Multiscale Materials Modeling

Lecture 02

Capabilities of Classical Molecular Simulation

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Fundamentals of Sustainable Technology

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Capabilities of Classical Molecular Simulations

What are Classical Molecular Simulations?

Classical Molecular Dynamics simulations provide the distribution of atoms and molecules in a material. They do not provide the distribution of electrons, in contrast to quantum mechanical calculations. The “classical” in classical molecular dynamics indicates that the simulations are governed by classical mechanics, i.e. Newton’s equation of motion,

force = mass * acceleration

Thus quantum effects are generally neglected.

What are Molecular Dynamics?

Molecular Dynamics simply accepts that the trajectory (position and velocity) of each atom is given by

$$\underline{F} = m\underline{a} = m\frac{d^2\underline{r}}{dt^2}$$

The force is defined in classical mechanics to be the gradient of the potential energy

$$\underline{F} \equiv -\nabla U(\underline{r})$$

Thus for a system of N atoms in 3-dimensional space, we have 3N second-order nonlinear ODEs of the form

$$m\frac{d^2 r_x}{dt^2} = -\frac{\partial U(\underline{r})}{\partial x}$$

Molecular Dynamics is the numerical solution of this set of ODEs.
It is crucial to understand that the potential, $U(r)$, is an input.
The simulation results are only as good as the interaction potential.

What are Monte Carlo Simulations?

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The Monte Carlo technique takes a very different approach to obtaining the distribution of atomic positions than molecular dynamics. The Monte Carlo (MC) technique relies on statistical mechanics to give a weighting to each configuration based on its energy. The configuration is counted in the simulation average based on a Boltzmann probability,

$$p \propto \exp\left[-\frac{U(\underline{r})}{k_B T}\right]$$

Where k_B is the Boltzmann constant and T is the temperature. Millions of configurations are randomly generated and a statistical average of the system and its associated properties are generated. This procedure generates positions but not velocities. There is no time associated with Monte Carlo, so this method does not generate transport properties. Note again that just as in molecular dynamics, the interaction potential is an input. The simulations are only as good as the interaction potential.

Dynamics in MD and MC

Molecular Dynamics (MD) has an intrinsic time scale in it. Monte Carlo (MC) has no absolute time scale associated with it. Therefore, real dynamics are observed in MD simulations. This has advantages and disadvantages.

Advantages to MD

dynamic properties such as viscosity, diffusivity, thermal conductivity and structural relaxation times can be obtained unambiguously from MD simulations

Disadvantages to MD

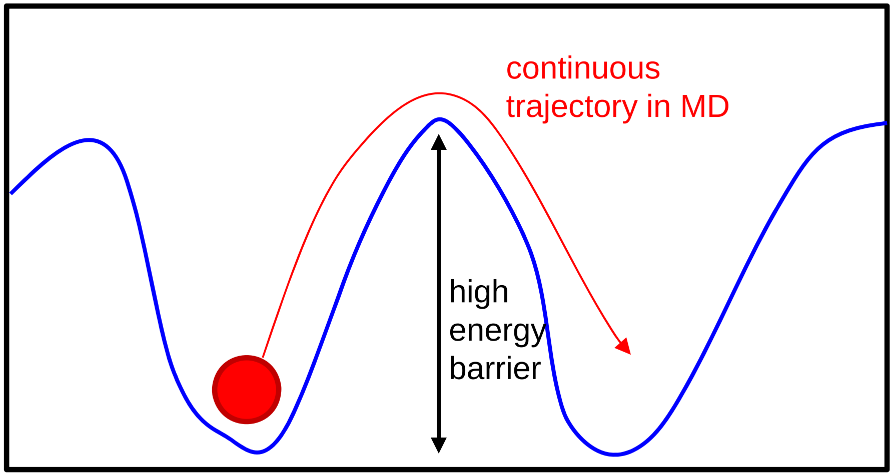
MD simulations typically run from 1 to 100 ns.

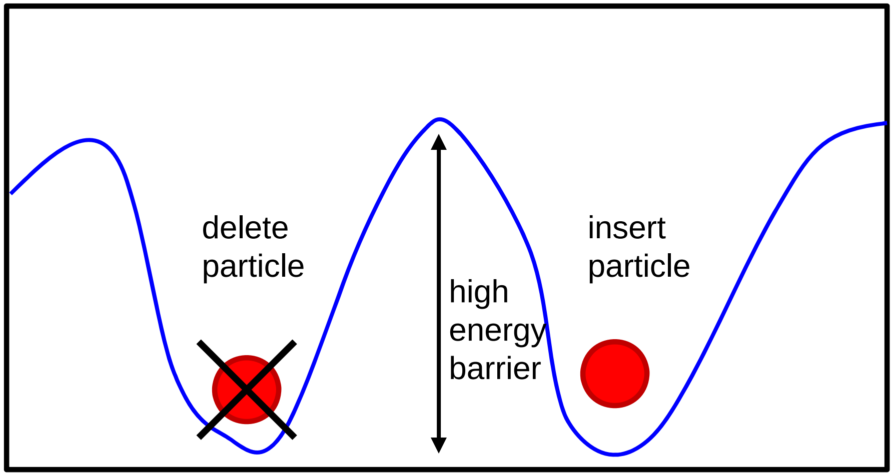
Any phenomena that occurs on a time scale greater than the duration of the simulation will not be captured by the simulation. Very slow relaxation or diffusion processes will not be modeled by MD. Example: relaxation of long polymer chains.

Any phenomena that occur very rarely will not be sampled in a statistically valid manner due to few observations of the phenomena. Example: transitions with high energy barriers leading to very low rates.

Dynamics in MD and MC

Example of diffusion among deep energy wells.





In molecular dynamics because the system obeys physical laws such as the conservation of energy and momentum, particles follow a continuous path. If a particle rarely has sufficient energy to overcome a barrier, then the observed passings are very few.

In Monte Carlo simulations, one employs unphysical moves, where a particle is deleted at one location and inserted at another location. The move is accepted based not on the path but on the stability of the two endpoints. Thus states isolated by very slow processes can still be studied.

Ensembles in MD and MC

Molecular Dynamics simulations naturally occur in the NVE (or microcanonical) ensemble, in which the number of particles, N, the volume, V, and the energy, E is constant. This is natural because the equations conserve energy.
MD simulations can easily be run in the NVT (canonical) ensemble by the introduction of a thermostat that adds or removes heat from the system to maintain the correct temperature. Furthermore, MD simulations can be easily run in the (NpT) ensemble by the introduction of a barostat that regulates the pressure by controlling the volume of the simulation. All of these simulations have a constant number of particles, N.

Monte Carlo simulations are naturally run in the NVT ensemble, where the temperature, a parameter in MC is constant. However, unlike MD, Monte Carlo simulations can also be run in the μVT (grand canonical) ensemble, in which the chemical potential is held constant and the number of particles is allowed to vary. This is easy to accomplish since unphysical moves are allowed and particles can be deleted and inserted in Monte Carlo. The ability to run in the grand canonical ensemble makes MC simulations ideal for modeling multiphase equilibrium. (Examples follow.)

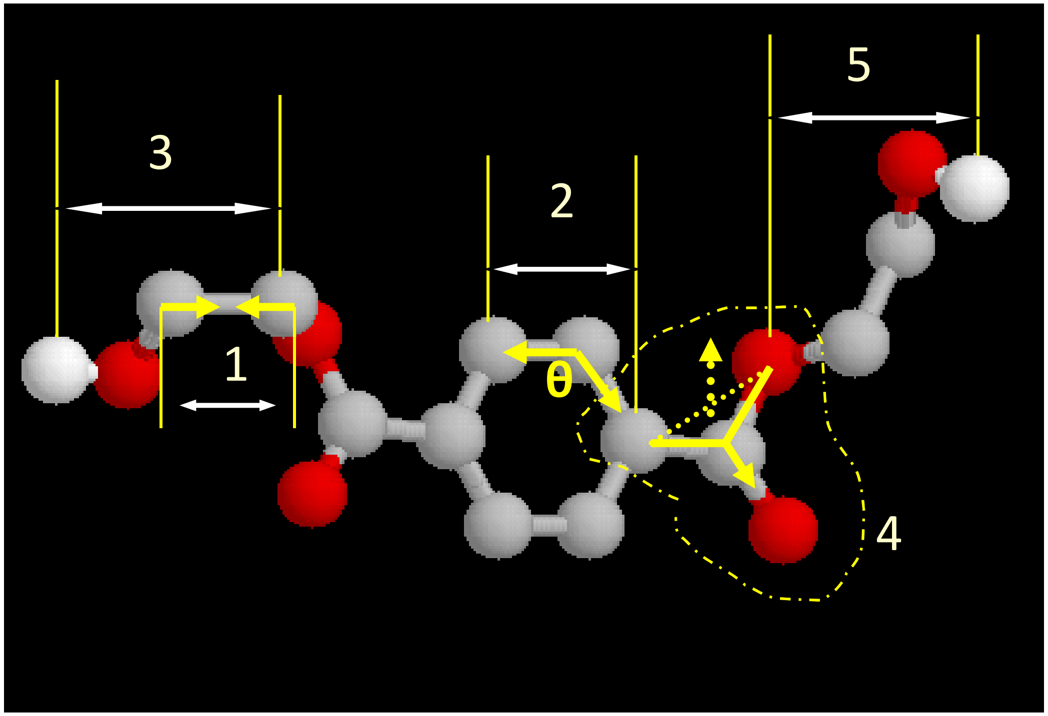
Outline

Capabilities of Classical Molecular Simulations

- I. What are Classical Molecular Simulations?
  - I.A. Molecular Dynamics Simulation
  - I.B. Monte Carlo Simulation
- II. Applications
  - II.A. PET Properties
  - II.B. Adsorption Isotherms for RDX in MOFs
  - II.C. Nonequilibrium Molecular Dynamics of Polymers
  - II.D. Reactive Molecular Dynamics
  - II.E. Two Phase Simulations
- III. Strengths and Weaknesses
  - III.A. Theoretical Limitations
  - III.B. Computational Limitations
- IV. References

PET Properties

Molecular Dynamics simulations can be used to generate structural, thermodynamic, mechanical and transport properties of materials.
In this example, we look at the generation of the physical properties of the polymer, PET, from which plastic bottles (among many other things) are made.



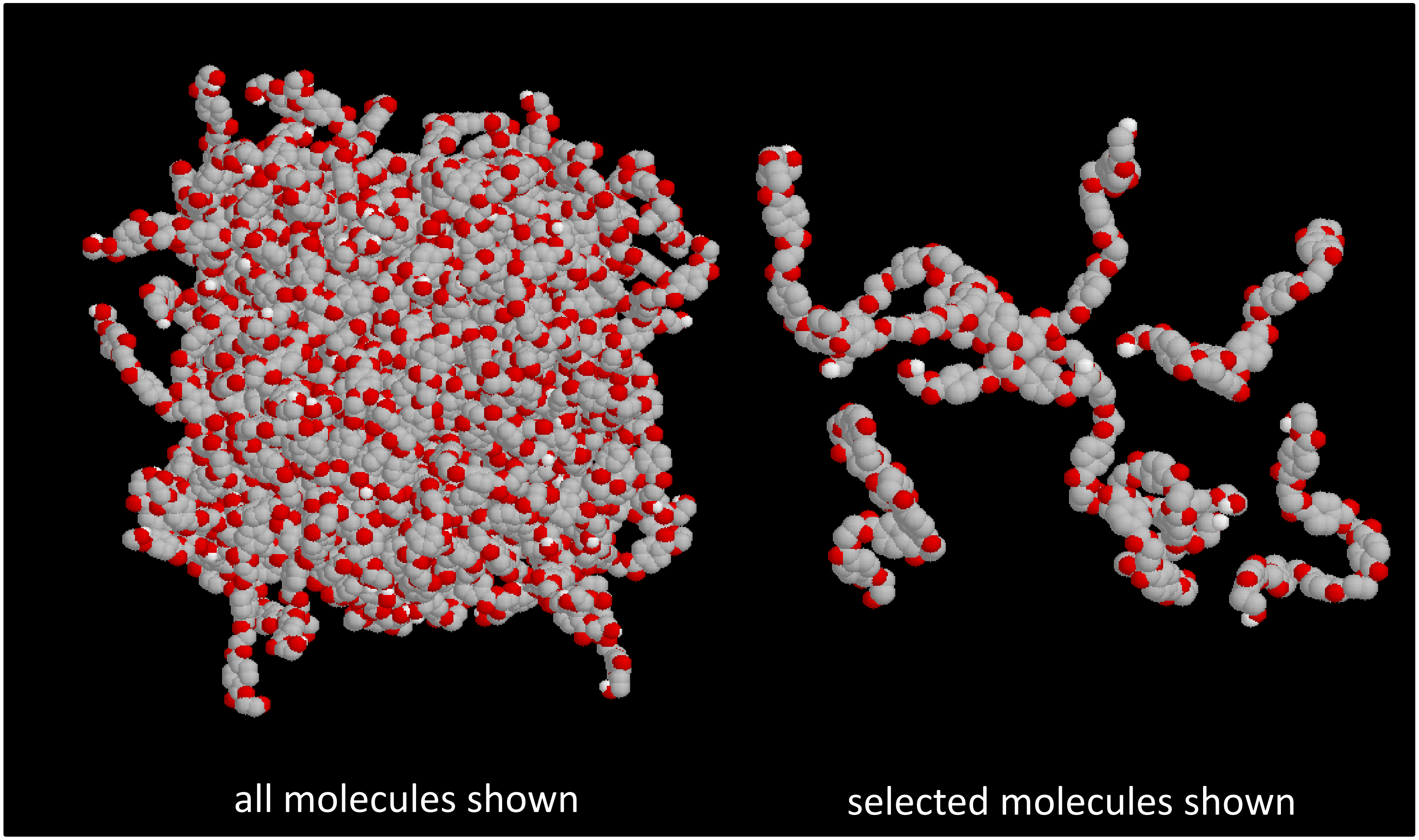
1: bond stretching
2: bond bending
3: bond torsion
4: out of plane bending
5: intramolecular L-J and electrostatic potential
(for atoms over four bonds)

Note: not all pairs are listed
O: red; C: grey; H: white

The potential we provide must include all physically significant modes of interaction.

PET Properties

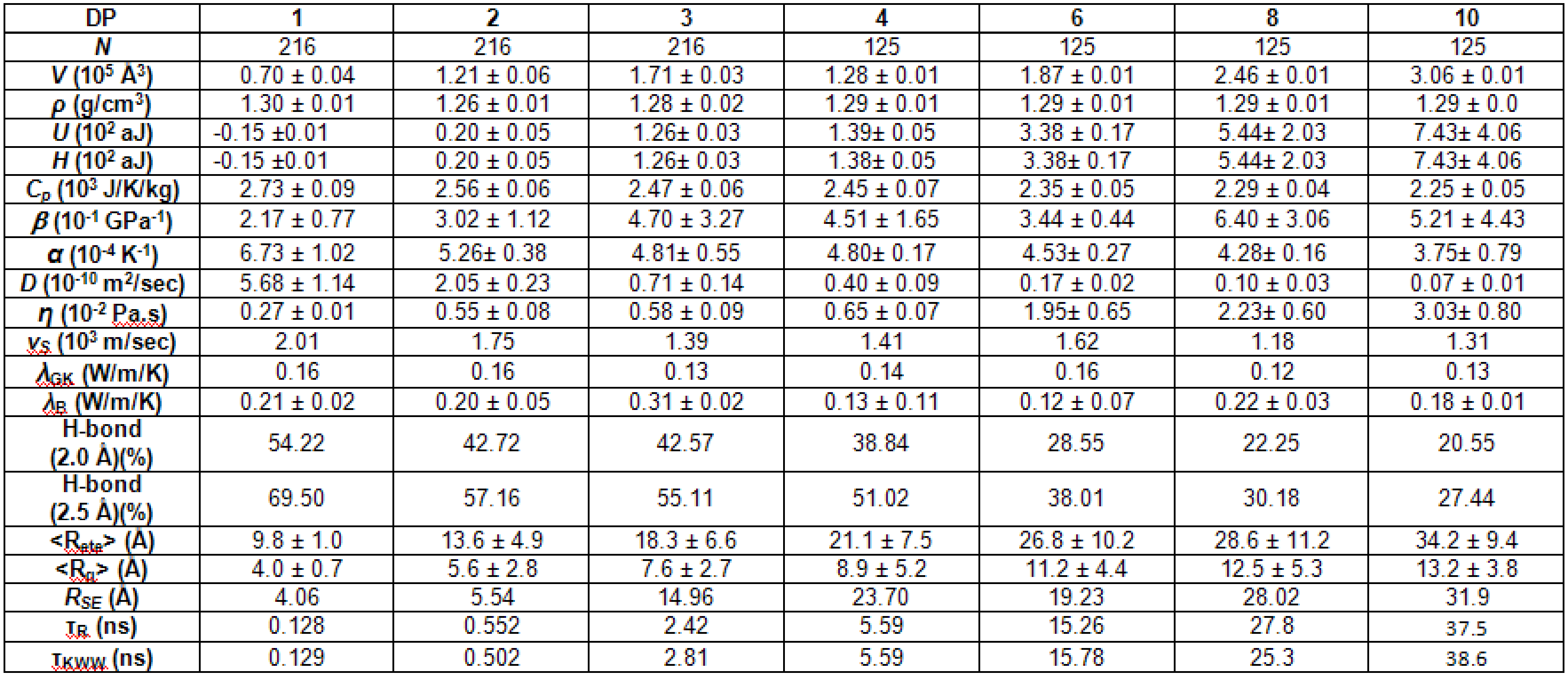
Molecular Dynamic Simulation Snapshots



Snapshots of PET hexamer at T = 563 K and p = 0.13 kPa.

PET Properties

MD Simulation data for PET (DP = 1, 2, 3, 4, 6, 8 and 10) at p = 0.13 kPa, T = 563 K.

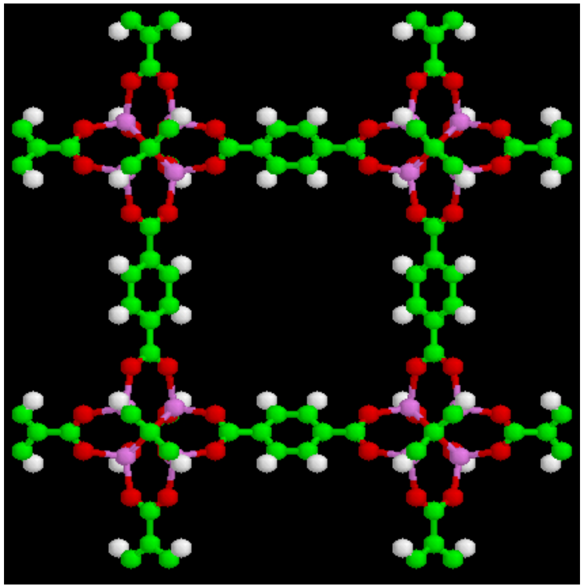


DP	**1**	**2**	**3**	**4**	**6**	**8**	**10**
N	216	216	216	125	125	125	125
V (10^5 Å^3)	0.70 ± 0.04	1.21 ± 0.06	1.71 ± 0.03	1.28 ± 0.01	1.87 ± 0.01	2.46 ± 0.01	3.06 ± 0.01
ρ (g/cm^3)	1.30 ± 0.01	1.26 ± 0.01	1.28 ± 0.02	1.29 ± 0.01	1.29 ± 0.01	1.29 ± 0.01	1.29 ± 0.0
U (10^2 aJ)	-0.15 ±0.01	0.20 ± 0.05	1.26± 0.03	1.39± 0.05	3.38 ± 0.17	5.44± 2.03	7.43± 4.06
H (10^2 aJ)	-0.15 ±0.01	0.20 ± 0.05	1.26± 0.03	1.38± 0.05	3.38± 0.17	5.44± 2.03	7.43± 4.06
C_p (10^3 J/K/kg)	2.73 ± 0.09	2.56 ± 0.06	2.47 ± 0.06	2.45 ± 0.07	2.35 ± 0.05	2.29 ± 0.04	2.25 ± 0.05
β (10^{-1} GPa^{-1})	2.17 ± 0.77	3.02 ± 1.12	4.70 ± 3.27	4.51 ± 1.65	3.44 ± 0.44	6.40 ± 3.06	5.21 ± 4.43
α (10^{-4} K^{-1})	6.73 ± 1.02	5.26± 0.38	4.81± 0.55	4.80± 0.17	4.53± 0.27	4.28± 0.16	3.75± 0.79
D (10^{-10} m^2/sec)	5.68 ± 1.14	2.05 ± 0.23	0.71 ± 0.14	0.40 ± 0.09	0.17 ± 0.02	0.10 ± 0.03	0.07 ± 0.01
η (10^{-2} Pa.s)	0.27 ± 0.01	0.55 ± 0.08	0.58 ± 0.09	0.65 ± 0.07	1.95± 0.65	2.23± 0.60	3.03± 0.80
v_S (10^3 m/sec)	2.01	1.75	1.39	1.41	1.62	1.18	1.31
λ_{GK} (W/m/K)	0.16	0.16	0.13	0.14	0.16	0.12	0.13
λ_B (W/m/K)	0.21 ± 0.02	0.20 ± 0.05	0.31 ± 0.02	0.13 ± 0.11	0.12 ± 0.07	0.22 ± 0.03	0.18 ± 0.01
H-bond (2.0 Å)(%)	54.22	42.72	42.57	38.84	28.55	22.25	20.55
H-bond (2.5 Å)(%)	69.50	57.16	55.11	51.02	38.01	30.18	27.44
$\langle R_{ete} \rangle$ (Å)	9.8 ± 1.0	13.6 ± 4.9	18.3 ± 6.6	21.1 ± 7.5	26.8 ± 10.2	28.6 ± 11.2	34.2 ± 9.4
$\langle R_g \rangle$ (Å)	4.0 ± 0.7	5.6 ± 2.8	7.6 ± 2.7	8.9 ± 5.2	11.2 ± 4.4	12.5 ± 5.3	13.2 ± 3.8
R_{SE} (Å)	4.06	5.54	14.96	23.70	19.23	28.02	31.9
τ_R (ns)	0.128	0.552	2.42	5.59	15.26	27.8	37.5
τ_{KWW} (ns)	0.129	0.502	2.81	5.59	15.78	25.3	38.6

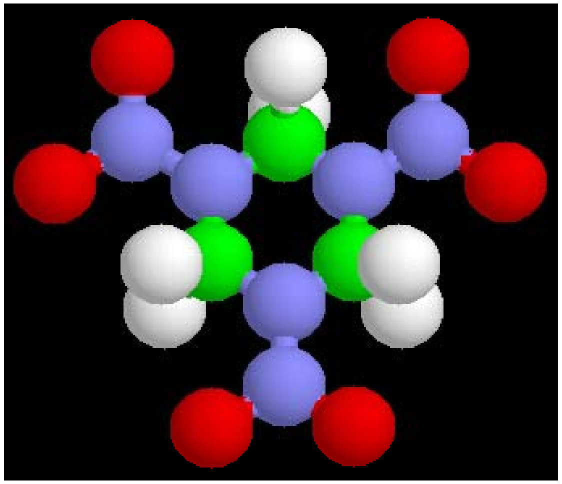
Wang, Q., Keffer, D.J., Petrovan, S., Thomas, J.B., in preparation, 2009.

Adsorption Isotherms for RDX in IRMOF-1

Grand Canonical Monte Carlo simulations can be used to generate adsorption properties for fluids adsorbed in nanoporous materials. In this example, we examine the ability of IsoReticular Metal Organic Framework #1 (IRMOF-1) to adsorb the explosive compound, RDX.



IRMOF-1 Li et al. Nature 1999.

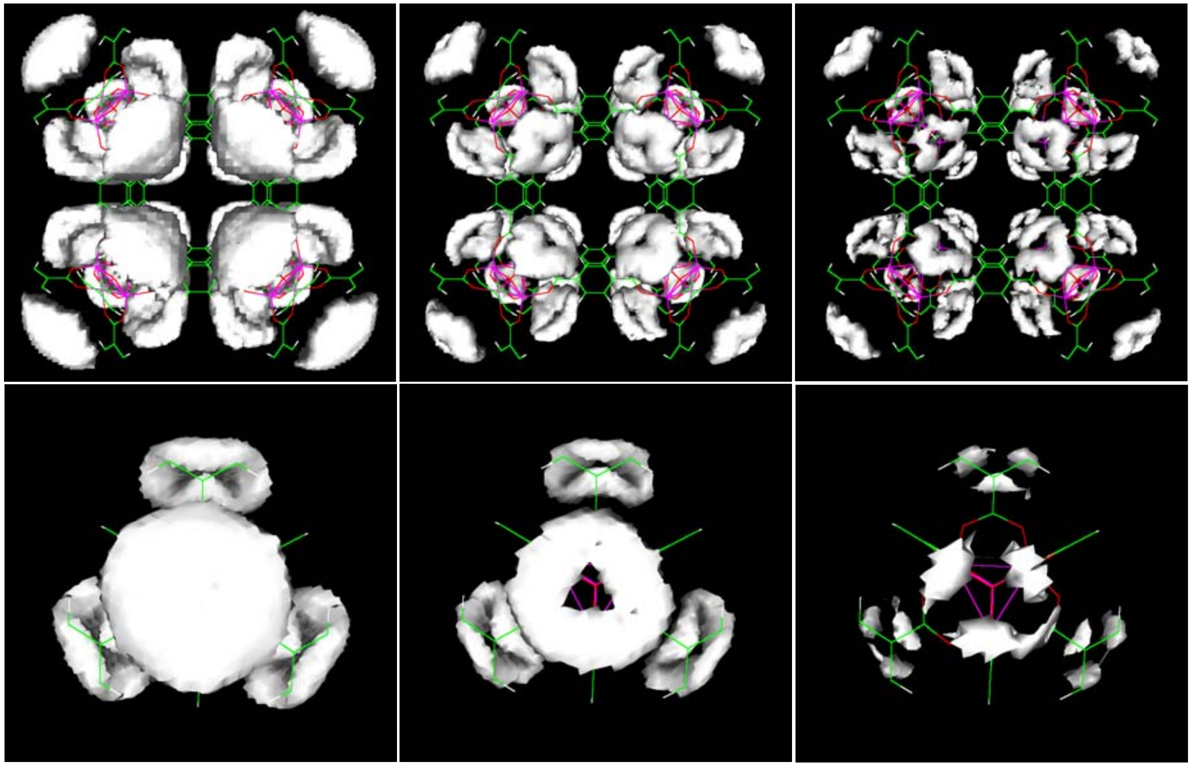


RDX

violet-Zn, red-O, green-C, white-H, blue-N

Adsorption Isotherms for RDX in IRMOF-1

RDX Adsorption Sites in MOF-5



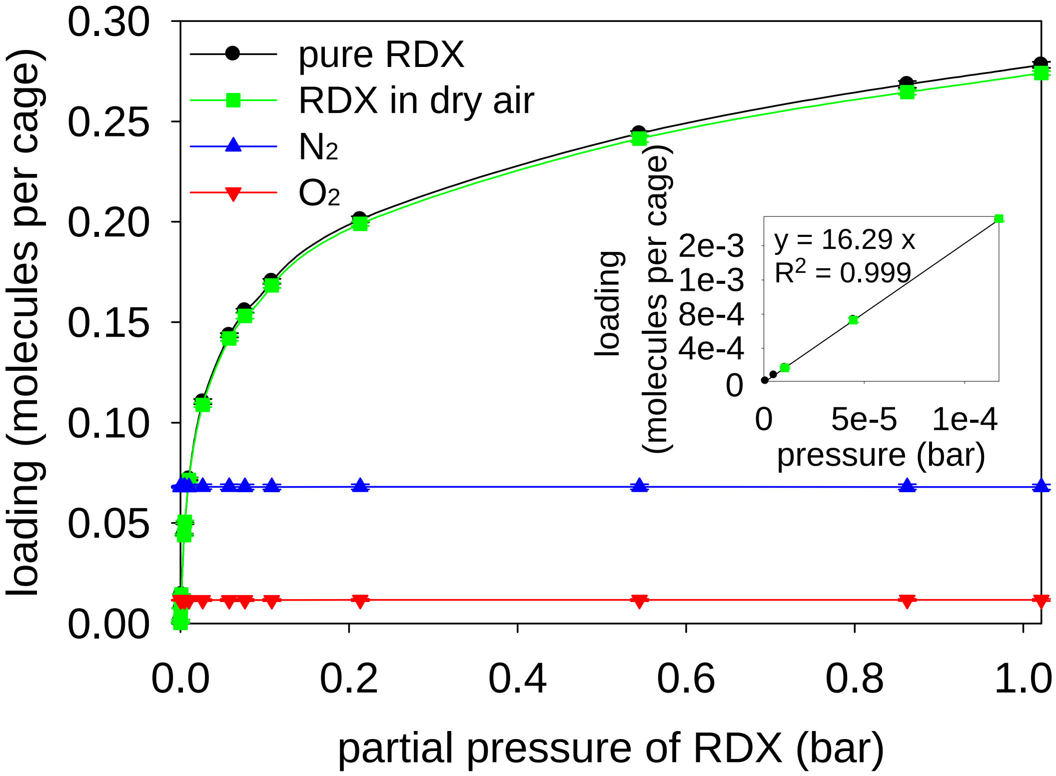
These simulations provide density distribution of the RDX that show where the RDX sits inside the cage. These are called adsorption sites.

Xiong, R., Fern, J.T., Keffer, D.J., Nicholson, D.M., Fuentes-Cabrera, M.A., Mol. Sim., 2009.

Adsorption Isotherms for RDX in IRMOF-1

Adsorption isotherms and energies

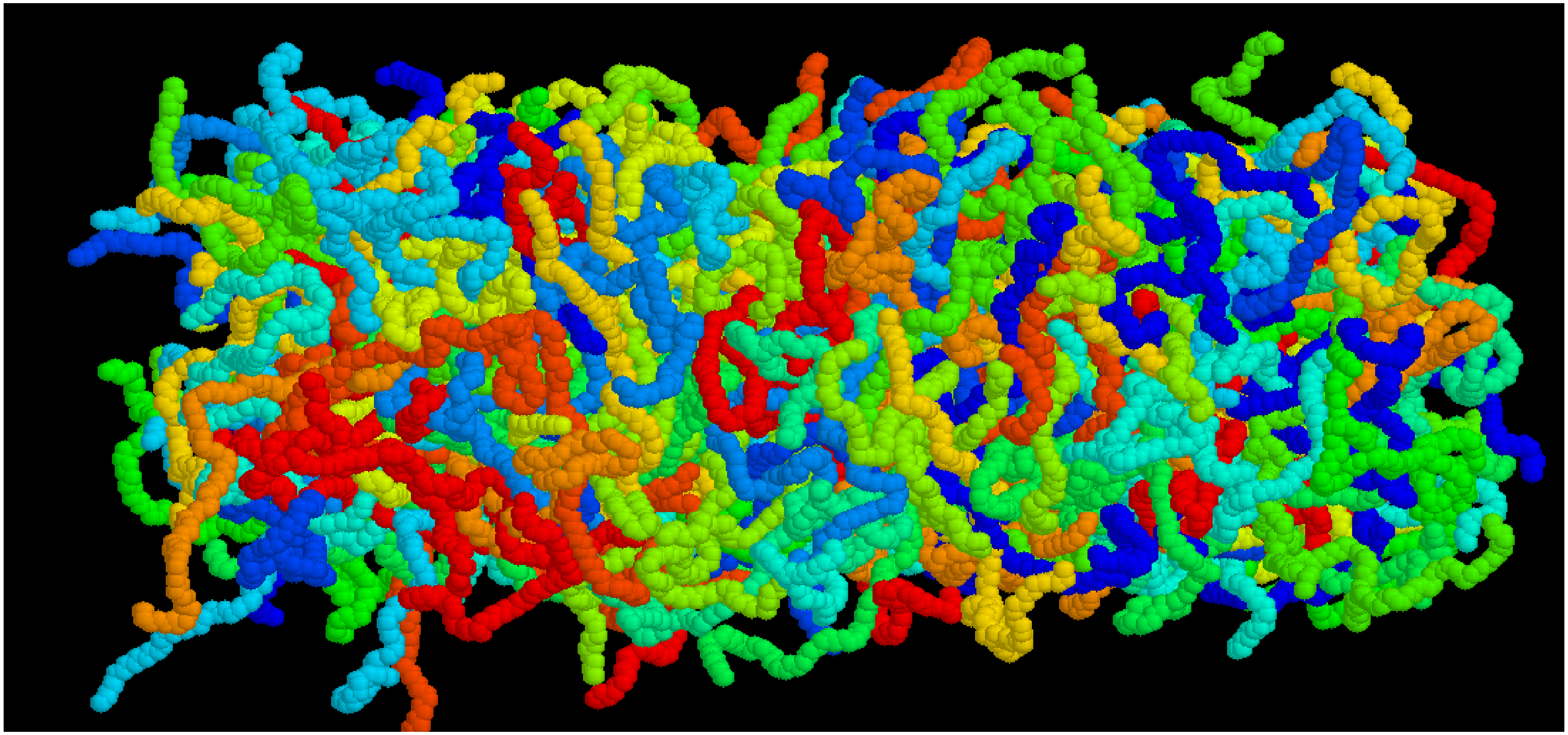
- The highest loading is less than 0.3 RDX/cage.
- The linear regime extends to about 1×10^{-4} bar, which is well above realistic RDX partial pressures.
- The linear regime is defined by a Henry's law constant of 16.3 molecules/cage•bar.



- RDX adsorption isotherm in dry air is virtually the same as that of pure RDX, especially in the low pressure limit of practical interest.
- The binding energy of RDX is about -9.2 kcal/mol, which is in good agreement with quantum chemistry calculation of -9.8 kcal/mol*.

Nonequilibrium MD of Polyethylene

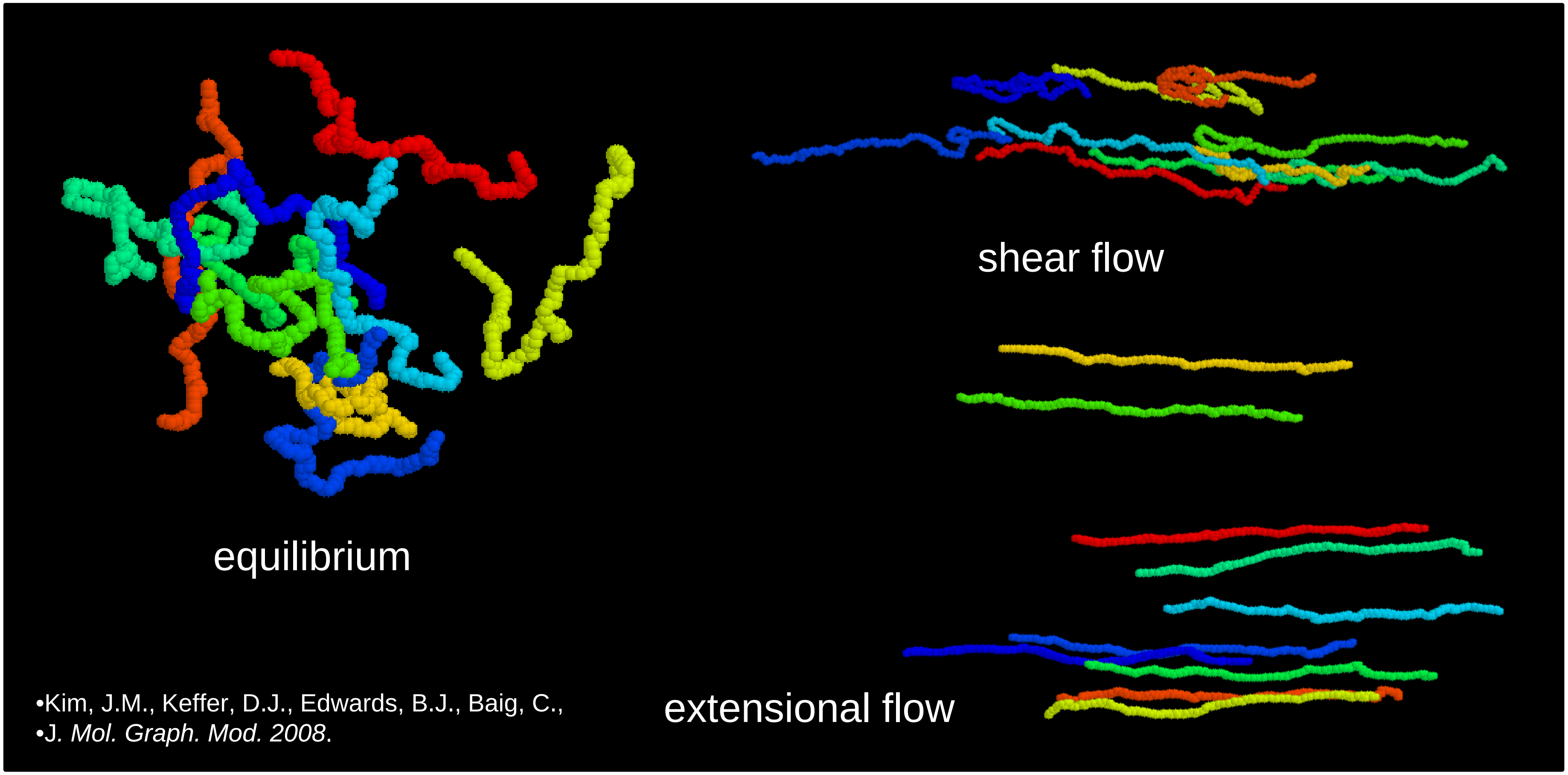
Nonequilibrium Molecular Dynamics simulations can incorporate a flow field so that one can understand how the presence of a flow field changes the molecular structure of the flowing fluid. This is particularly important for polymers.



Polyethylene ($C_{128}H_{258}$) at T = 450 K and p = 1 atm. The coloring is used to show different chains.

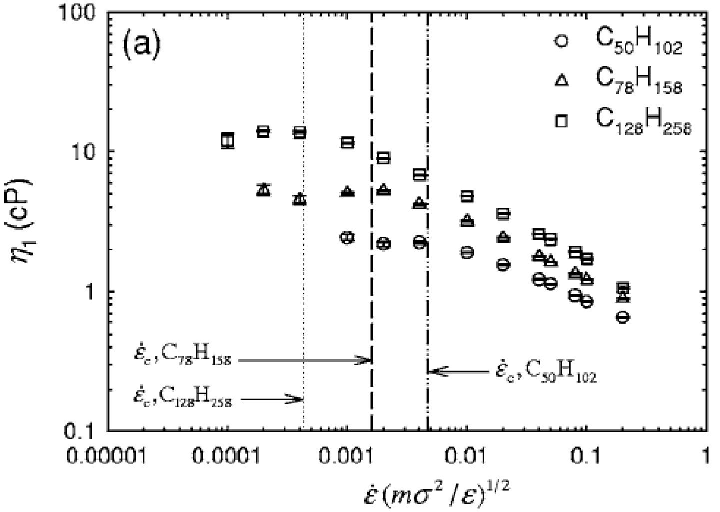
Nonequilibrium MD of Polyethylene

At equilibrium (no flow), the chains are coiled. Under a shear flow, the chains align and extend, but some are folded due to chain tumbling induced by the vorticity of the shear flow. In a vorticity free extensional flow, the chains just align with the flow field and extend.



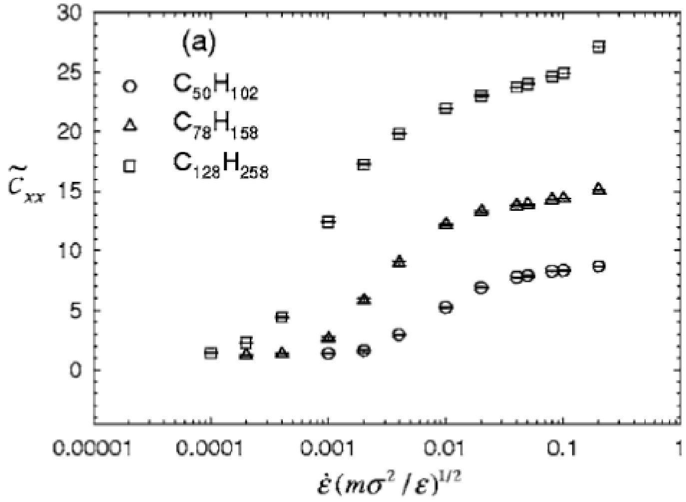
- Kim, J.M., Keffer, D.J., Edwards, B.J., Baig, C.,
- J. *Mol. Graph. Mod. 2008*.

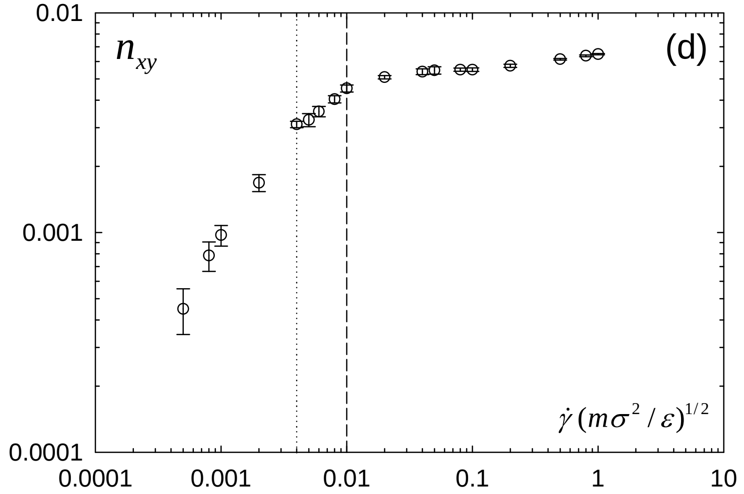
Nonequilibrium MD of Polyethylene



rheological properties (elongational viscosities)

structural properties (conformation tensor)





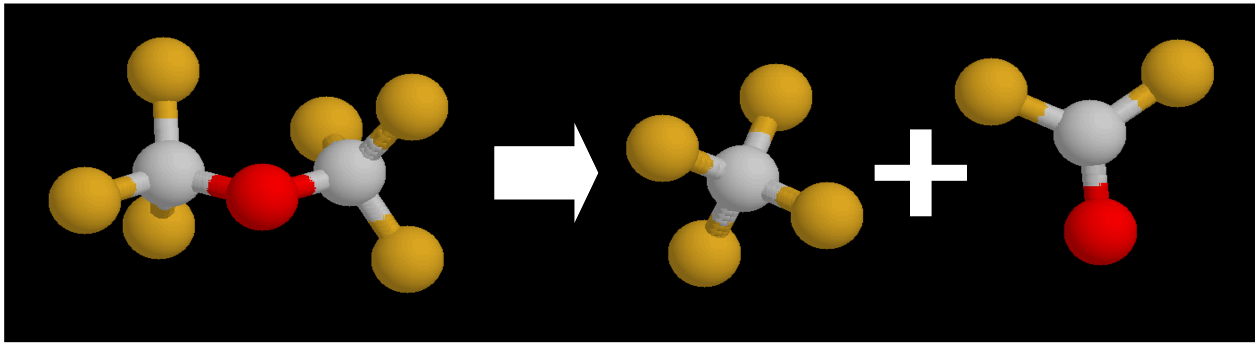
optical properties (birefringence tensor)

Baig, C., Edwards, B.J., Keffer, D.J., Cochran, H.D., Harmandaris, V.A.,, *J. Chem. Phys.*, 2006.
Baig, C., Jiang, B., Edwards, B.J., Keffer, D.J., Cochran, H.D., *J. Rheol.* **2006**.
Baig, C., Edwards, B.J., Keffer, D.J., *Rheologica Acta* 2007.

Reactive Molecular Dynamics

MD doesn't generate electron distributions. Chemical reaction involves the redistribution of electrons. Therefore, conventional MD doesn't incorporate chemical reactions. It can be made to approximate chemical reaction, however.

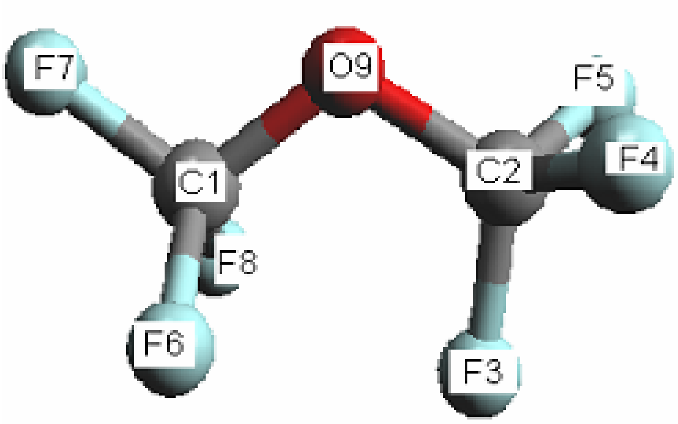
Thermal decomposition of perfluorinated ether



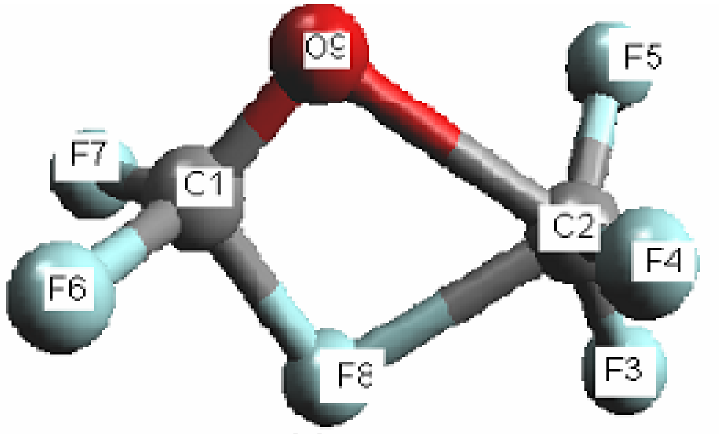
1. Stoichiometry $CF_3OCF_3 \rightarrow CF_4 + CF_2O$
2. Rate expression $rate = k\left[CF_3OCF_3\right]$
3. Reaction rate constants $k = k_o \exp\left(-\frac{E_a}{RT}\right)$
4. Reaction heat: ΔH_R

Reactive Molecular Dynamics

Quantum mechanics provides the ground state and transition state of the isolated molecule.



ground state



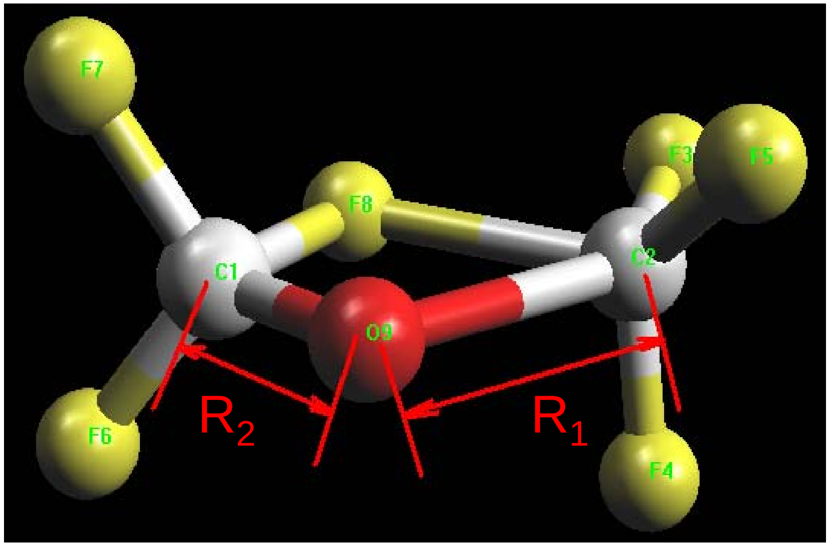
transition state

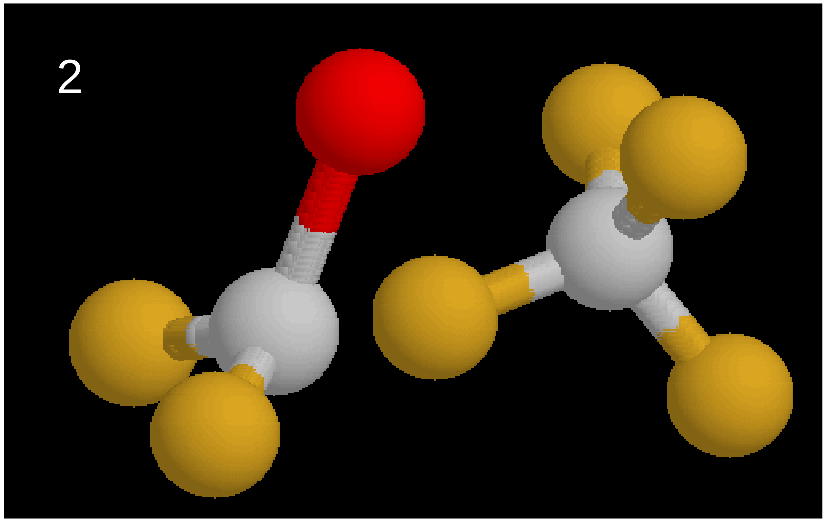
One must find a way to map this change in geometry in the classical MD simulation into a reaction, while satisfying the characteristics of the reaction (like activation energy) and basic physical constaints (like conservation of energy).

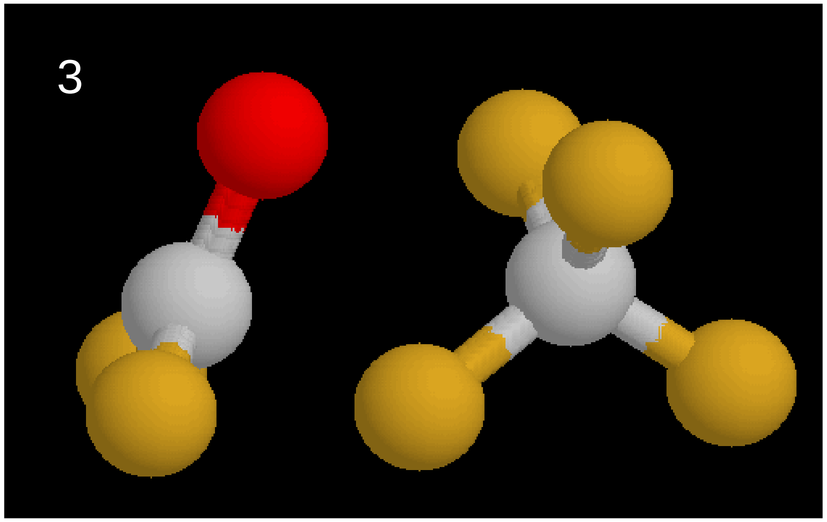
Reactive Molecular Dynamics

We map the QM results onto a simple set of configurations in which reaction occurs.

1. reaction triggers: R_1, R_2
2. instantaneous transformation from reactant to product
3. local relaxation







red: O; gold: F; white: C

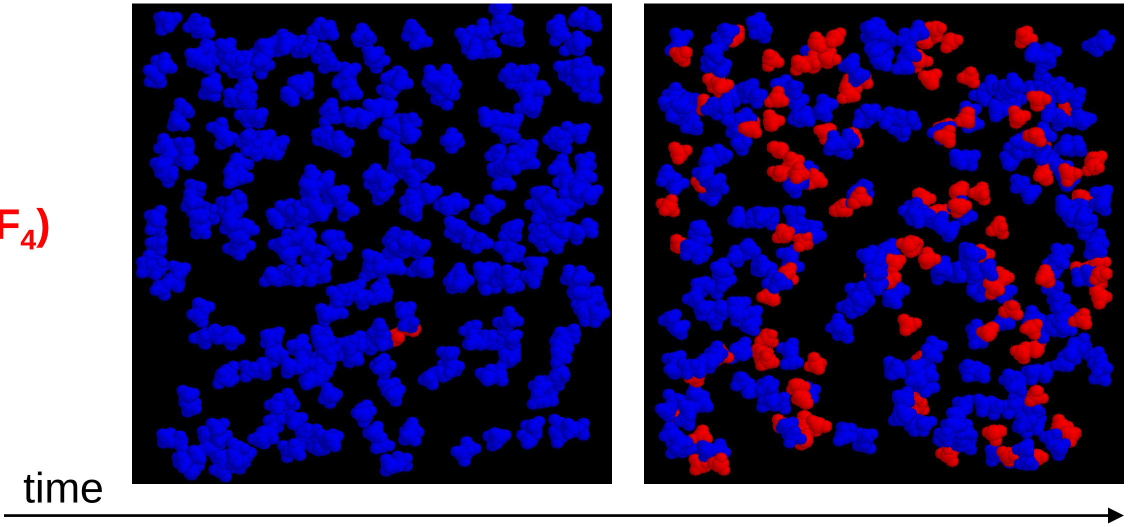
Reactive Molecular Dynamics

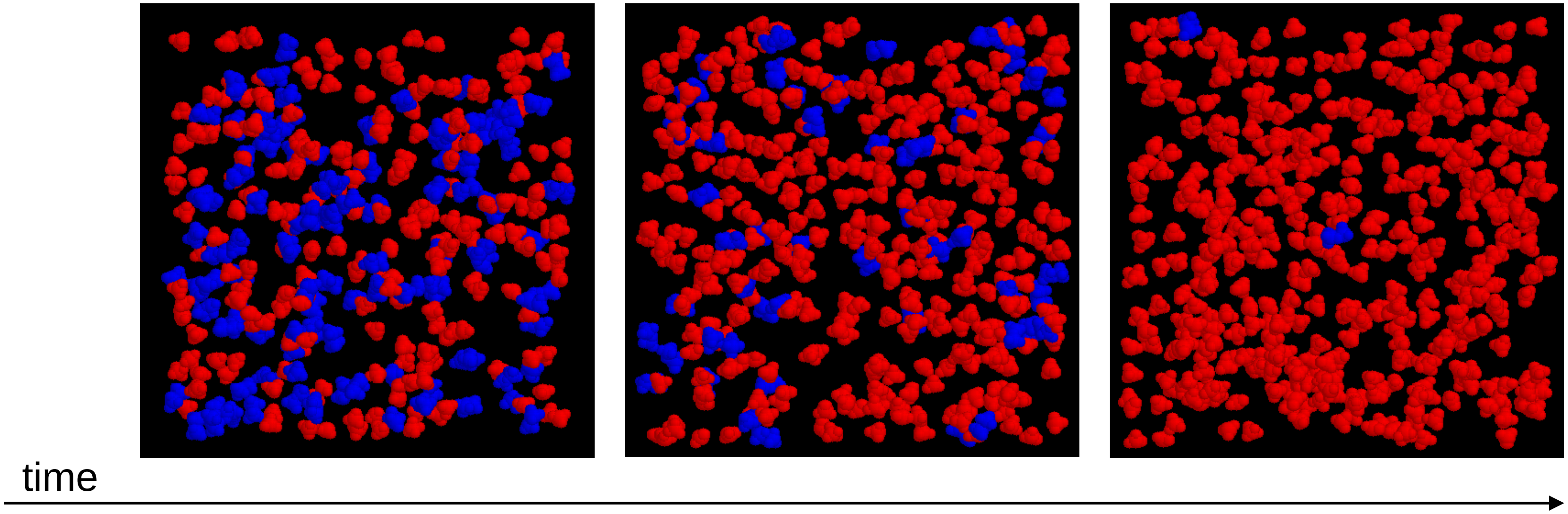
Over time, the reactant (blue) is converted into product (red).

Snapshots from RMD simulation:

blue = reactant (CF_3OCF_3)

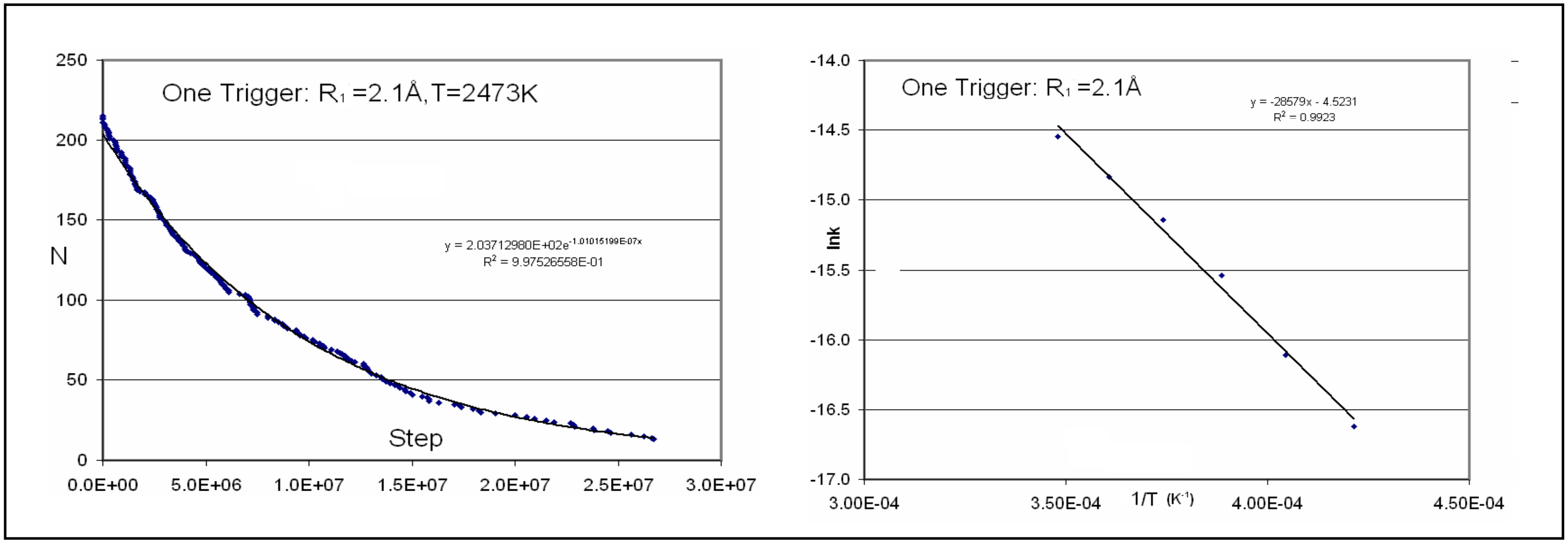
red = products (CF_2O & CF_4)





Reactive Molecular Dynamics

Over time, the reactant is converted into product.



$$N_0 - N = N_0 \exp(-kt)$$

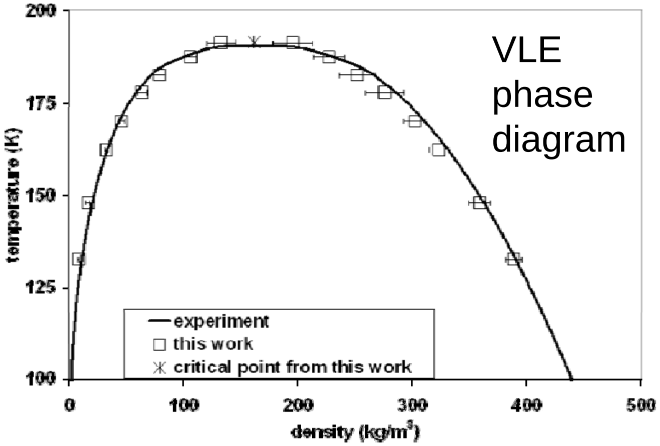
$$k = k_o \exp\left(-\frac{E_a}{RT}\right)$$

RMD simulation obeys macroscopic rate equation.
Consequently, macroscopic rate constants can be extracted from RMD simulation.

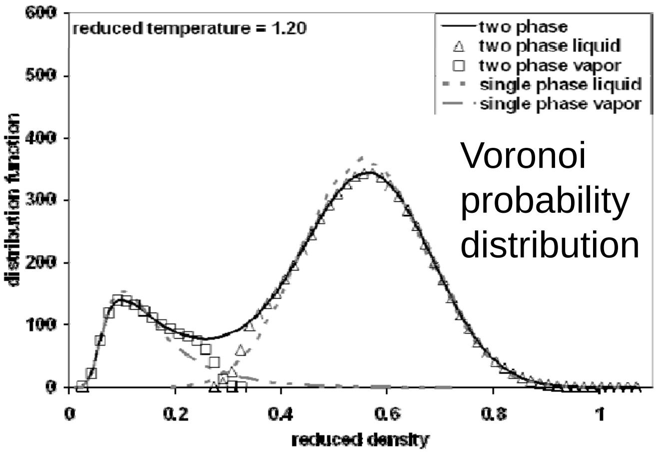
Jiang, B., Esai Selvan, M., Keffer, D.J., Edwards, B.J., J. Chem. Phys B., 2009.

Two-Phase Simulation

MD simulations can also be used to model multiphase systems.



VLE phase diagram

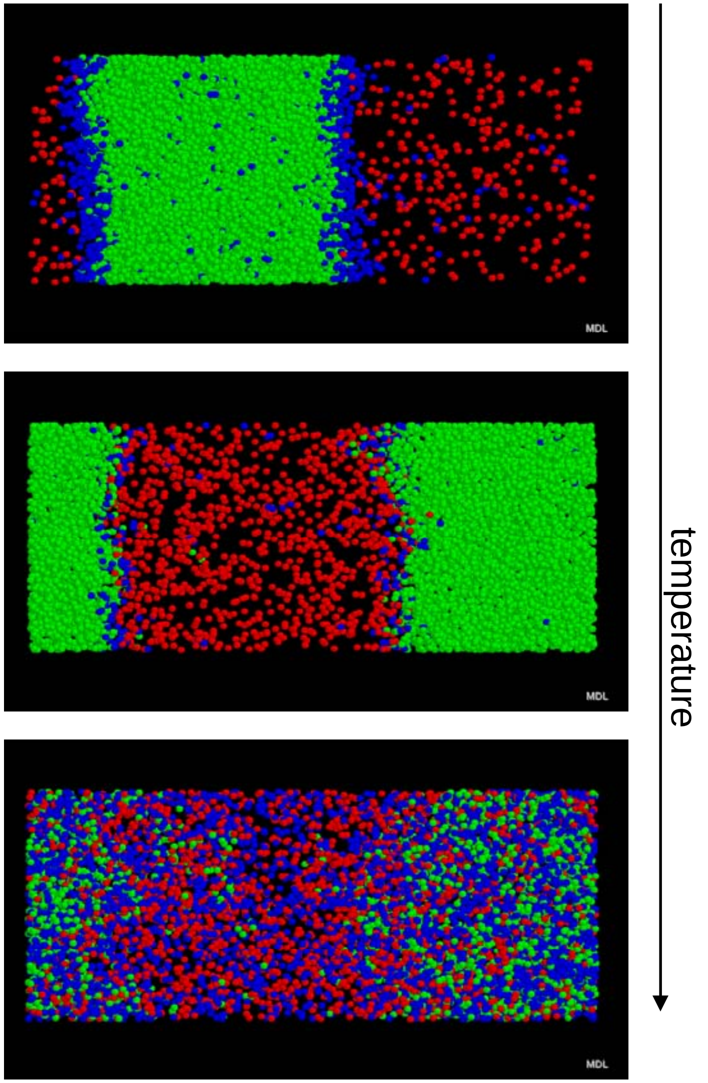


Voronoi probability distribution

green = liquid
red = vapor
blue = interface

At low T, interface is neither liquid nor vapor.

Below the critical point, interface is both liquid and vapor.



Fern, J.T., Keffer, D.J., Steele, W.V., *J. Phys. Chem. B* **2007**.

Strengths & Weaknesses

Strengths:

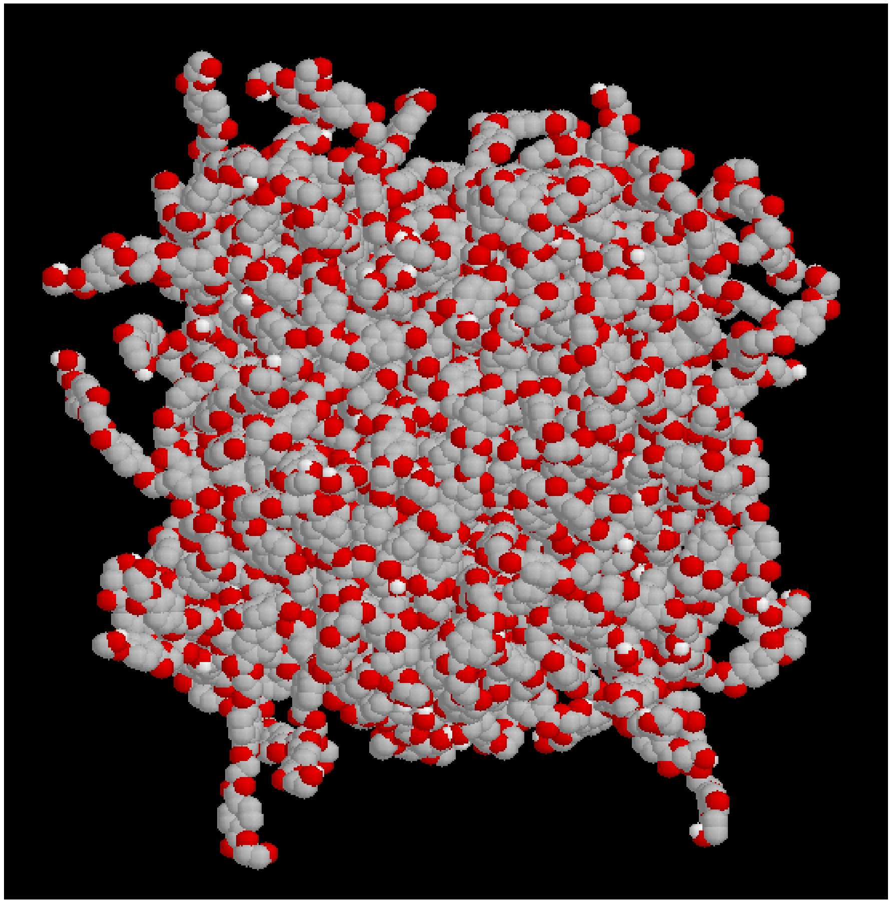
- an easily adaptable tool that provides molecular level insight into material properties
- acts as a third approach to research, complementing experiment and theory

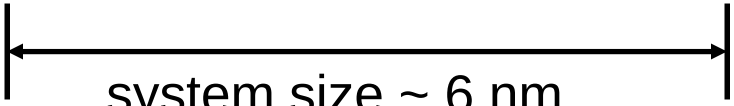
Weaknesses:

- results are only as good as the interaction potential provided to the simulation
- computationally intensive (requires supercomputers for large systems)
- incorporates redistribution of electrons in an approximate manner at best

Strengths & Weaknesses

Atomistic MD simulation: Small system, short time.





number of oligomers
125 to 216

number of atoms
4320 to 18250

simulation duration
1 to 100 ns

The use of periodic boundary conditions allows bulk properties to be extracted from these simulations.

References

1. Haile, J.M., “Molecular Dynamics Simulation”, John Wiley & Sons, Inc., New York, 1992.
2. Allen, M.P., Tildesley, D.J., “Computer Simulation of Liquids”, Oxford Science Publications, Oxford, 1987.
3. Frenkel, D., Smit B., “Understanding Molecular Simulation”, Academic Press, San Diego, 1996.
4. Keffer, D.J., “A Working Person’s Guide to Molecular Dynamics”, http://utkstair.org/clausius/docs/che548/pdf/md_sim.pdf.