Lecture 1: Introduction to Molecular Simulation

August 29, 2016

Outline

- Syllabus and introductions
- Perspective: Why molecular simulation?
- Computer logistics

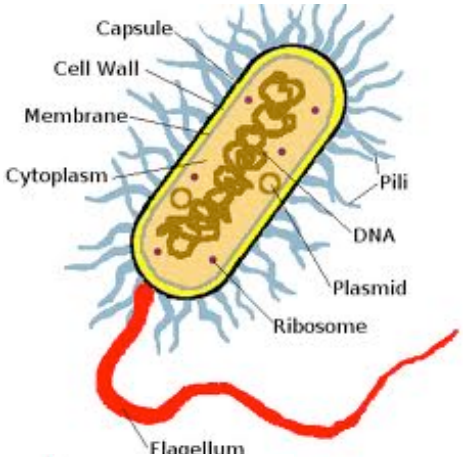
- Break, fill out survey.

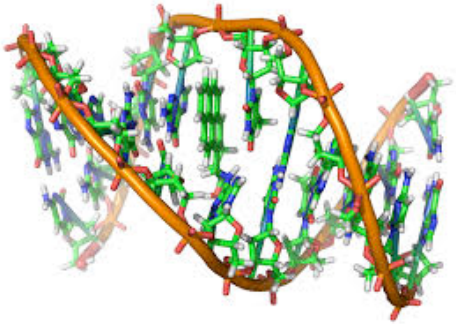
- Simulation techniques

- Files related to the course can be found on Blackboard.

What is Nano?

- 1 meter
  - about 3.3 feet
  - a very tall person is 2 m tall
- 1 millimeter = 0.001 meters
  - smallest division on your ruler
  - a typed period is about 0.5 mm in dia
- 1 micrometer (micron) = 0.000001 meters
  - average human hair diameter is 80 microns
  - a bacterium cell is 1 micron in length
- 1 nanometer = 0.000000001 meters
  - diameter of a DNA molecule is 2 nm
  - atomic bonds are less than 1 nm long
- Also interested in short time scales (fs-ns)
- http://en.wikipedia.org/wiki/Orders_of_magnitude_(length)
  http://scaleofuniverse.com/





Energy Scale

- Energy = mass x length^2 / time^2
  - Mass scale ~ 1E-26 kg

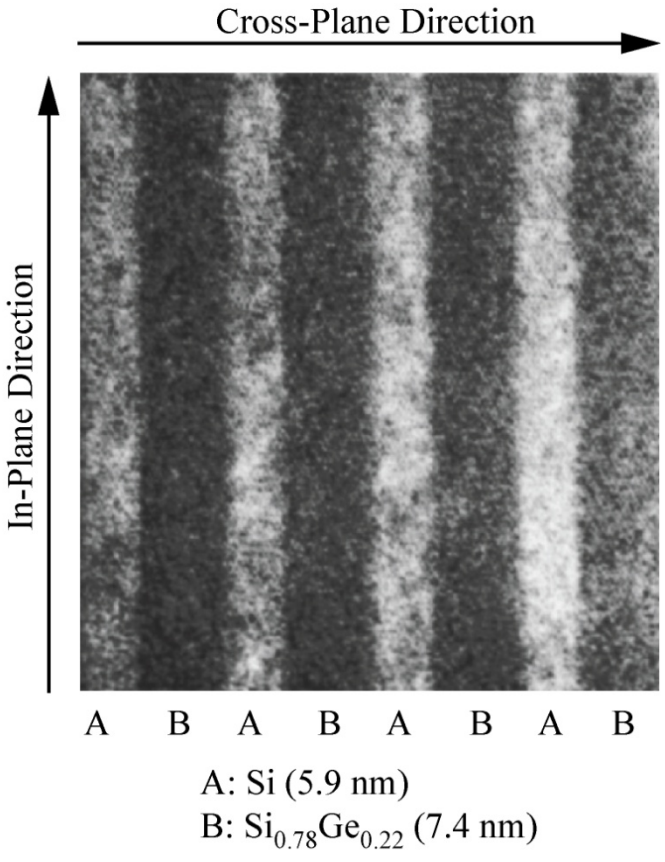
- Results are often reported in electron-Volts (eV)
  - 1 eV = 1.60219E-19 J

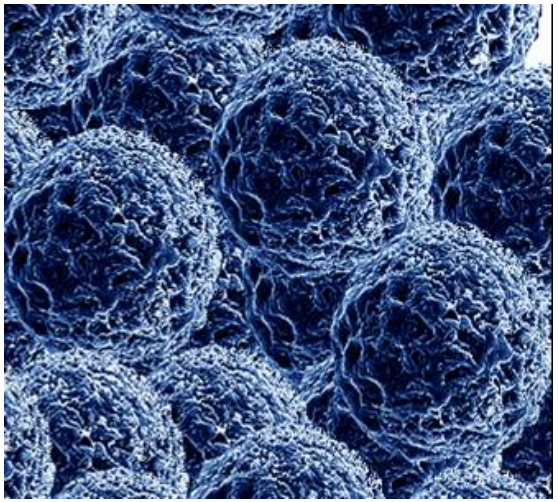
- You may also see energies in terms of $k_B T$ (thermal fluctuation reference point)
  - k_B = Boltzmann constant = 1.3806E-23 J/K (related to the ideal gas law)
  - at T = 300 K, $k_B T$ = 4.14E-21 J = 0.025 eV = 1/40 eV

- Atomic-level energies are typically between 0.01 eV and 100 eV.

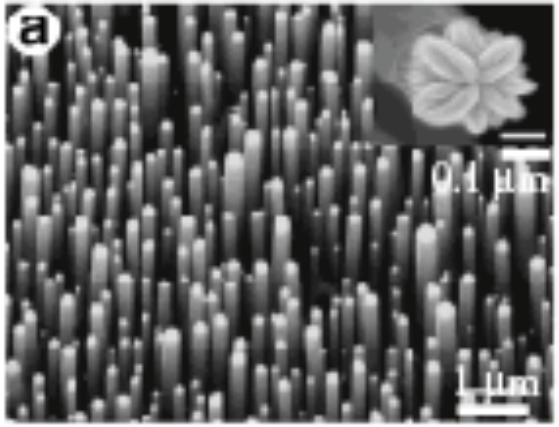
Nanomaterials

Superlattice



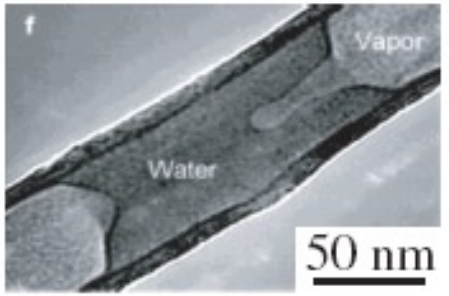


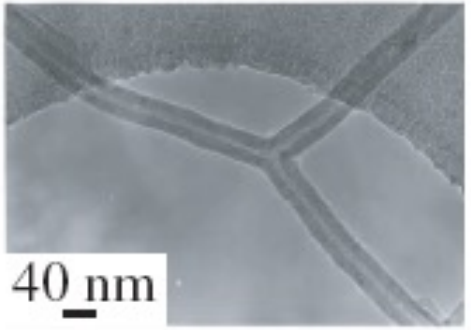
Metallic Nanoparticles



Silicon-Germanium Nanowires

Carbon Nanotubes

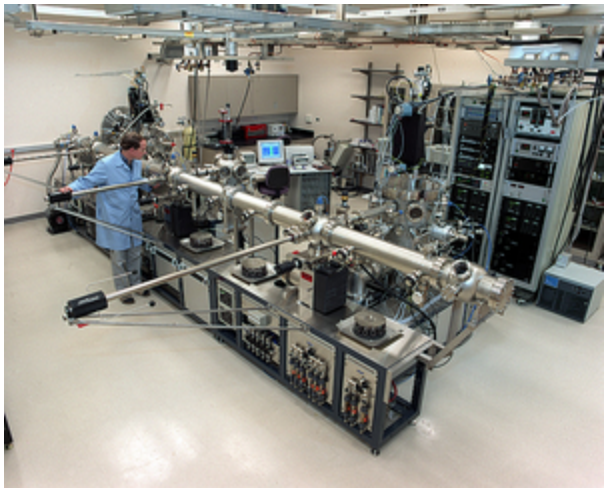




… quantum dots, nanofluids, nanoribbons, nanopipes …

Fabrication and Characterization

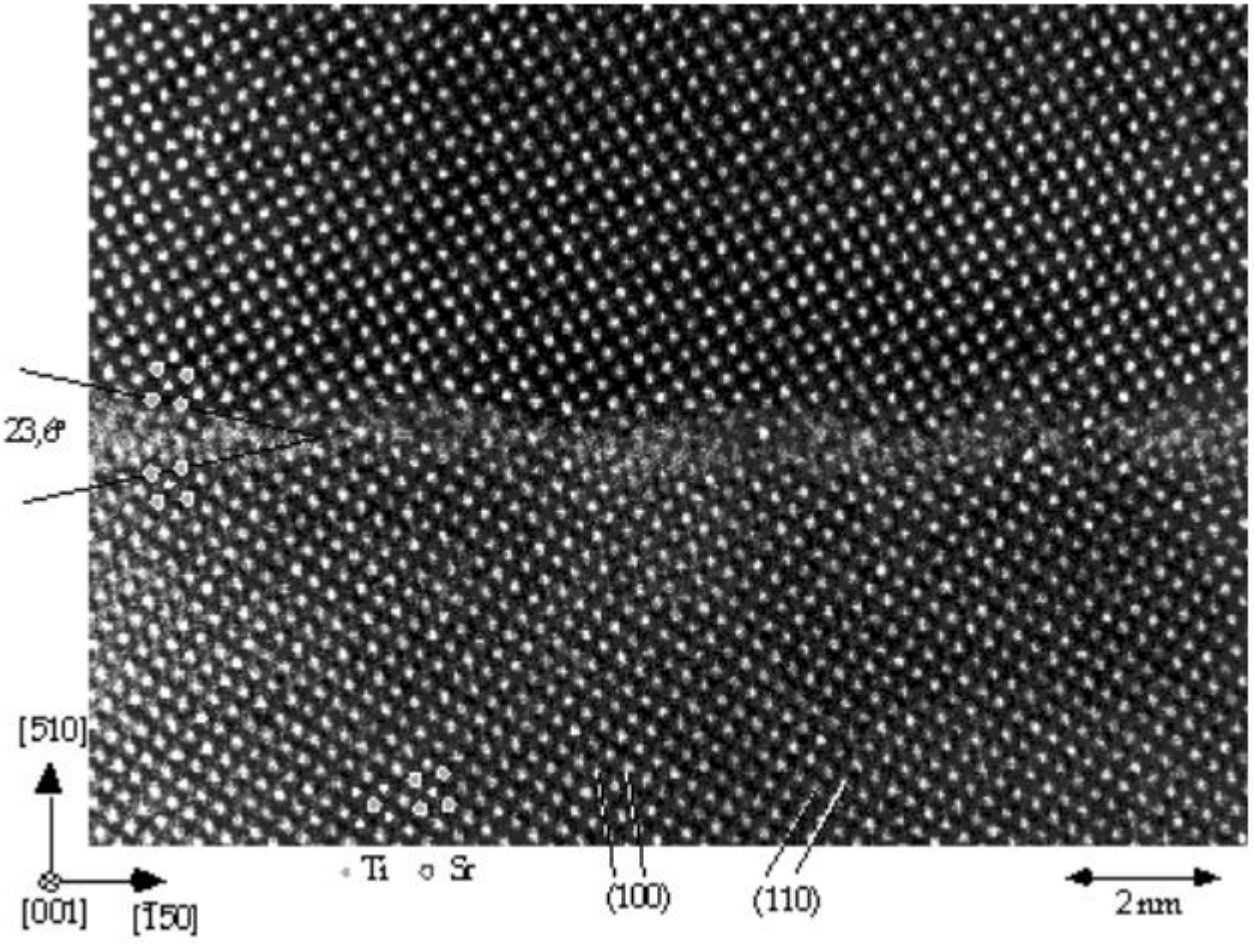
- Structures are built from the bottom-up:
  - chemical vapor deposition
  - molecular beam epitaxy
  - sputtering
  - …



- We can't see things this small. Images are obtained using *electron microscopy*.
- Sample preparation is challenging.

What About Experiments?

- Electron microscopy can generate images with sub-micron resolution
  - *In situ* time resolution ~ ms (maybe)

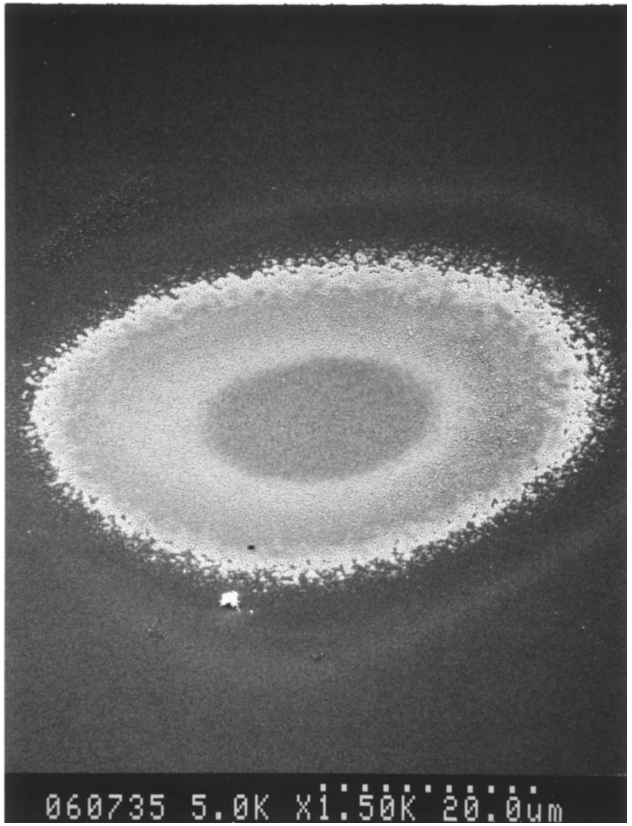


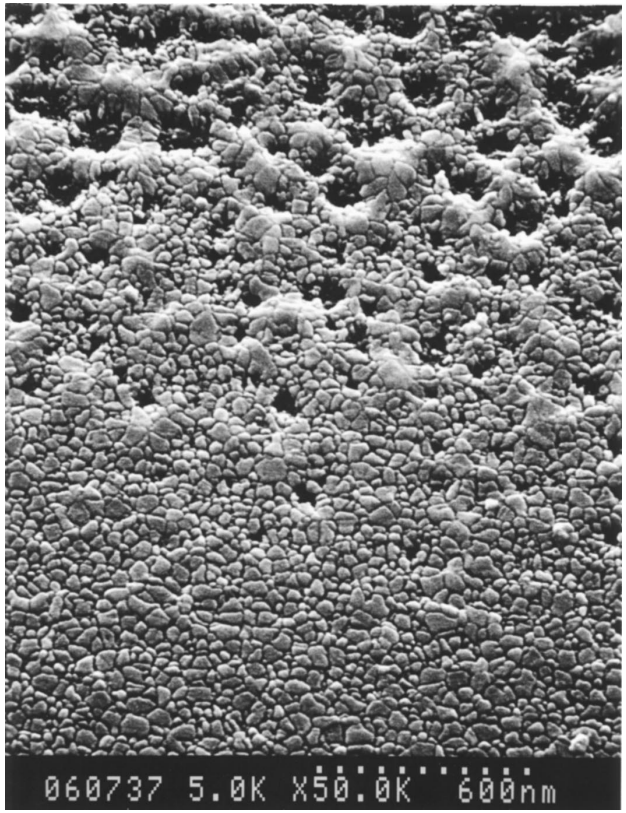
Grain boundary in strontium titanate

pruffle.mit.edu/~ccarter/NANOAM/images/

What About Experiments? (2)

- Lasers can resolve phenomena down to picoseconds (10^{-12} s), femtoseconds (10^{-15} s)
  - measuring thermal conductivity (Malen), materials processing (ablation)
  - spatial resolution ~ μm





Femtosecond pulsed laser recrystallization of a-Si film on quartz substrate

http://www.me.berkeley.edu/ltl/research/fs.html

Why Modeling?

- Experiments can be time- and resource-intensive
- Nanoscale phenomena are challenging to observe experimentally
  - Small length (10^{-10} m) and time (10^{-15} s) scales
  - Difficult to measure properties and elucidate physics
- Properties not available in handbooks or textbooks
  - New bulk materials and nanostructures, extreme conditions (geophysics)
- Fundamental understanding
  - Why does one material have a higher thermal conductivity than another?
  - How to design materials with tailored thermal properties?

Why Simulation?

- Exact solutions are the exception. Need numerical solutions!

$$m_i a_i = \sum_{j=1, j \neq i}^{N} F_{ij}$$

- Closed form (algebraic) solution only for $N = 1$ or 2.
- We are interested in hundreds, thousands, millions of atoms.

Why at the Molecular Level?

- A route from the microscopic (atoms and their interactions) to the macroscopic (equation of state, transport coefficients).
- Length and time scales not describable by continuum approaches (e.g., energy equation, Navier Stokes, beam equations, …).

Perspective

- **A simulation is a computer experiment.**
  - Make measurements, identify mechanisms.
  - Not just a calculation, like taking the Fourier transform
  - Inherent uncertainty due to finite sampling
    (we will see this point a lot)

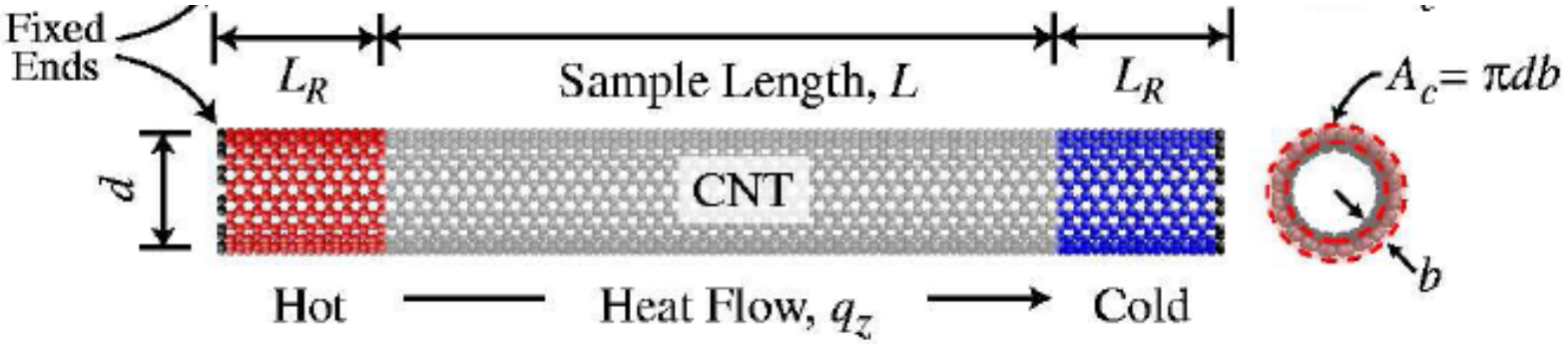
- As with an experiment, you need to understand the capabilities and limitations of your simulation technique.

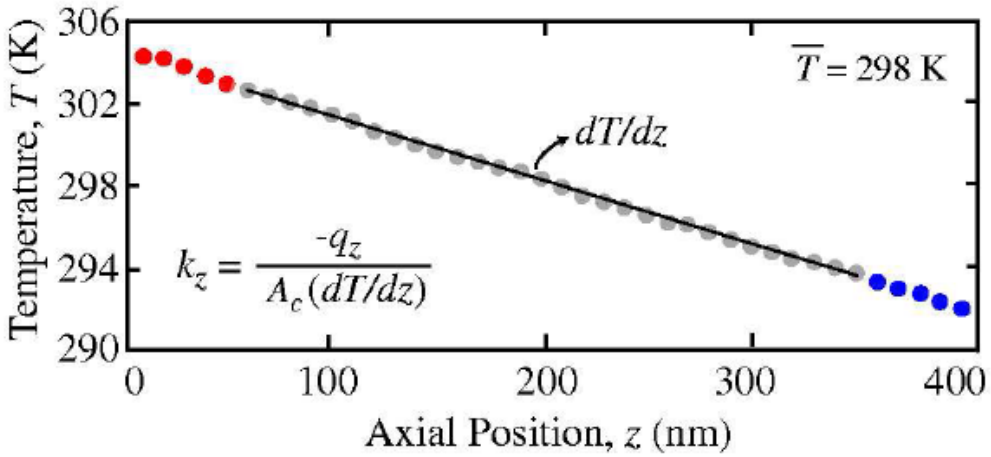
Which Class to Take? Both!

24-623/12-623 (this class)	06-640 (John Kitchin in ChemE)
Classical molecular dynamics/Monte Carlo	Quantum mechanics-based methods (density functional theory)
Classical limit: no quantum effects, limited to "high" temperature	All temperature accessible, but trajectories in dynamics are classical
Millions (billions?) of atoms	Hundreds/thousands of atoms (size effects may still be present)
Nanoseconds of simulation	Picoseconds of simulation
Energetics, transport, mechanics Reaction (breaking/forming bonds) is difficult	Predicting energies and energy barriers, relaxing structures, reaction pathways Limited access to dynamics

Predicting the Thermal Conductivity of CNT

- How long does the CNT need to be?
- How much time is needed to get the system to steady state?
- How much time is needed to obtain enough data to get good averages?
- How do these quantities depend on temperature and CNT diameter?
- What is the resulting uncertainty?

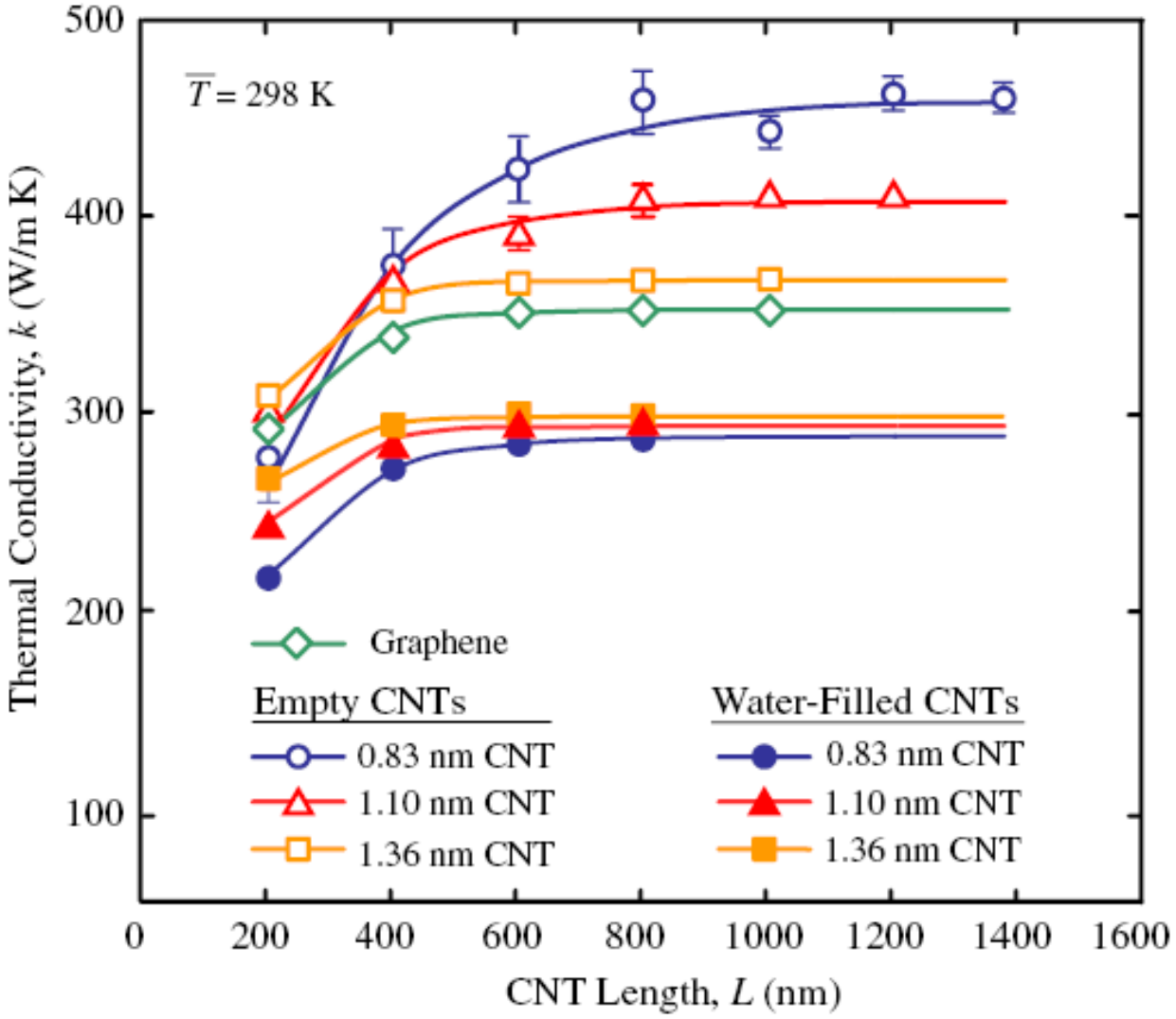




Thomas, Iutzi, and McGaughey, *Physical Review B*. **81**, 045413 (2010).

Results

You won't know the answers to any of these questions when you start.



Computer Logistics

- Writing code from scratch (don't use parts of a code from your research group). You will be submitting your code. It must compile and run.
- Options: C++, Fortran. DO NOT USE A MATH PROGRAM.
- Class examples will be in C++.
- Don't make code any more complicated than it needs to be.
- Comment! (you will forget how/why you did something).
- Spreadsheet program (Excel) and/or
  math program (Matlab, Mathematica).

- See the file computer.pdf on the website for more details.

- ***Establish your computer presence.***

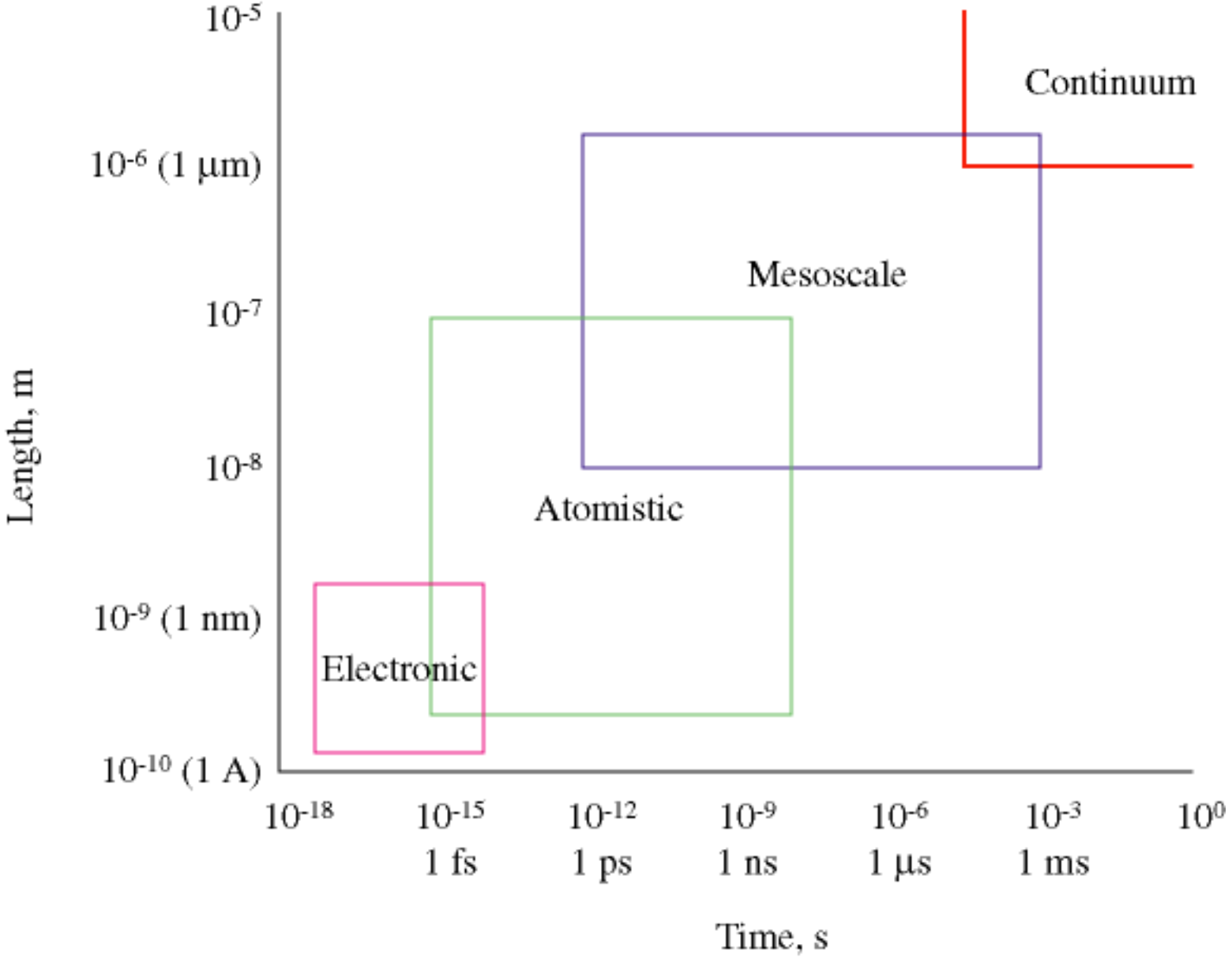
Wednesday Coding Workshop

- Bring your laptop to class if you have one.
- No problem if you don't, we will be working in pairs.

- Before: Download and install an editor and compiler. Test it out if you know how.

- We will go through how to compile and run C++ on a Mac.
- Explain a simple code line-by-line.
- Then you will modify.

Simulation Techniques



More Perspective

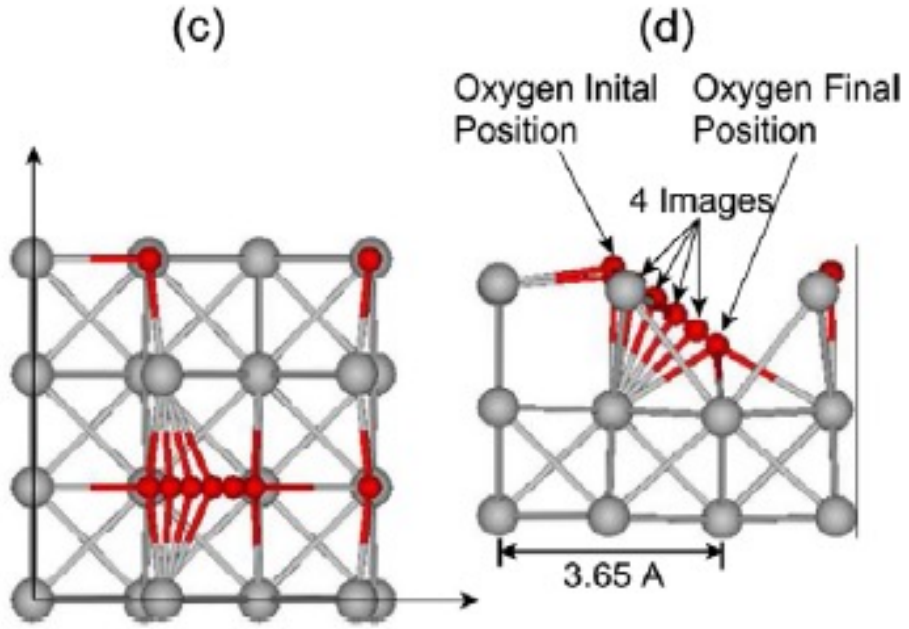
- Purpose of a simulation: qualitative or semi-quantitative comparison to experiments.
  - Simulations can be tuned but this can cause a loss of generality.
  - Identify trends and mechanisms

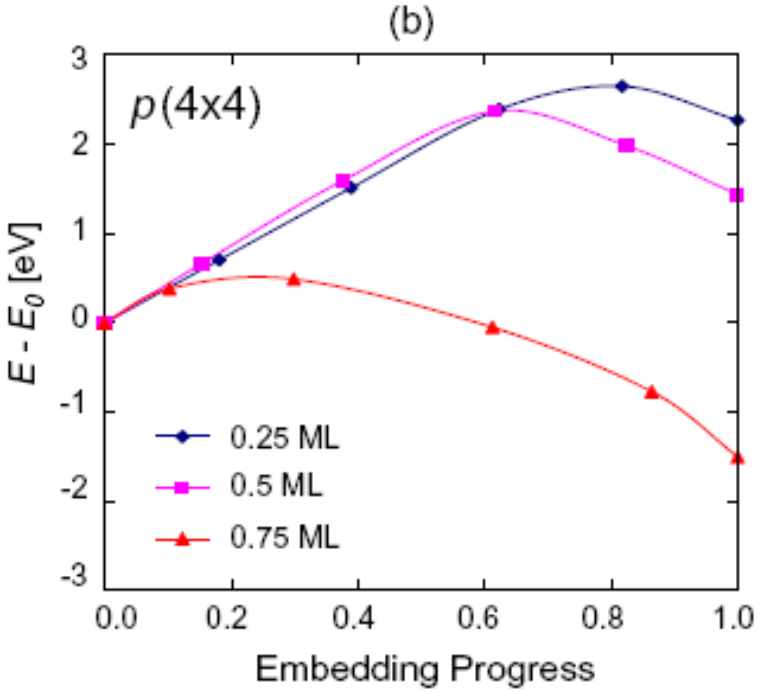
- Compromise between accuracy and computational time.
  - Depends on what you are trying to do

Electronic Structure Calculations

- Electronic degrees of freedom are considered
  - Quantum mechanics -> Solve the Schrödinger Equation.
- Theory is very complicated.
  - All-electron, density functional theory, tight-binding
  - Commercial/academic codes (would take far too long to write one yourself). Quantum Espresso (free), VASP (license), GAUSSIAN (license), ABINIT (free), SIESTA (free)
  - courses at CMU (06-640) and Pitt (Chemistry Dept.)
- Can be easy to use, but garbage in = garbage out!
- Typically scales as the cube of the number of electrons.
  - Limited access to dynamics.
  - Systems with more than a few thousand atoms rarely considered.

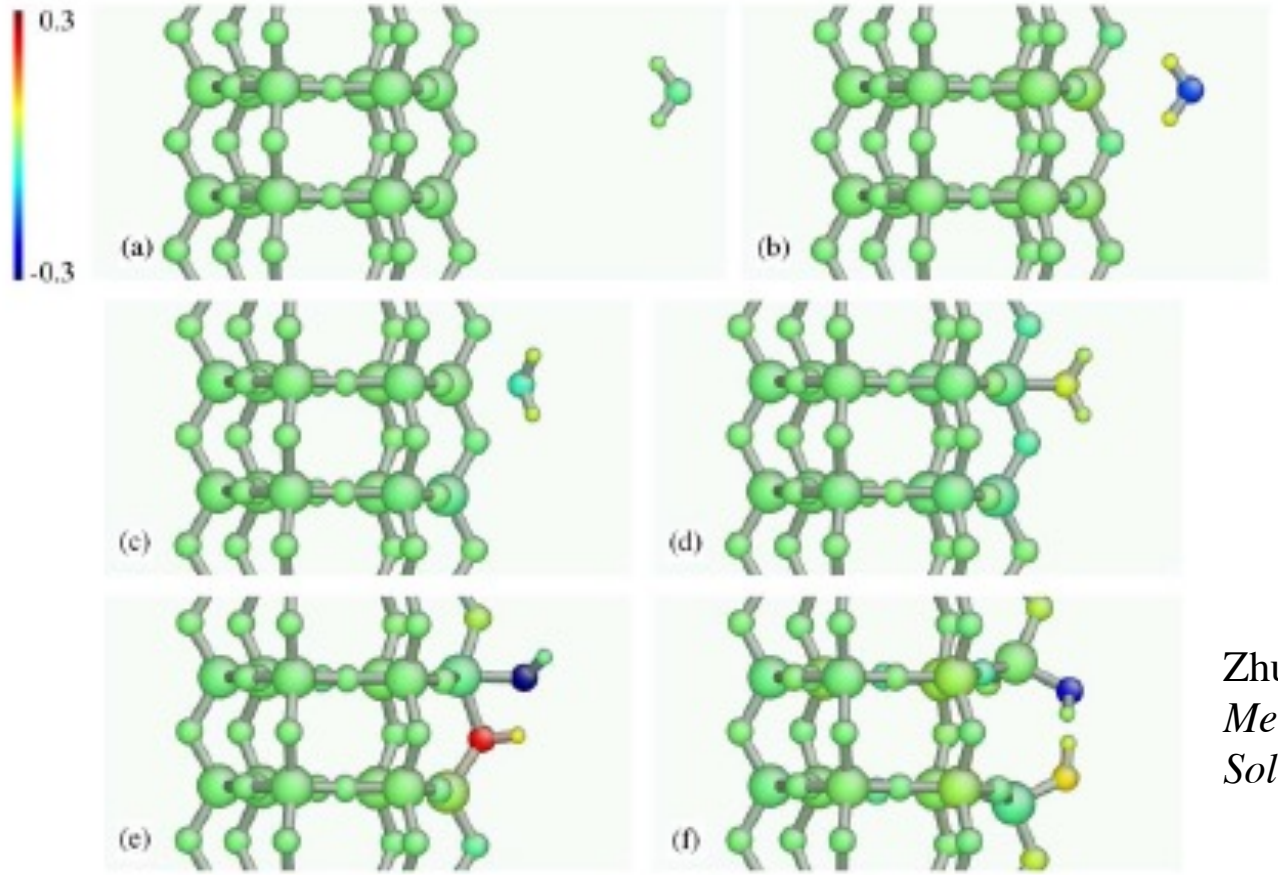
Oxidation of Copper Surfaces (DFT calculations)





Lee and McGaughey, *Surface Science* **603** (2009) 3404-3409.

Water Interacting with a Silica Nanowire (Semi-Empirical Molecular Orbital Theory)



Zhu et al., *Journal of the Mechanics and Physics of Solids* **53** (2005) 1597-1623.

Fig. 6. Atomic configurations along the transition pathway of hydrolysis under a stress of $0.3\sigma_{cr}$. Mechanism II: (a) initial state, (b) physisorbed state, (c) the first saddle-point configuration, (d) metastable molecularly adsorbed state, (e) the second saddle-point configuration, and (f) final chemisorbed state. Atoms are color-coded by charge variation relative to the initial configuration (a).

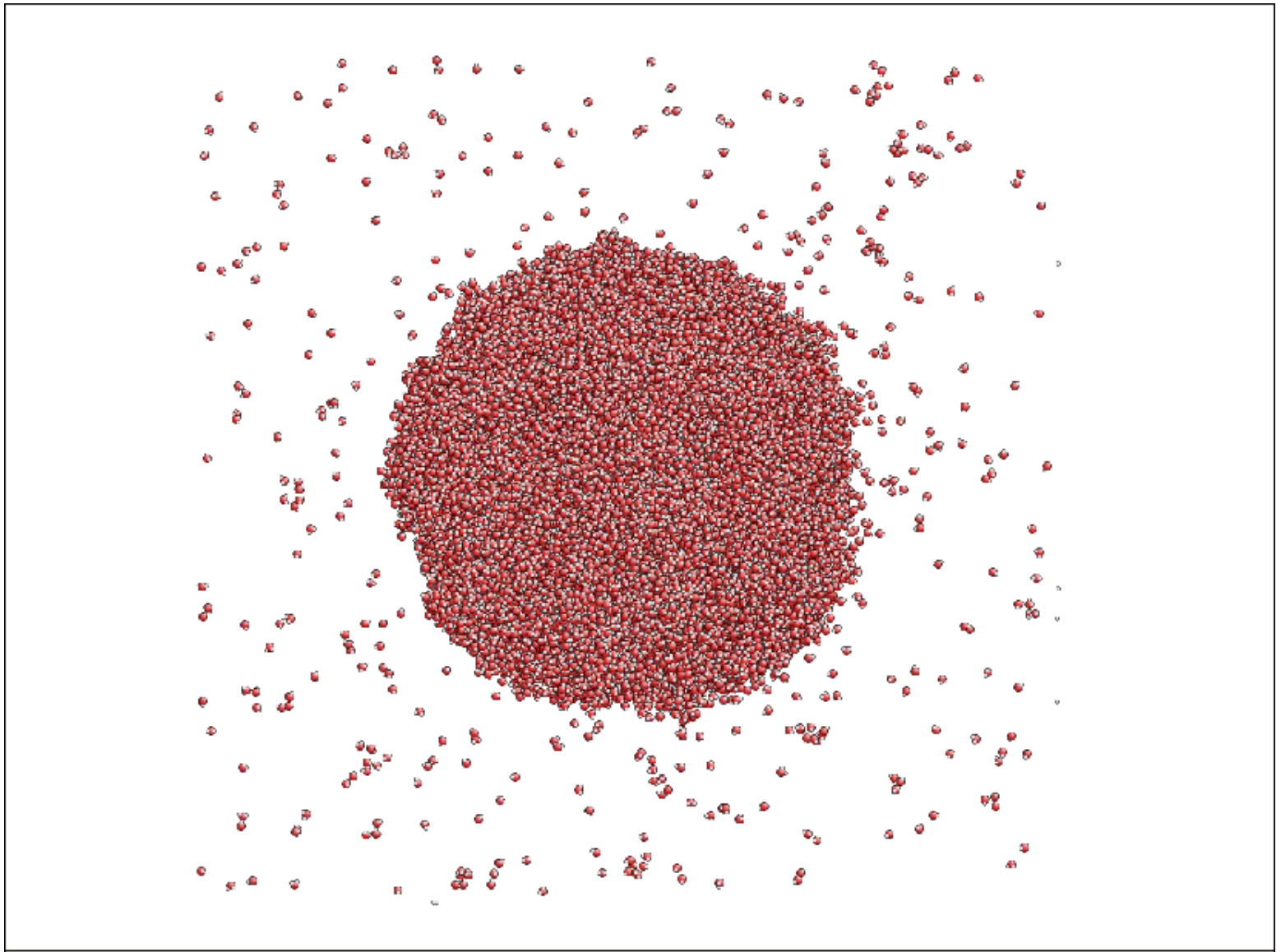
Atomistic Simulation (MD and MC)

- Electrons not explicitly considered, atom-by-atom
  - Larger lengths and times than ES methods.
    The adiabatic (Born-Oppenheimer) approximation.

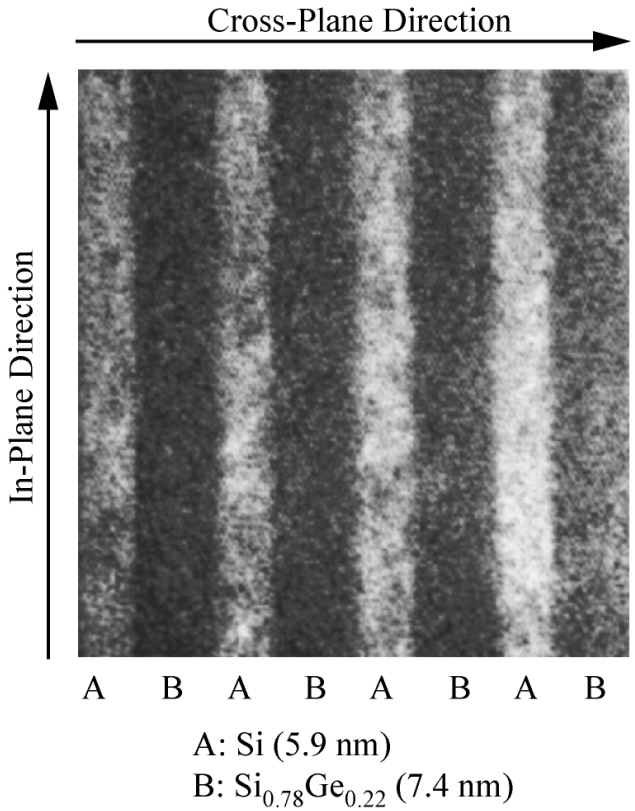
- Most common approaches: Molecular dynamics (MD) and Monte Carlo (MC).
- Techniques based in classical statistical mechanics.
- Quantum effects cannot be considered (that's the whole point!)

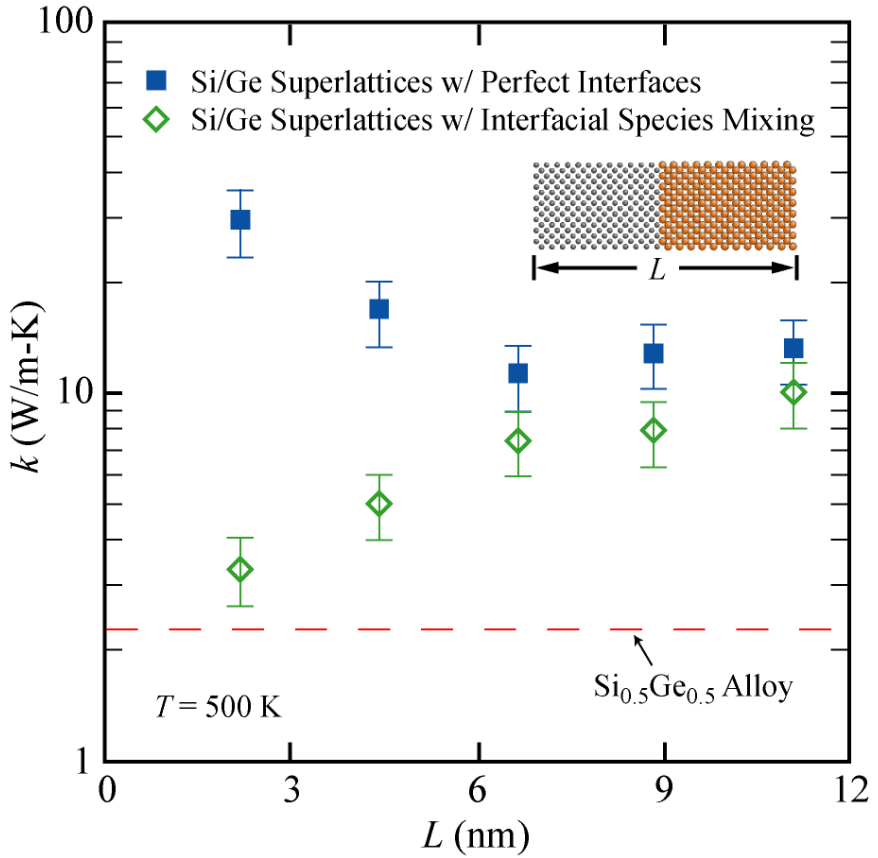
- Need a way to predict how the atoms will interact:
  an interatomic potential (Lecture 3)

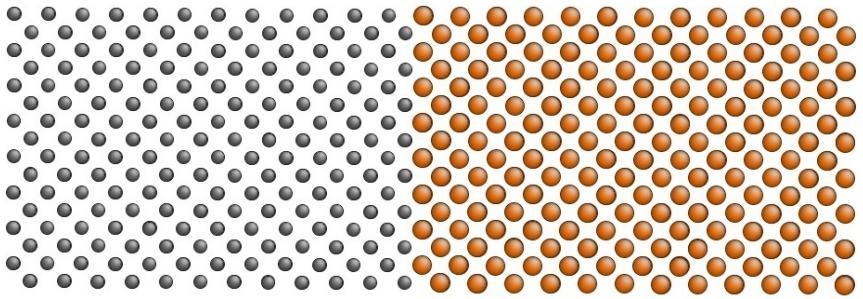
MD Simulation of a Water Droplet

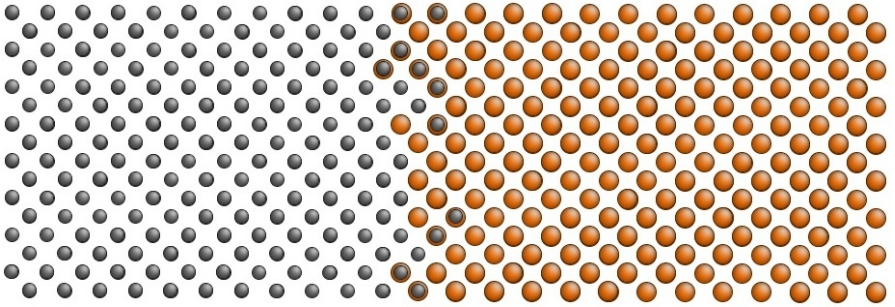


Heat Transfer in Superlattices









Landry and McGaughey, *Physical Review B* **79** (2009) 075316.

Reality?

- MD/MC have nothing to do with modern physics.
  - They directly contradict relativity and quantum mechanics!
  - Relativity predicts the finite times needed to transfer information. In MD, it is instantaneous.
  - QM says that it is impossible to know both a particle's position and momentum at the same time (the uncertainty principle), while this is exactly what we do in MD.

- Don't worry. For what we will do, these approaches are fine.

Mesoscale Simulation

- Information about every atom may not be necessary.
- There may be a larger length/time scale that is appropriate to the problem (e.g., in granular flow).
- May not need to explicitly model the fluid surrounding a molecule. Still require discrete information, though.
- Introduce random, dissipative forces, and effective potentials.

Continuum Modeling

- Traditional engineering analysis tools: CFD, FEA.
- Do not have specific information about atoms.
- Material properties must be specified in advance.
- Some hybrid methods exist. Significant challenges at interfaces.