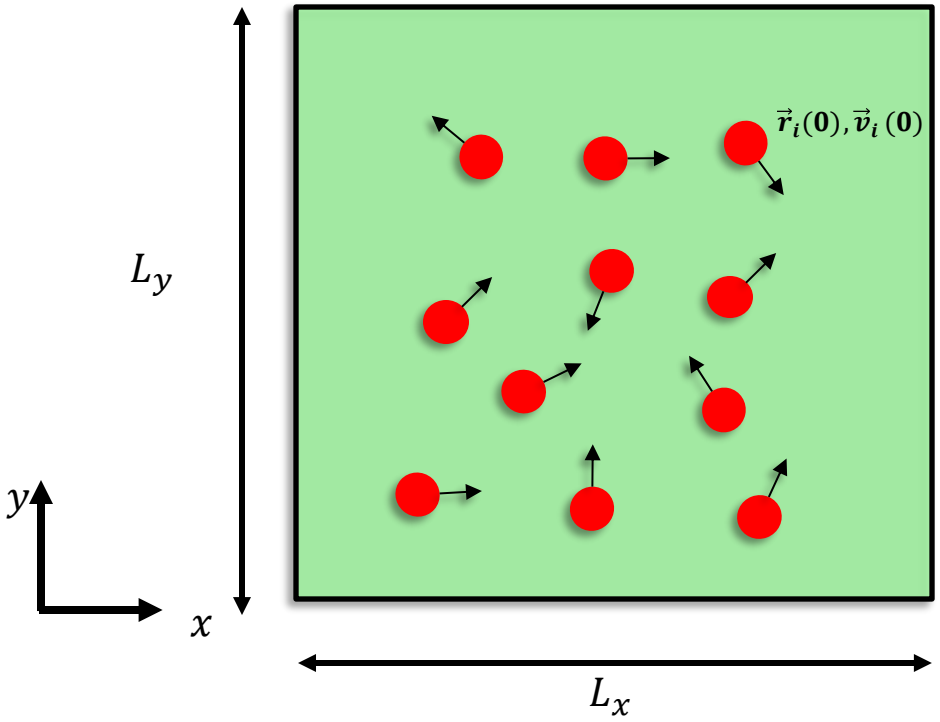

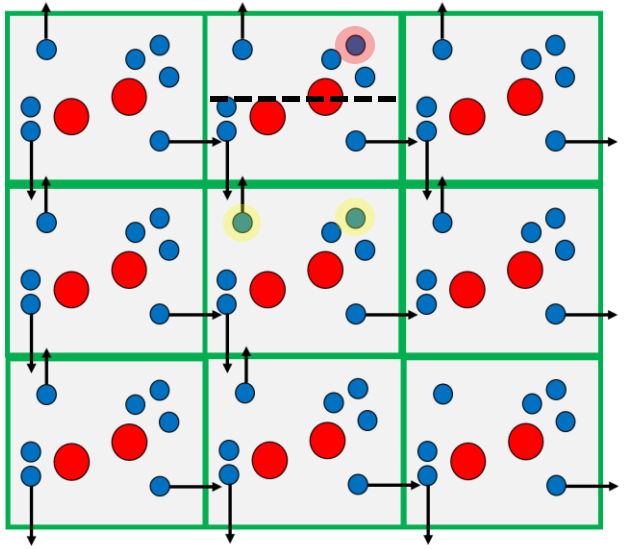

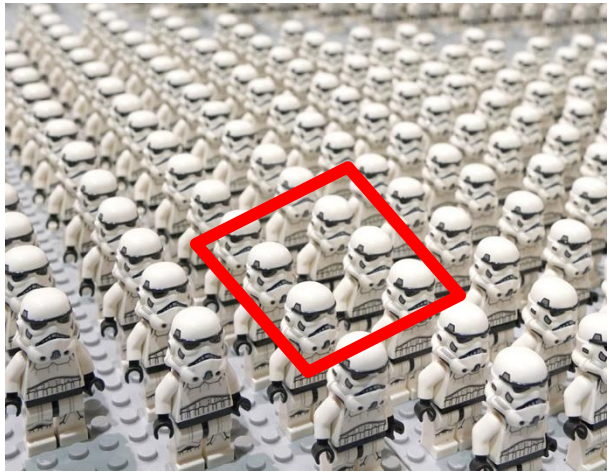

A periodic boundary condition assumes atoms interact in an infinite-boundary box. By the minimum image convention, each individual particle interacts with the closest image of the remaining particles in the system.

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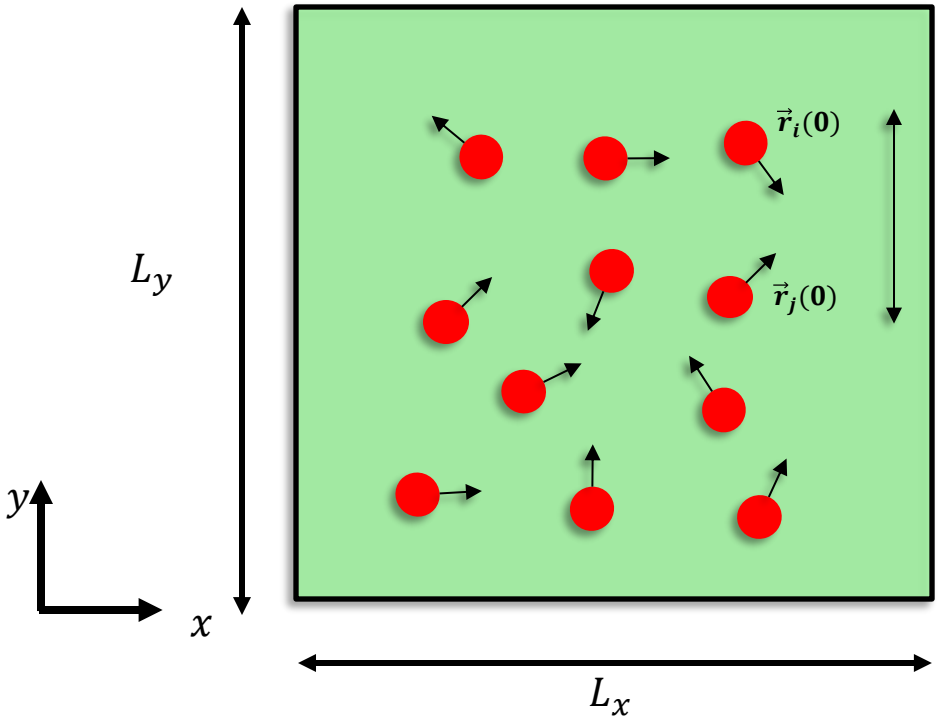
$$U_{tot} = \sum_{j \neq i} U_{ij}(\vec{r}_{ij})$$

$$\vec{F}_{j \to i} = -\nabla U_{ij}(\vec{r}_{ij})$$

$$\vec{F}_i = \sum_{j \neq i} \vec{F}_{j \to i}$$



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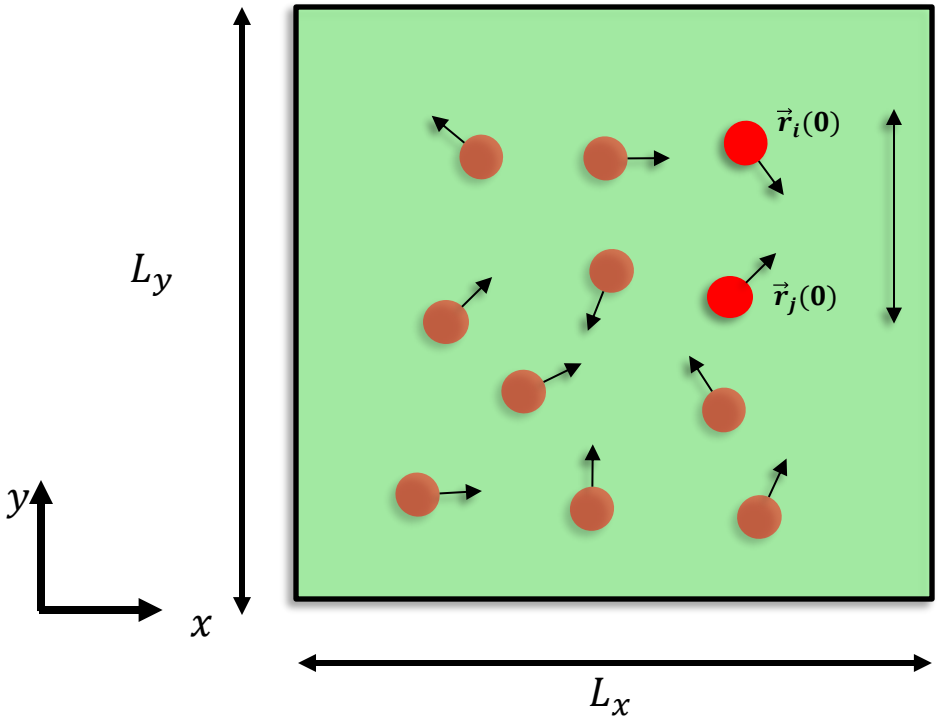

$$U_{ij}(r_{ij}) = U_b + U_{nb}$$

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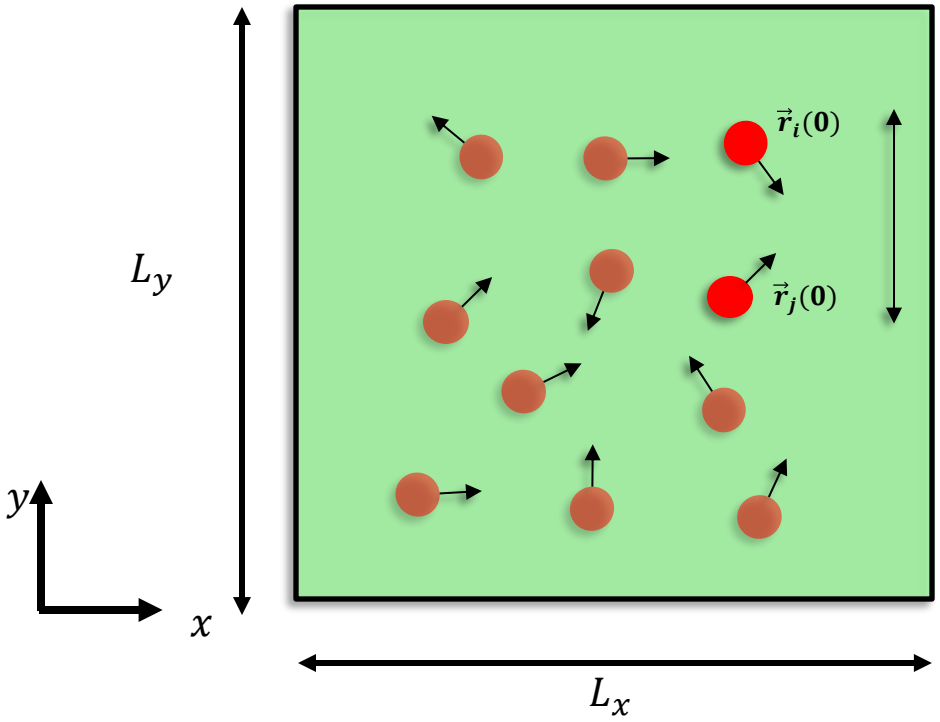
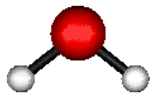


$$U_{ij}(r_{ij}) = U_b + U_{nb}$$

$$= \sum_{bonds} \frac{1}{2} k_b (r - r_0)^2$$



GIFs from http://www2.ess.ucla.edu/~schauble/molecular_vibrations.htm

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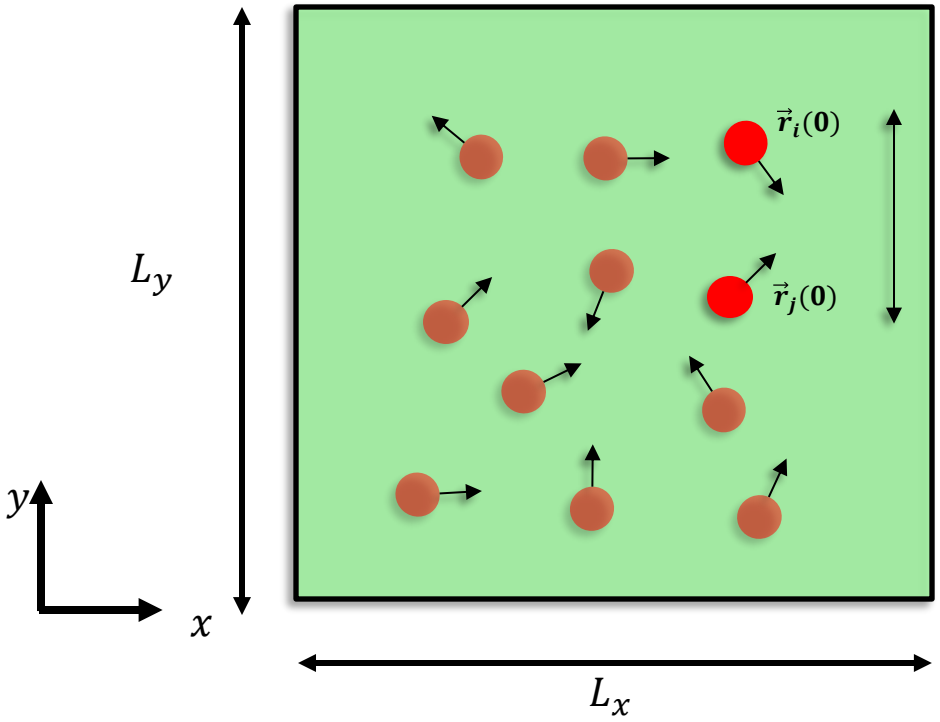

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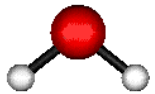

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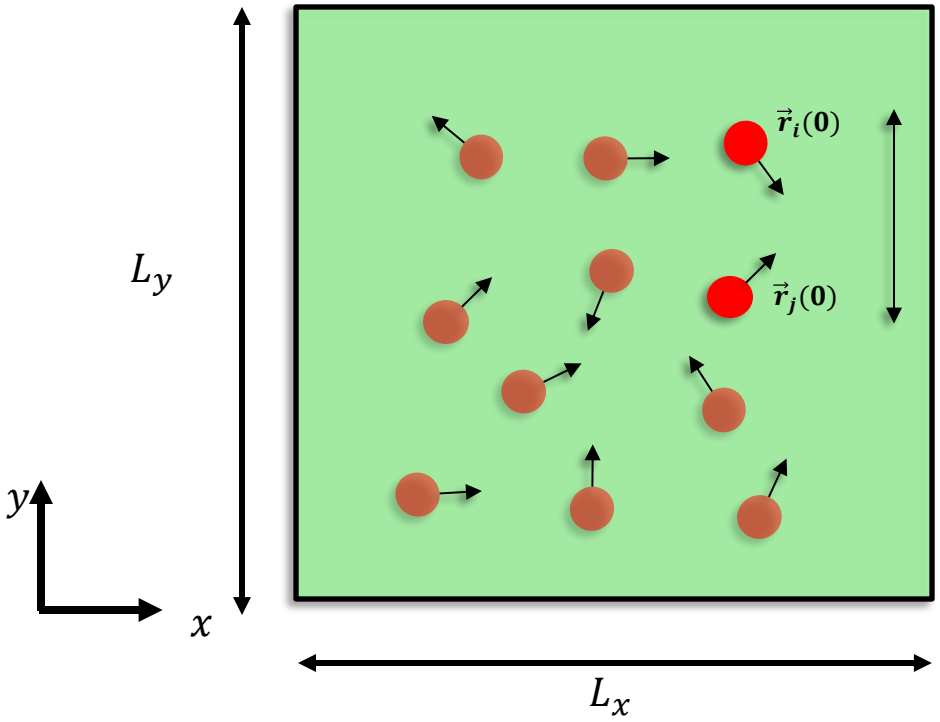

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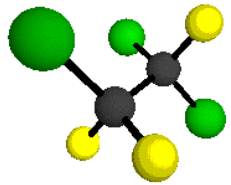

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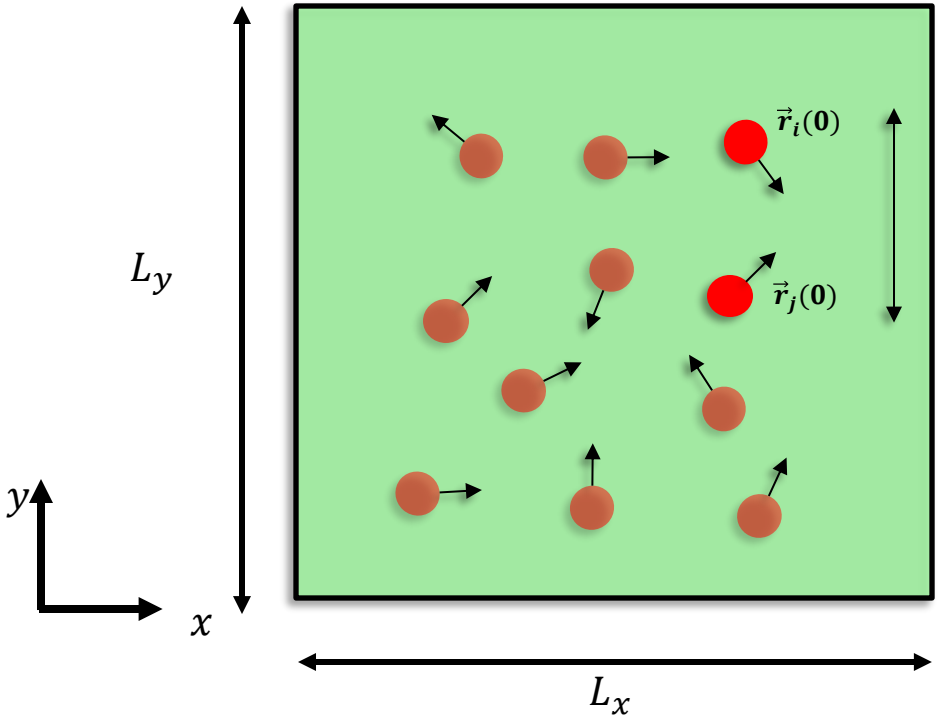

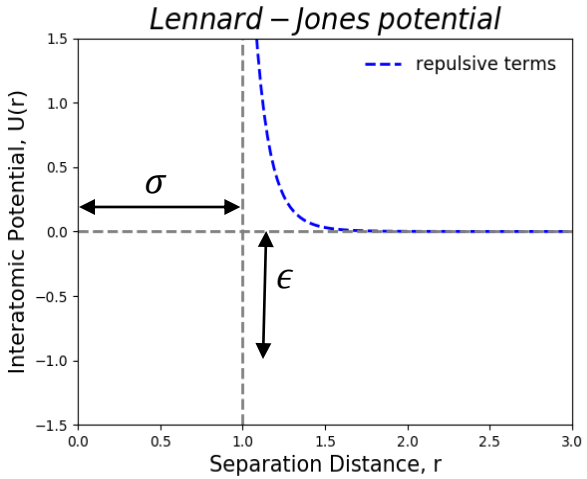

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$$+ \frac{1}{4\pi\epsilon_0} \sum_{i \neq j} \sum \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij} \sum_{i \neq j} \sum \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]$$

Repulsive terms

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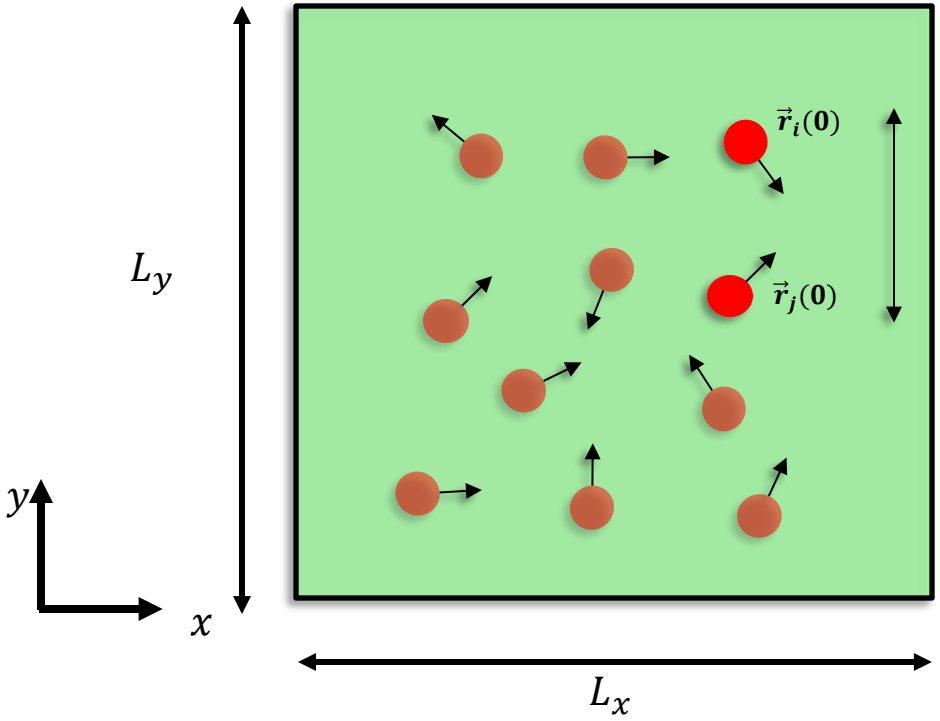

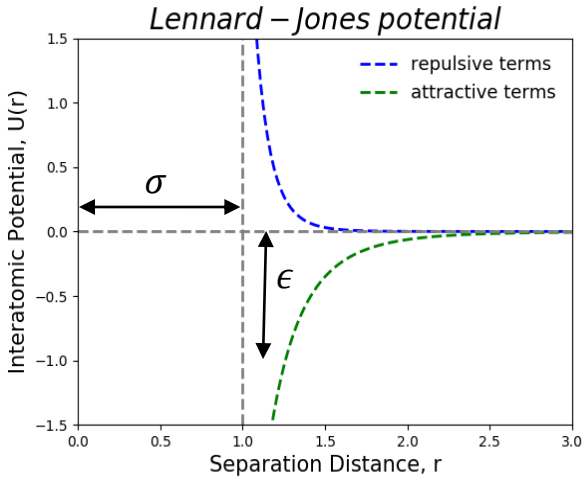

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Repulsive terms **Attractive terms**

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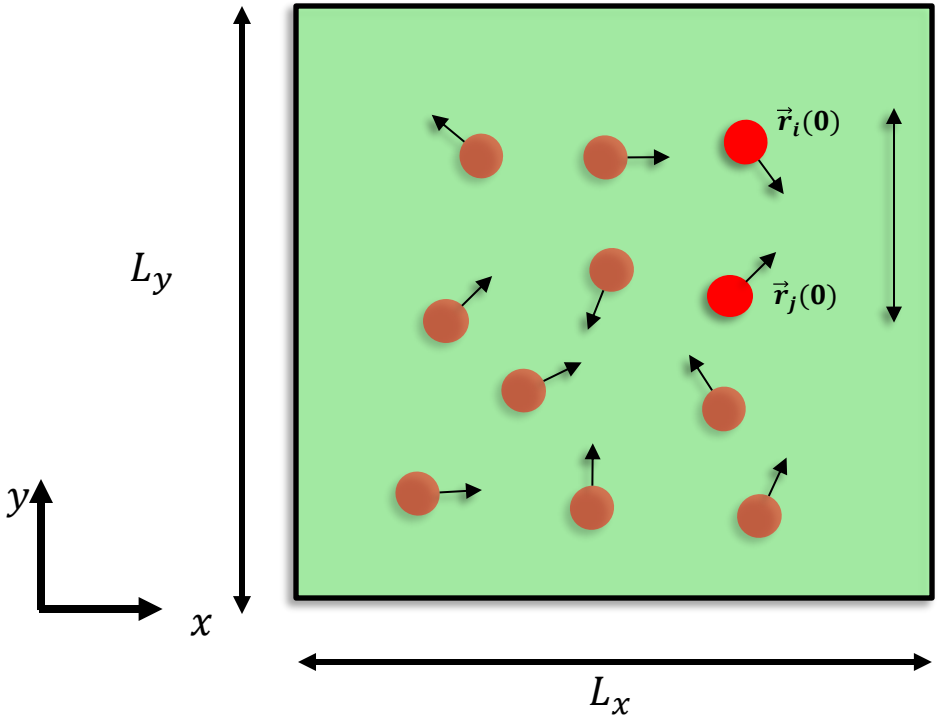

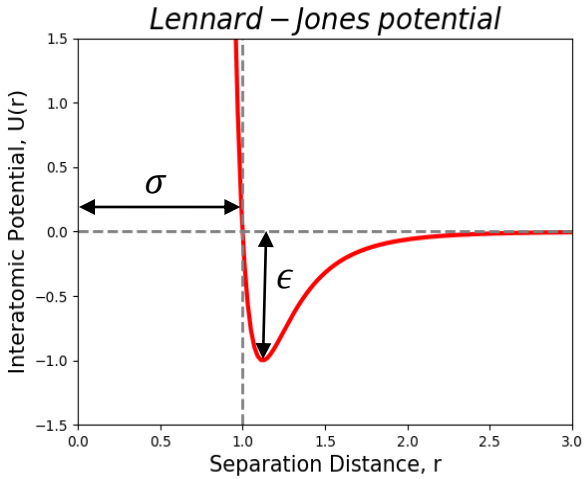

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A force field includes the set of empirically-determined parameters for the chosen potential.

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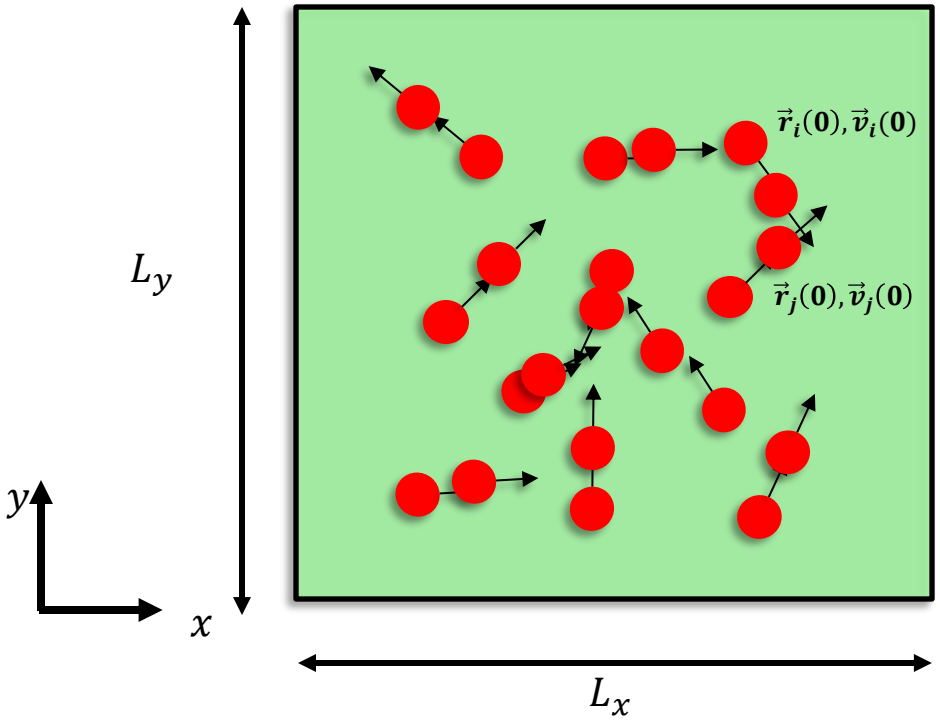
Move Atoms

$\vec{r}_i(t + \Delta t), \vec{v}_i(t + \Delta t)$
- Based on numerical integration scheme (e.g. Verlet algorithm)



Verlet Algorithm

1. $\vec{a}_i(t) = \frac{1}{m} \vec{F}_i(\vec{r}_i(t))$
2. $\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \vec{v}_i(t)\Delta t + \frac{1}{2}\vec{a}_i(t)\Delta t^2$
3. $\vec{v}_i\left(t + \frac{\Delta t}{2}\right) = \vec{v}_i(t) + \frac{\Delta t}{2}\vec{a}_i(t)$
4. $\vec{a}_i(t + \Delta t) = \frac{1}{m}\vec{F}_i(r_i(t + \Delta t))$
5. $\vec{v}_i(t + \Delta t) = \vec{v}_i\left(t + \frac{\Delta t}{2}\right) + \frac{1}{2}\vec{a}_i(t + \Delta t)\Delta t$

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Move Atoms

$\vec{r}_i(t + \Delta t), \vec{v}_i(t + \Delta t)$
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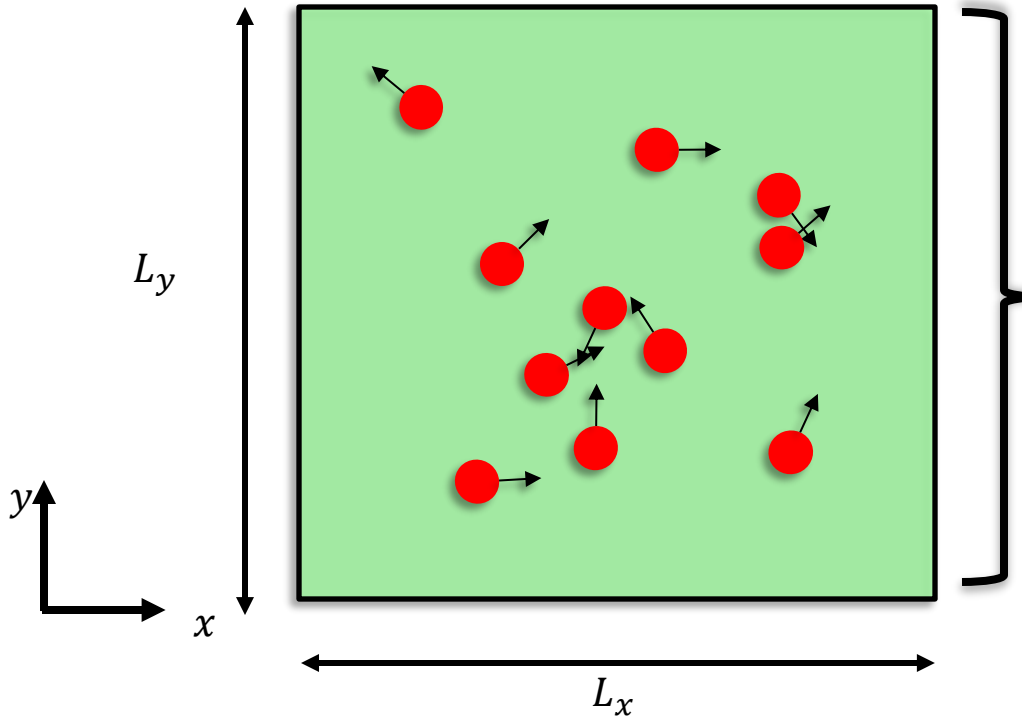
Adjust Thermodynamics
- NVT/NVE/NPT Ensemble
- Based on equilibration or production conditions

Simulation Complete

Update Timestep

$t = t + \Delta t$



Kinetic Energy: $\langle KE \rangle = \left\langle \frac{1}{2} \sum_i^N m_i v_i^2 \right\rangle$

Temperature: $T = \frac{2}{3Nk_b} \langle KE \rangle$

Configuration Energy: $\langle U_c \rangle = \langle \sum_i \sum_{j>i}^N U(r_{ij}) \rangle$

Pressure: $PV = Nk_bT - \frac{1}{3} \langle \sum_{i=j}^{N-1} \sum_{j>1}^N \vec{r}_{ij} \cdot \vec{F}_{ij} \rangle$

Canonical (NVT): Constant number of atoms, volume, and temperature

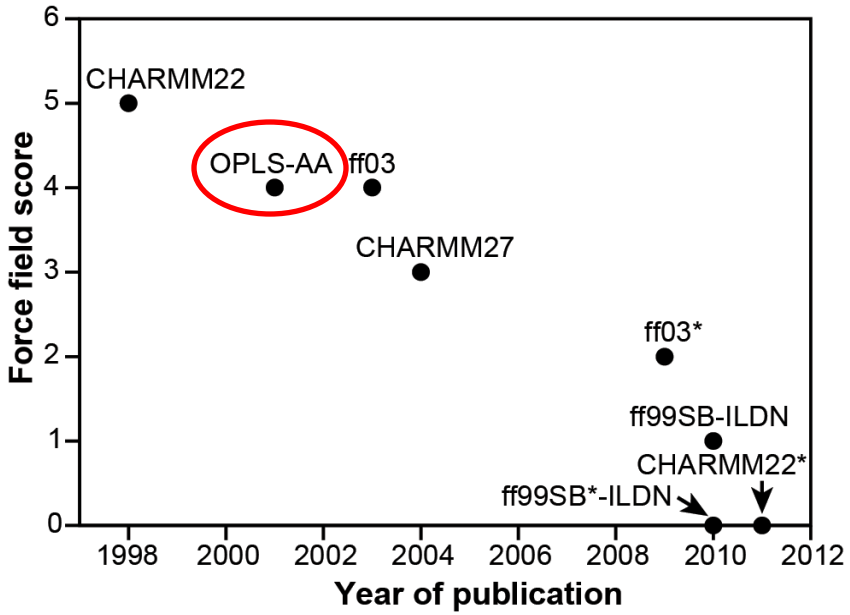
Microcanonical (NVE): Constant number of atoms, volume, and energy

Isothermal-Isobaric (NPT): Constant number of atoms, pressure, and temperature

An ensemble is a collection of systems described by the same set of microscopic interactions and sharing a common set of macroscopic properties

Force Fields – Classifications

- Force fields can be generally categorized in two ways:
  - **Material properties**
    - Organic compounds and biomolecules
    - Polymers
    - Advanced materials
    - Chemically reactive and catalytically activated systems
    - Granular or rigid bodied systems
  - **Underlying Physics and Chemistry (i.e. functional form)**
    - All-atom, unite-atom, bead-spring
    - Classical vs. reactive
    - Polarizable vs. nonpolarizable
    - Implicit vs. explicit solvent potentials
- An inadequate force field can produce inaccurate results as the simulation time increases



Different force fields "scored" based on ability to reproduce experimental data for protein dynamics, where lower scores indicate better agreement [1]

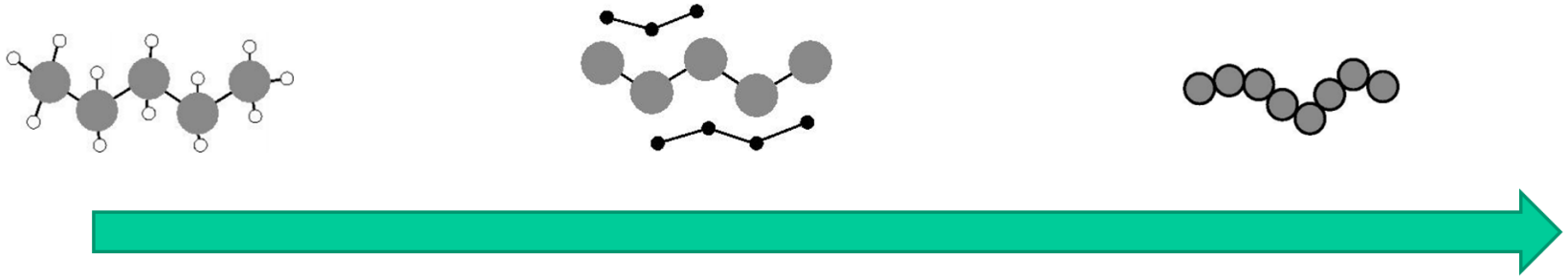
CHARMM, AMBER, and OPLS are commonly used, "universal" force fields for a wide range of organic molecules.

[1] K. Lindorff-Larsen, P. Maragakis, S. Piana, M. P. Eastwood, R. O. Dror, and D. E. Shaw, "Systematic Validation of Protein Force Fields against Experimental Data," PLoS One, vol. 7, no. 2, p. e32131, Feb. 2012, [Online]. Available: https://doi.org/10.1371/journal.pone.0032131.

Force Fields – Classifications

Underlying Physics and Chemistry (i.e. functional form)

- All-atom, united-atom, bead-spring
- Classical vs. reactive
- Polarizable vs. nonpolarizable



All-atom

- Includes parameters for every type of atom in the system

United-atom

- Approximates molecular properties combining atoms into groups (i.e. hydrogen and carbon form a methyl group)
- Computational cost improved by 20-30x

Bead-Spring

- Example of further, coarse-grained interatomic potential
- Offers significant reduction in computational cost and allows for mesoscale-type simulations

Molecular dynamics coarse-graining (Images from https://lammps.sandia.gov/tutorials.html)

Force fields can be coarse-grained to simplify necessary terms in the potential function and achieve higher computational efficiency.

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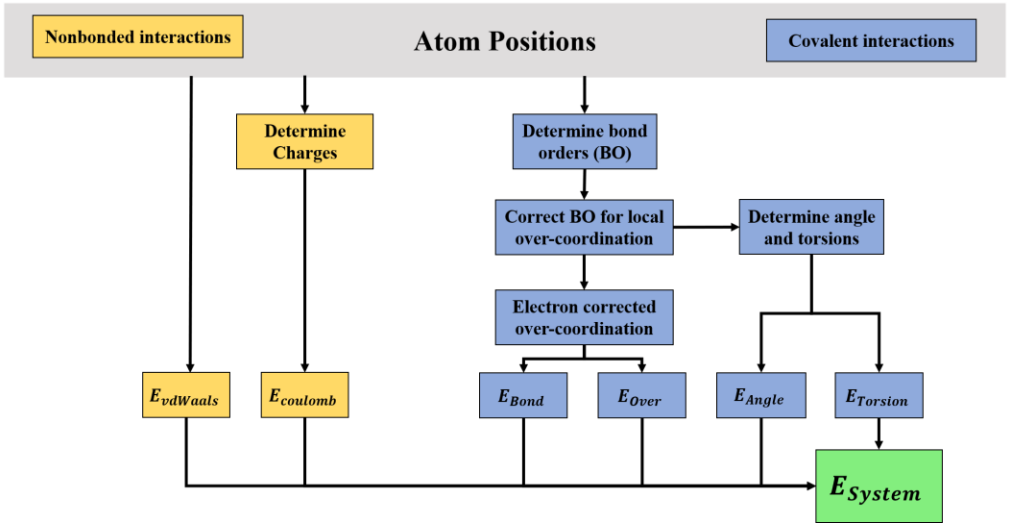

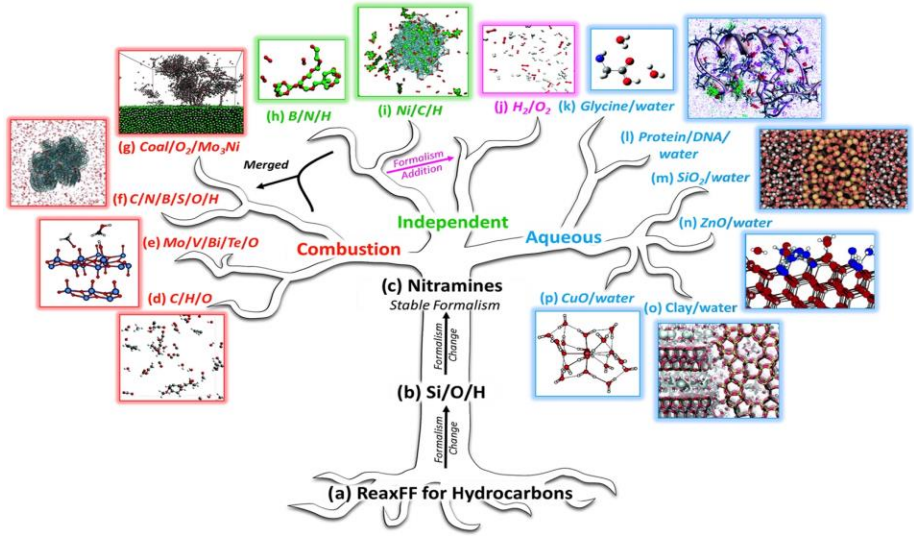

Iterative methodology of ReaxFF force field MD simulations (left) and ReaxFF development tree, where each branch represents a transferable set of parameters for hydrocarbon applications (right) [1,2]

$$BO_{ij} = \exp\left[p_{bo,1}\left(\frac{r_{ij}}{r_0^{\sigma}}\right)^{p_{bo,2}}\right] + \exp\left[p_{bo,3}\left(\frac{r_{ij}}{r_0^{\pi}}\right)^{p_{bo,4}}\right] + \exp\left[p_{bo,5}\left(\frac{r_{ij}}{r_0^{\pi\pi}}\right)^{p_{bo,6}}\right]$$

Single (Sigma) bond | Double (first pi) bond | Triple (second pi) bond

Reactive force fields, such as ReaxFF, employ a bond-order formalism to describe the formation and breaking of bonds.

[1] T. P. Senftle et al., "The ReaxFF reactive force-field: development, applications and future directions," npj Comput. Mater., vol. 2, no. 1, p. 15011, 2016, doi: 10.1038/npjcompumats.2015.11.
[2] M. F. Russo and A. C. T. van Duin, "Atomistic-scale simulations of chemical reactions: Bridging from quantum chemistry to engineering," Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms, vol. 269, no. 14, pp. 1549–1554, 2011, doi: https://doi.org/10.1016/j.nimb.2010.12.053.

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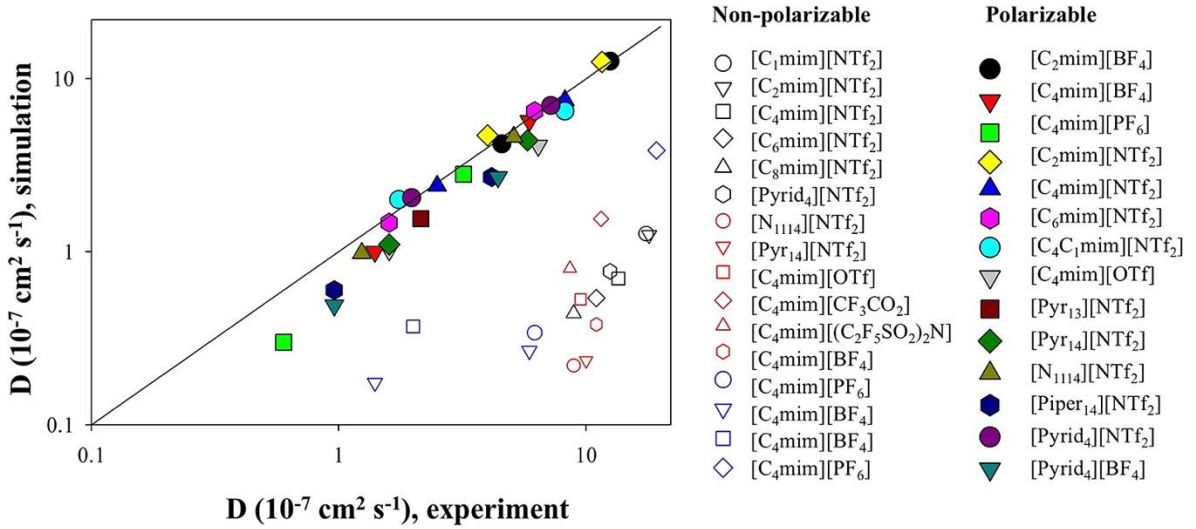
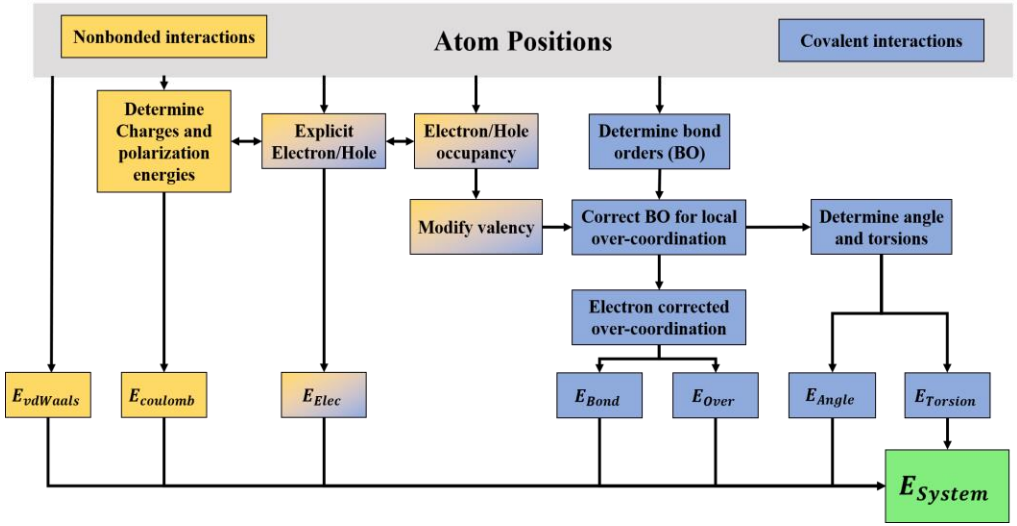


Comparison of polarizable and non-polarizable force fields based on self-diffusion coefficients obtained by MD simulations and experimental results. A C_2mim and C_4mim cation is equivalent to an EMIM and BMIM cation, respectively. [1]



Polarizable force fields, such as eReaxFF or APPLE&P, treat the electronic degrees of freedom explicitly.

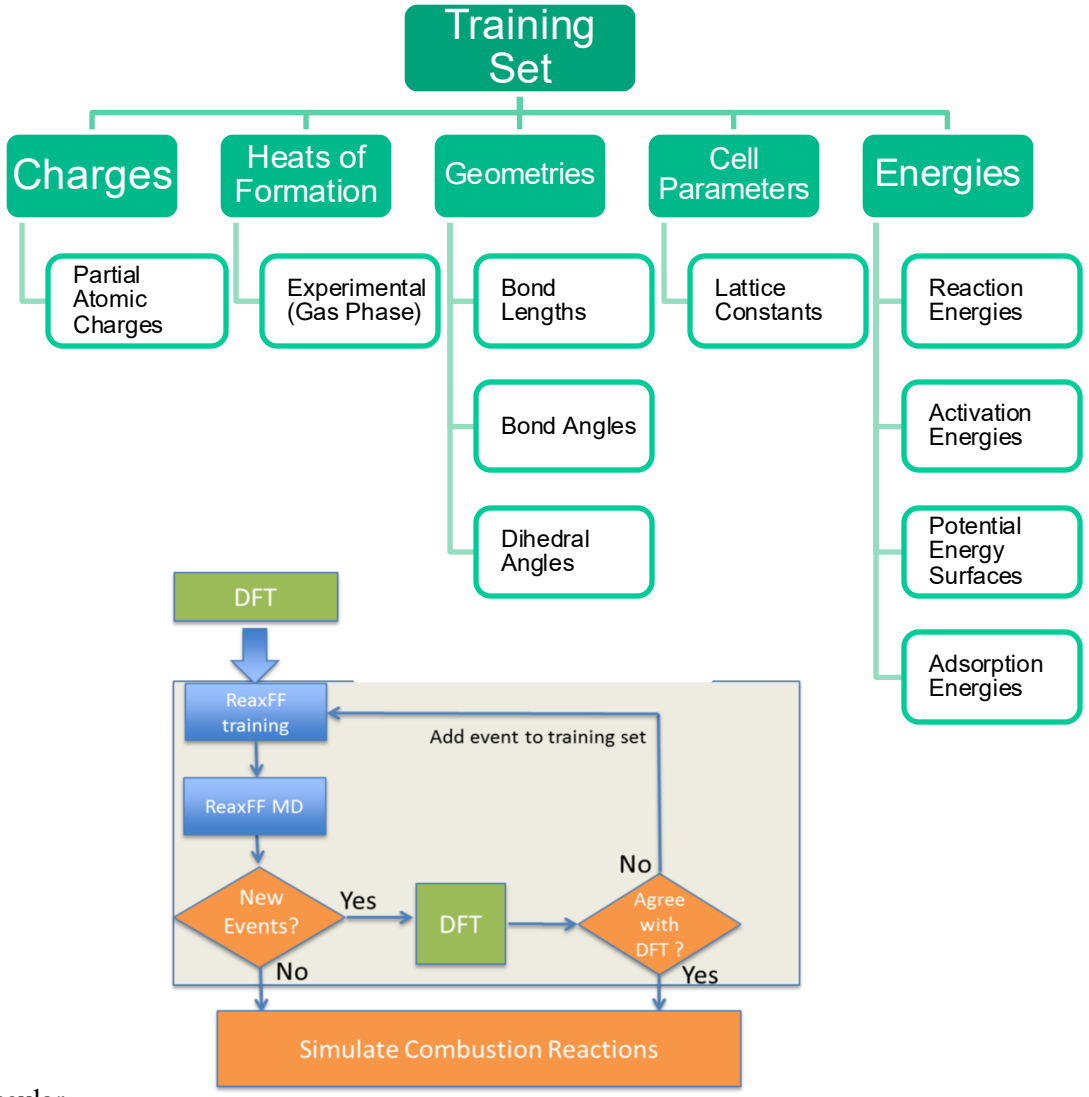
[1] D. Bedrov, J.-P. Piquemal, O. Borodin, A. D. MacKerell, B. Roux, and C. Schröder, "Molecular Dynamics Simulations of Ionic Liquids and Electrolytes Using Polarizable Force Fields," Chem. Rev., vol. 119, no. 13, pp. 7940–7995, Jul. 2019, doi: 10.1021/acs.chemrev.8b00763.
[2] M. M. Islam, G. Kolesov, T. Verstraelen, E. Kaxiras, and A. C. T. van Duin, "eReaxFF: A Pseudoclassical Treatment of Explicit Electrons within Reactive Force Field Simulations," J. Chem. Theory Comput., vol. 12, no. 8, pp. 3463–3472, Aug. 2016, doi: 10.1021/acs.jctc.6b00432.

Force Fields – Training Set Development

- A training set includes physical parameters derived experimentally or from quantum chemical calculations (i.e. density function theory) that characterize a specific system of interest
- Training set development is an iterative, optimization process aimed at minimizing an objective function (i.e. sum of squared differences between the set of the parameters and the values determined by the MD simulation)
- Large number of parameters and nonlinearities can lead to overparameterization and limits force field transferability

$$\textbf{error} = \sum_{i=1}^{n} \left[\frac{x_{i,QM} - x_{i,ReaxFF}}{\sigma} \right]^2$$

- Parameters x_i determined from quantum mechanical or MD simulations
- Accuracy of the training σ



[1] M. R. Weismiller, C. E. Junkermeier, M. F. Russo, M. R. Salazar, D. Bedrov, and A. C. T. van Duin, "ReaxFF molecular dynamics simulations of intermediate species in dicyanamide anion and nitric acid hypergolic combustion," *Model. Simul. Mater. Sci. Eng.*, vol. 23, no. 7, p. 74007, 2015, doi: 10.1088/0965-0393/23/7/074007.

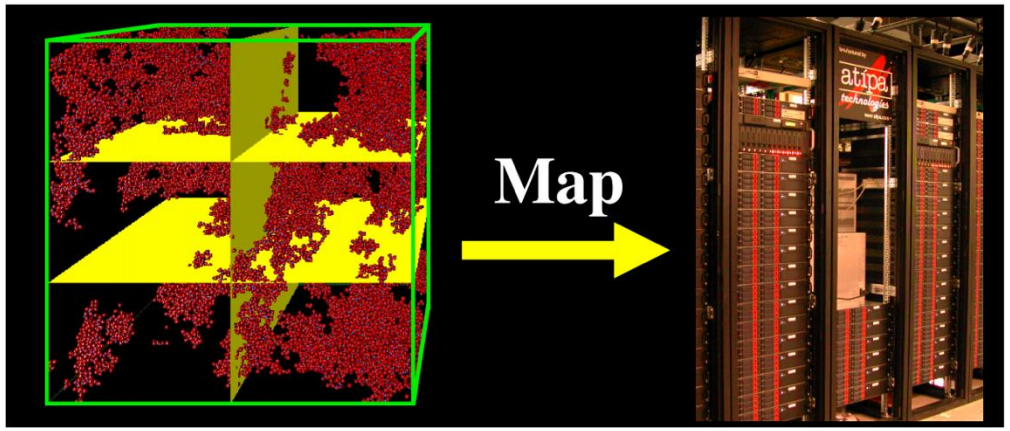
MD for Electrosprays in Literature

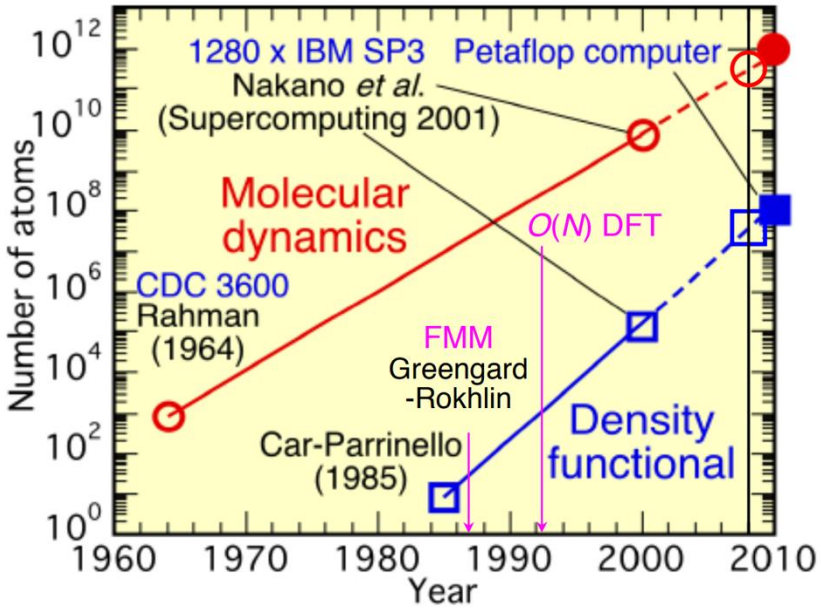
- Coarse-grain methods focus on achieving mesoscale-type simulation results
- High-fidelity force fields (i.e. polarizable) for ionic liquids require training set development
- Many ES MD publications for non-propulsion applications
- Limited MD studies on Emi-Im in ES

Researcher	Force Field or Potential Used	Application
M. Micci	Coarse-grained methods; ion-ion potentials fitted for specific materials	Liquid gallium
D. Levin	Coarse-grain methods (i.e. effective field coarse graining – EFCG)	EMI-BF4, EAN
P. Lozano	Assisted Model Building with Energy Refinement (AMBER)	EMI-BF4
Y. Takao	Optimized Potentials for Liquid Simulations-All Atom (OPLS-AA)	EMI-BF4, EMI-Im
M. Gamero	All-atom: Ziegler-Biersack-Littmark (ZBL) potential for close-range and Morse potential for long-range	EMI-Im nanodroplet impact on porous surfaces
B. Prince	DCA (dicyanamide) force field (made in-house)	Solvated ionic cluster dissociation (many different protic ILs)
D. Bedrov	APPLE&P (Atomistic Potential for Liquids, Electrolytes and Polymers); eReaxFF	Imidazolium-based ionic liquids for energy storage applications

Computational Considerations

- Main constraint: **timescale** (i.e. wall clock time per simulation Δt)
- Algorithm improvements
  - Verlet, Gears, Predictor-corrector,
  - Linked-list cells
- Parallelization
- Hardware improvements (GPUs)
  - Revolution from teraflops (10^{12} floating point operations per second) to petaflop (10^{15} flops) machines has led to many realistic simulations in materials, nanotechnology, and bioengineering





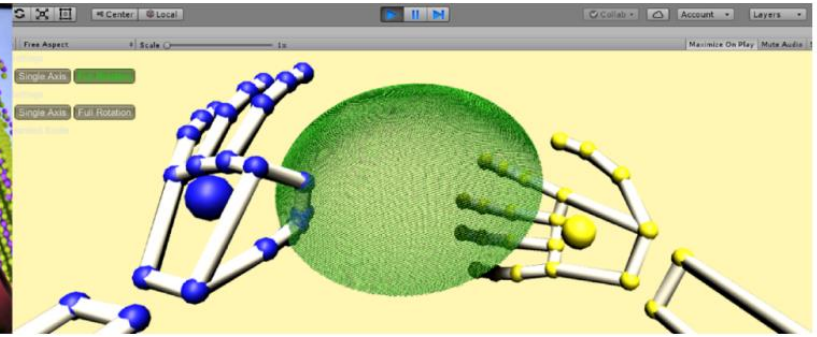
Images from http://cacs.usc.edu/education/cs596.html

Conclusions

- MD is a computational tool used to predict trajectories and material properties
- Choosing a force field is a crucial aspect of a successful MD simulation
- MD has benefitted from growing computational resources
- Questions?

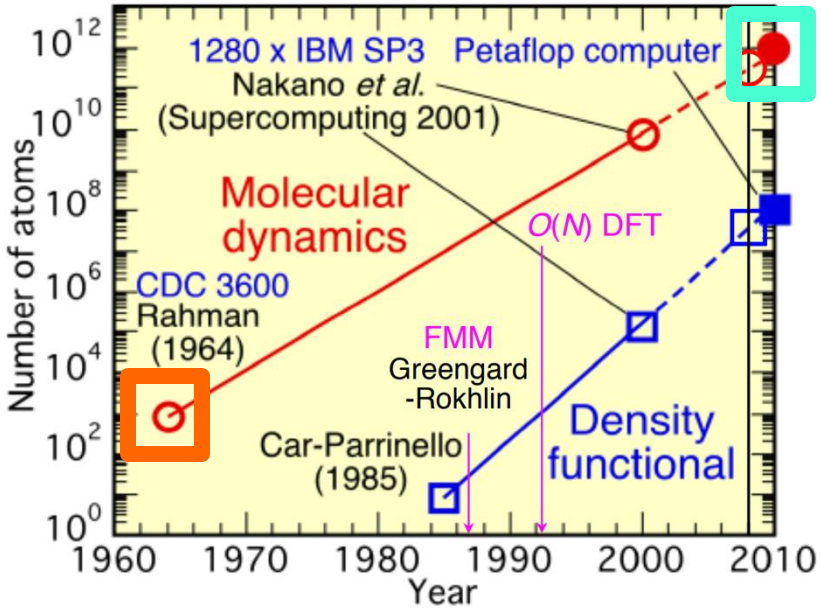
Backup: Common Tools

- MD Software Packages
  - LAMMPS, CHARMM, AMBER, NAMD, Gromacs, Desmond, OpenMM
- Post-Processing & Visualization
  - Jmol, Visual Molecular Dynamics (VMD), POV-Ray, GEARS (Game-Engine-Assisted Research platform for Scientific computing in Virtual Reality)



Backup: Computational Considerations

1960's



2018

Images from http://cacs.usc.edu/education/cs596.html

Backup: Ensembles and Thermostats