Lecture 1: Introduction to Molecular Simulation

January 11, 2010

Outline

- Syllabus and introductions.
- Perspective. Why molecular simulation?
- Length, time, mass, and energy scales

- Break. Fill out survey.

- Simulation techniques
- Classical vs. quantum systems
- Computer logistics

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

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 (you will see this point a lot)
- As with an experiment, you need to understand the capabilities and limitations of your simulation technique.

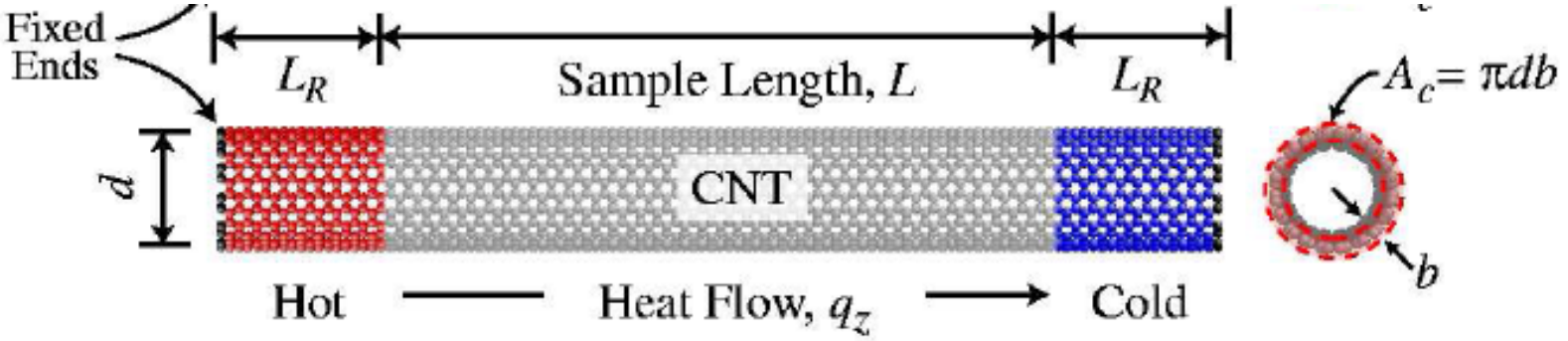
24-623 (this class)	06-640 (John Kitchin in ChemE)
Classical molecular dynamics/Monte Carlo	Quantum mechanics-based methods (density functional theory)
Classical limit: no quantum effects, limited to "high" temperature	All temperature accessible, but trajectories in dynamics are classical
Millions (billions?) 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

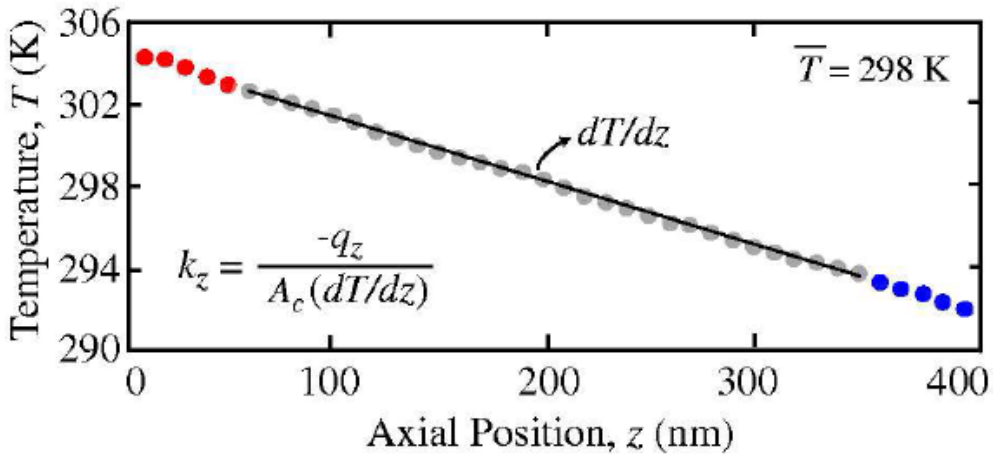
More Perspective

- Think of the purpose of a simulation as a qualitative or semi-quantitative comparison to experiments.
  - Simulations can be tuned (through the potentials) but this can cause a loss of generality.
  - Identify trends and mechanisms
- Compromise between desired accuracy and how long it takes to get results.
  - This balance depends on what you are trying to do with the simulations.

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?

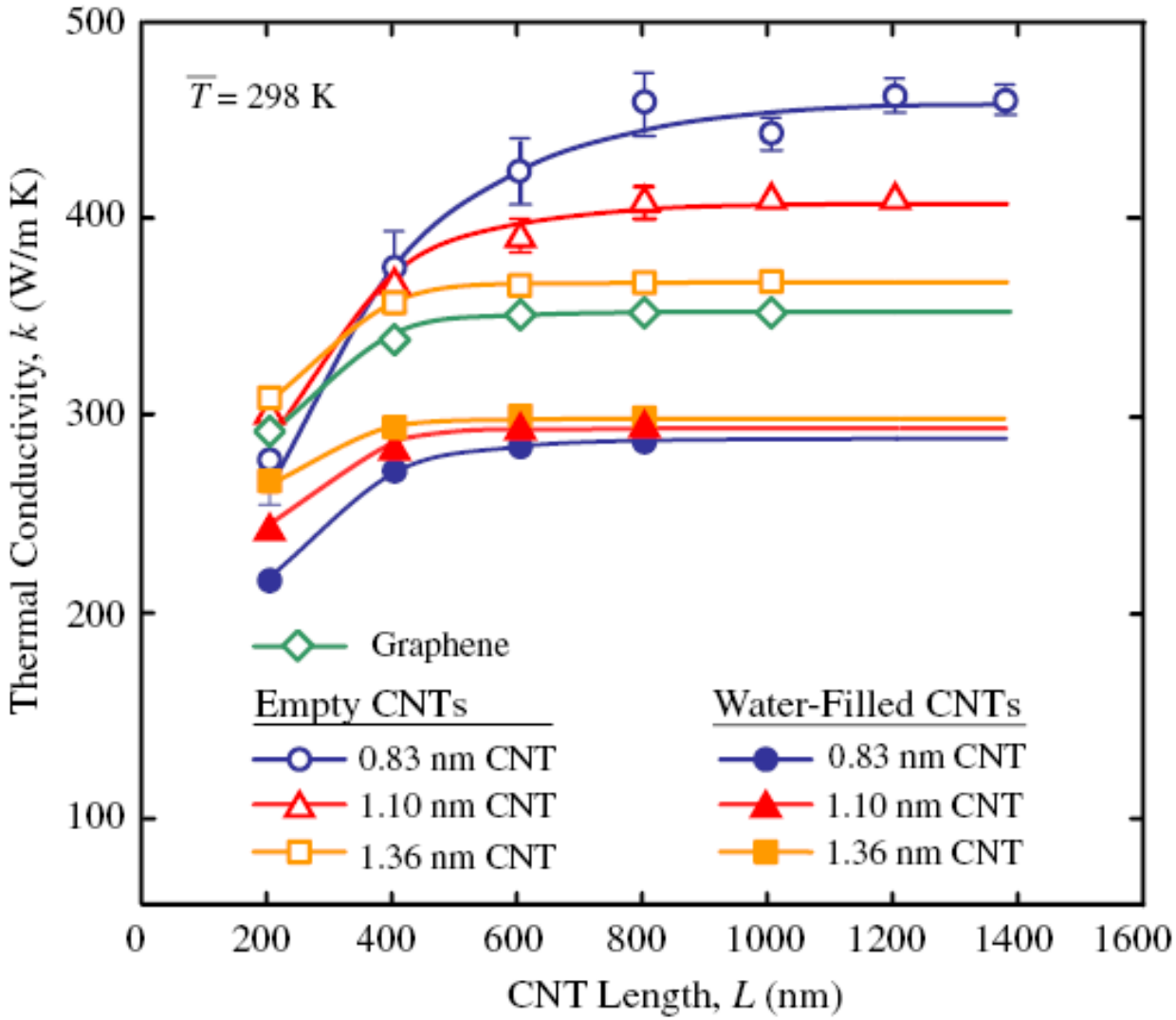




Thomas, Iutzi, and McGaughey, to appear in *Physical Review B*.

Results

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



Why simulation?

- Exact solutions are the exception in the real world. The need for numerical solutions is not unexpected.

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

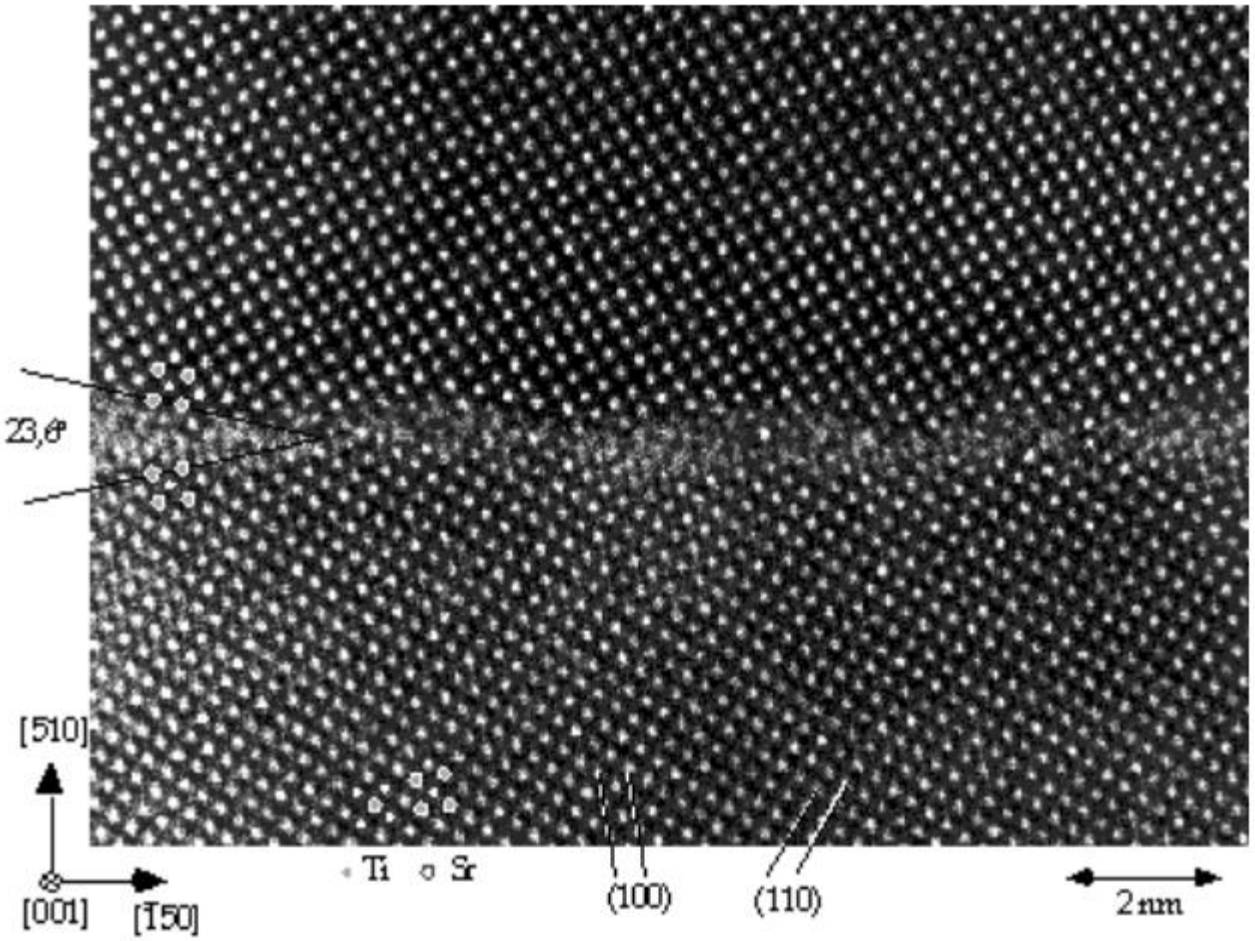
- Can only find a closed form (algebraic) solution for $N = 2$.
- We are interested in hundreds, thousands, millions of atoms.

Why at the molecular level?

- A route from the microscopic (atoms and their interactions) to the macroscopic (equation of state, transport coefficients, structural order).
- Systems in which the length and time scales are not accessible in continuum approaches (e.g., energy equation, Naview Stokes, beam equations, …).
- Determine material properties not easily accessible in experiments (size effects, new materials).

What about experiments?

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

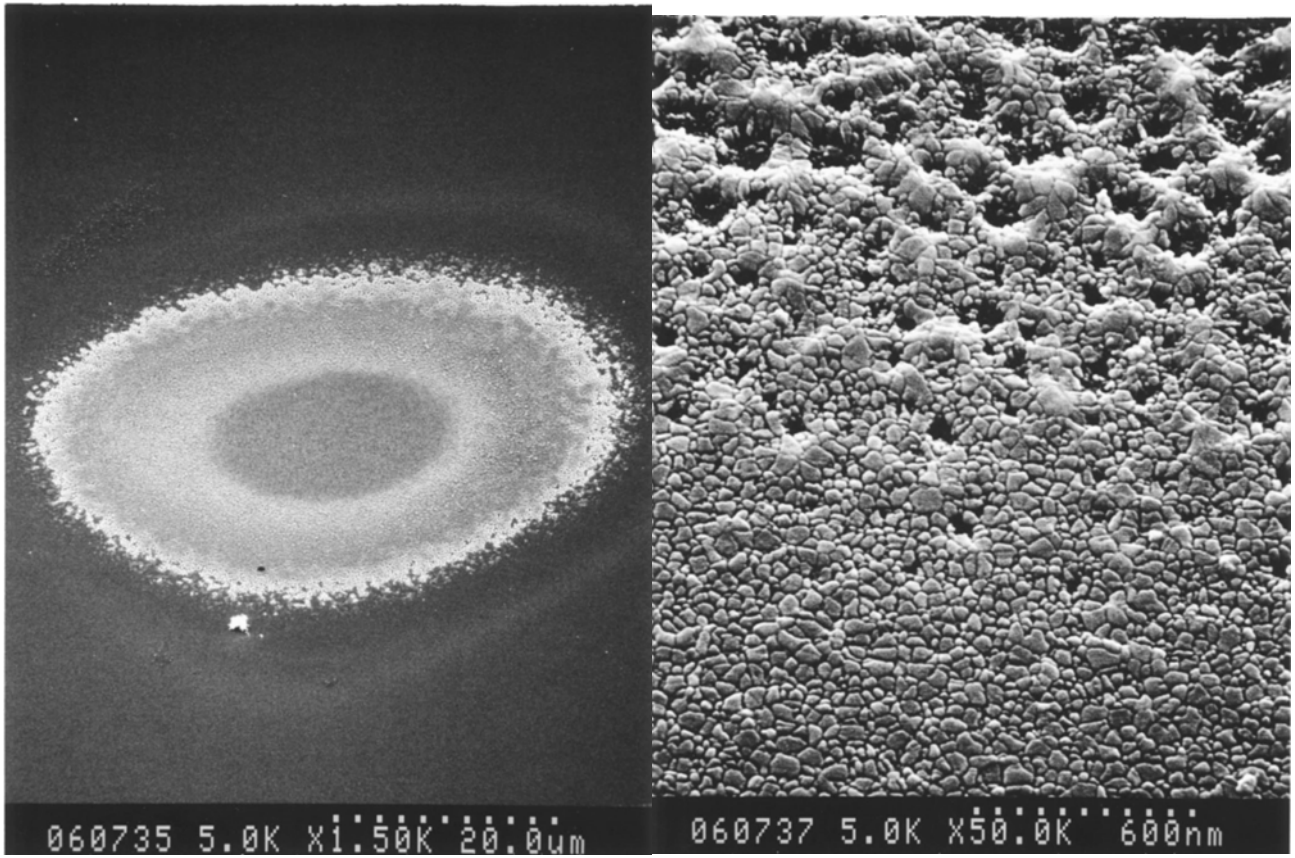


Grain boundary in strontium titanate

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
  - 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

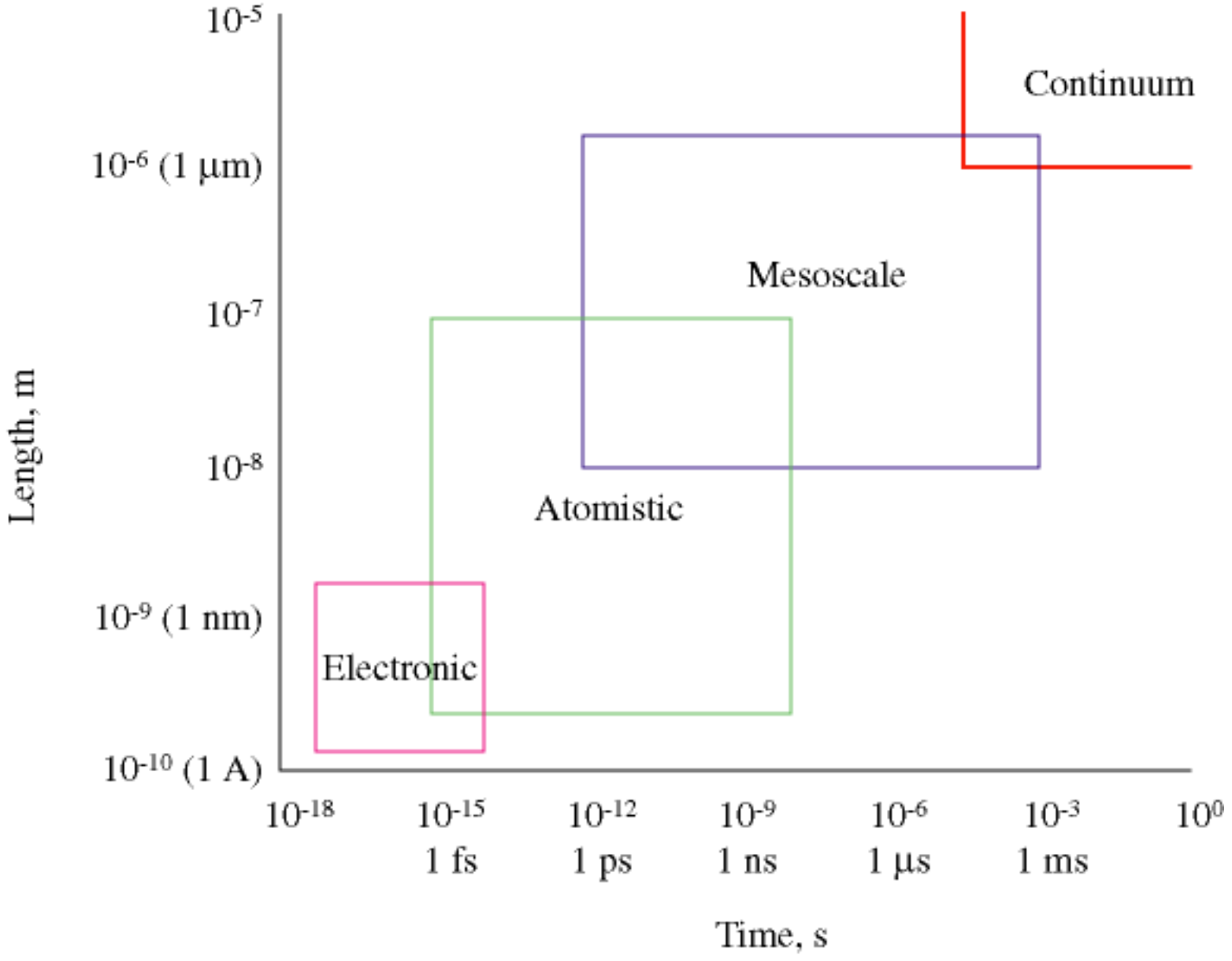
Length, Time, Mass, and Energy Scales

- Figures from *Principles of Heat Transfer* by M. Kaviany (Wiley, 2002).

Energy Scale

- Energy = mass x length^2 / time^2
  - (1E-26 kg)(1E-9 m)^2/(1E-13s)^2 = 1E-18 J
- 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 = 1.38E-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
- Energies at the atomic level are typically between 0.01 eV and 100 eV.

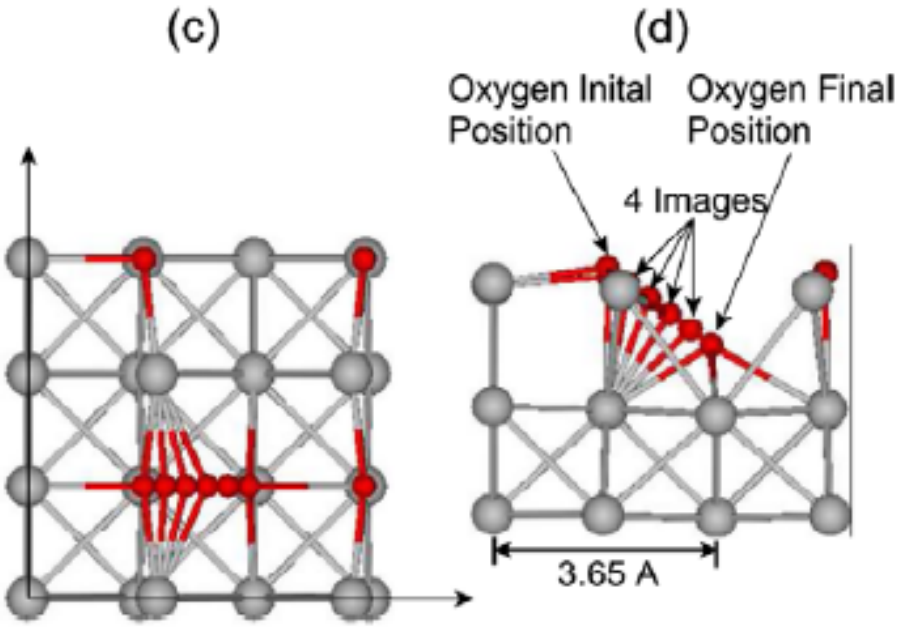
Simulation Techniques

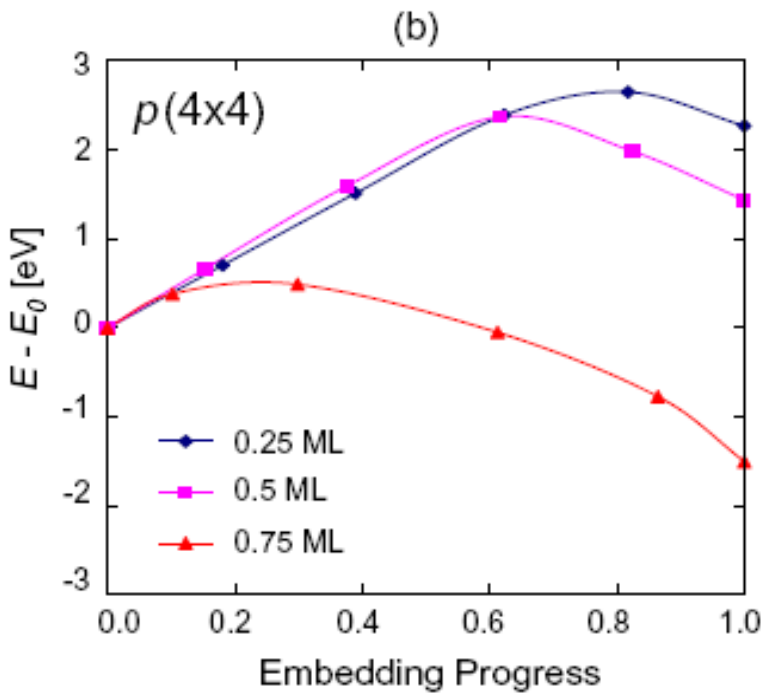


Electronic Structure Calculations

- Electronic degrees of freedom are considered
  - Quantum mechanics
  - Need to solve the Schrödinger Equation.
- Theory is very complicated.
  - all electron models, density functional theory, tight-binding models
  - Commercial/academic codes are typically used (would take far too long to write one yourself). VASP, GAUSSIAN, ABINIT, SIESTA
  - courses at CMU (06-640) and Pitt (Ken Jordan, Wissam al Saidi)
- These codes can be easy to use, but you need to know what you are doing or you will generate bad results! (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 are rarely considered.

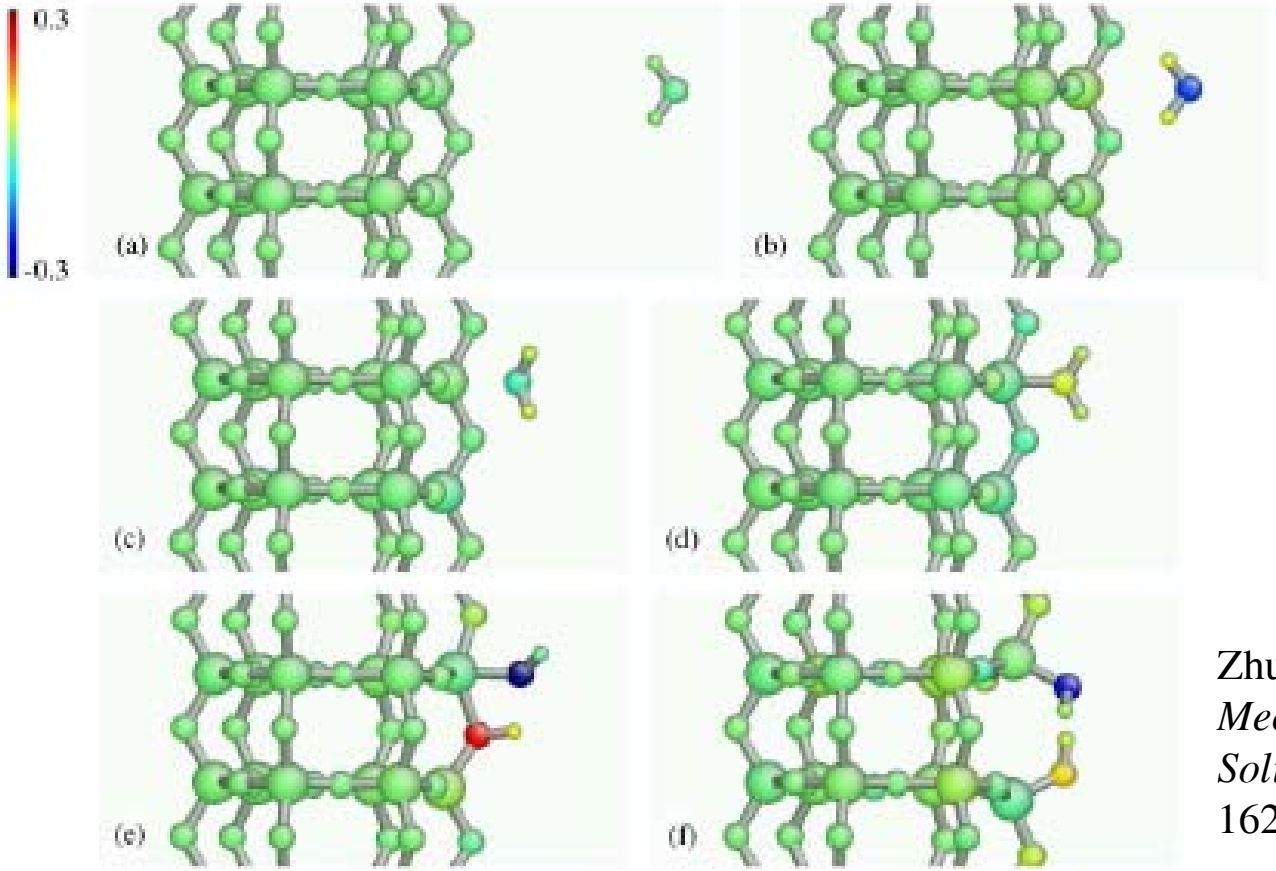
Oxidation of Copper Surfaces (DFT calculations)





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

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



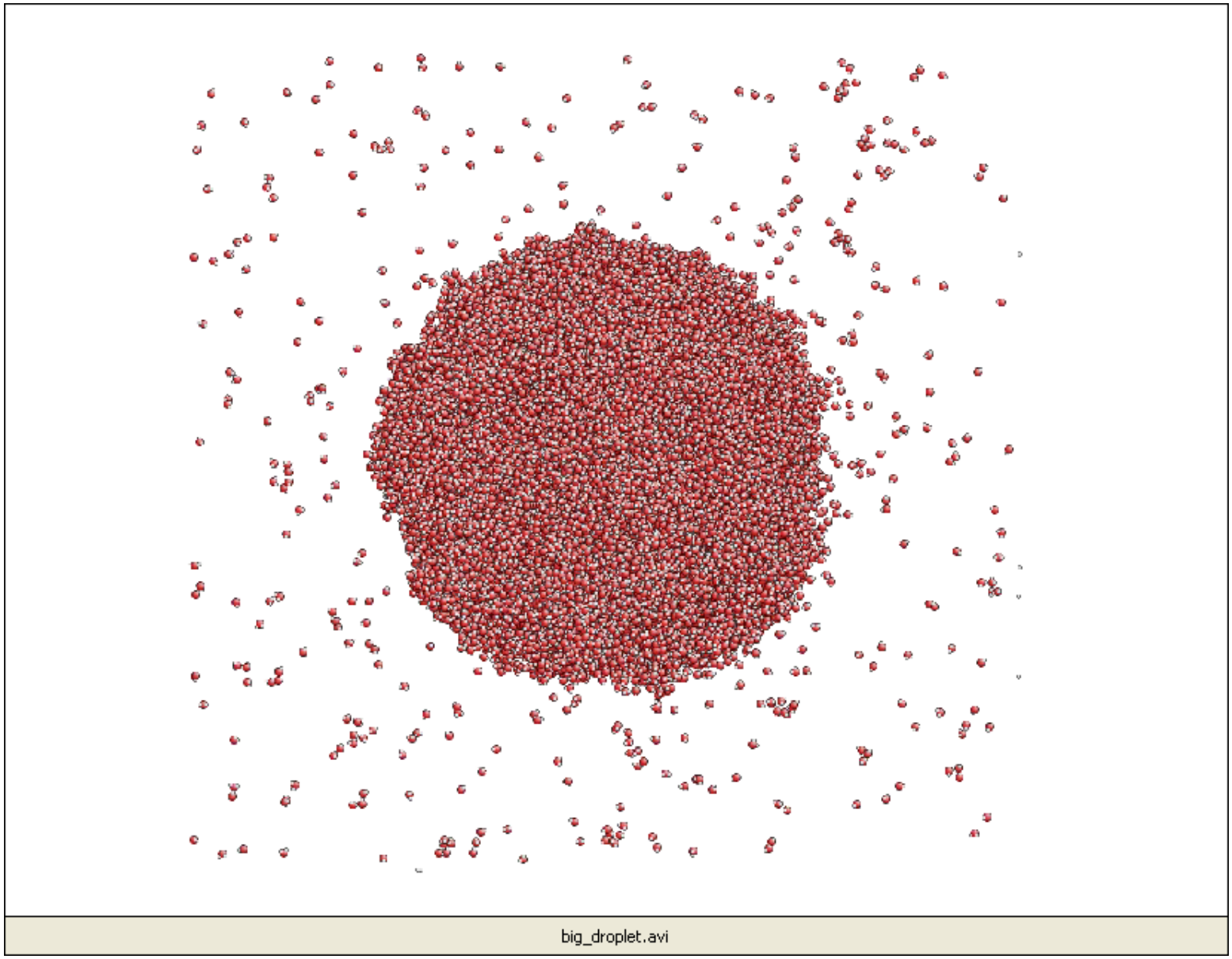
Zhu et al., *Journal of the Mechanics and Physics of Solids* **53** (2005) 1597-1623.

Fig. 6. Atomic configurations along the transition pathway of hydrolysis under a stress of $0.3\sigma_{ut}$. 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).

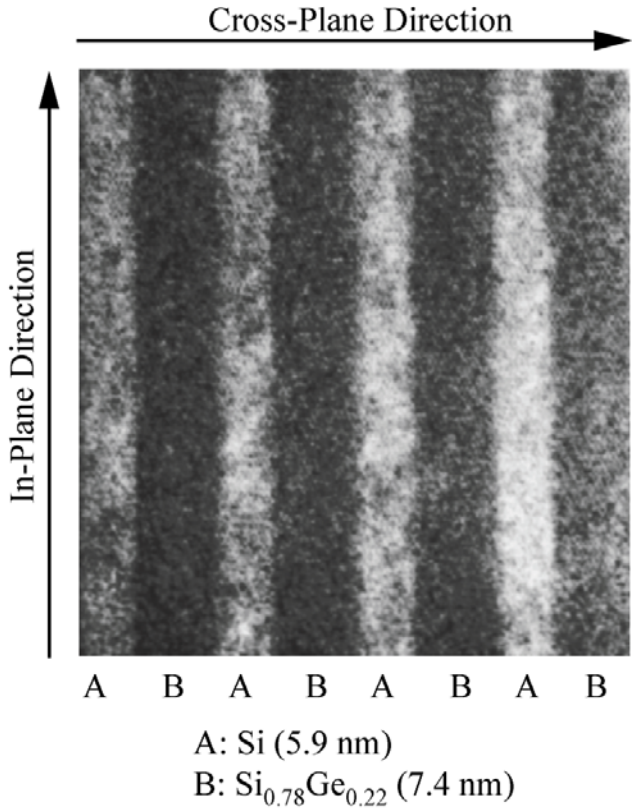
Atomistic Simulation (MD and MC)

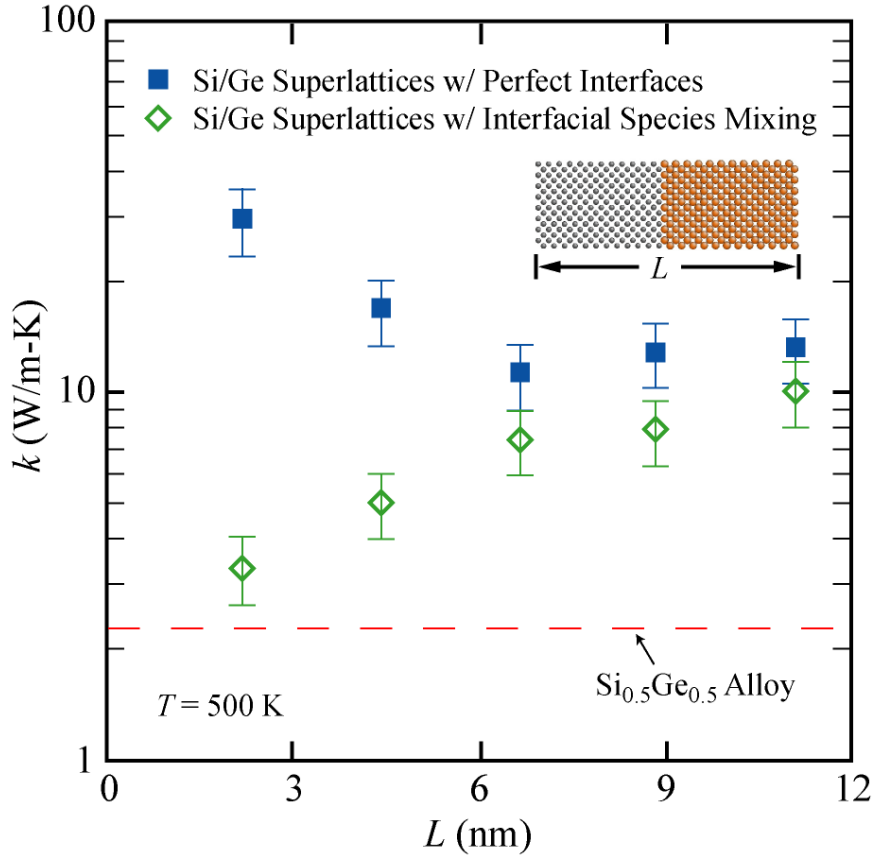
- Electrons not explicitly considered (these degrees of freedom may be much faster than the nuclei).
- Allows for consideration of much larger lengths and times than ES methods. *The adiabatic (Born-Oppenheimer) approximation*.
- Consider a system on an atom-by-atom basis.
- Most common approaches: molecular 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

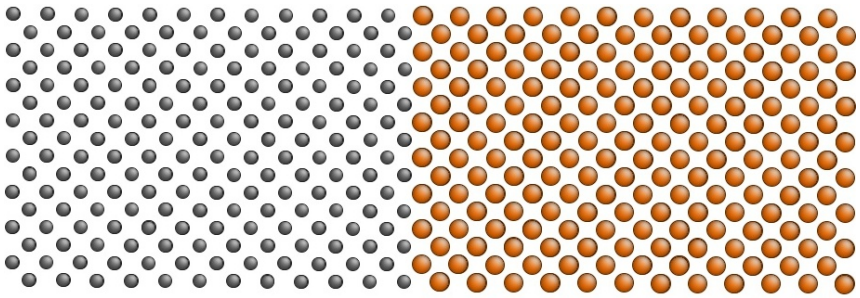
MD Simulation of a Water Droplet

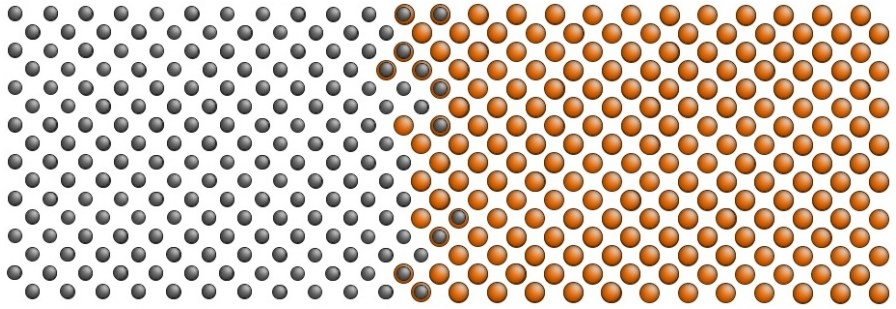


Heat Transfer in Superlattices









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

Reality?

- MD/MC have nothing to do with modern physics. In fact, they directly contradict both 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.

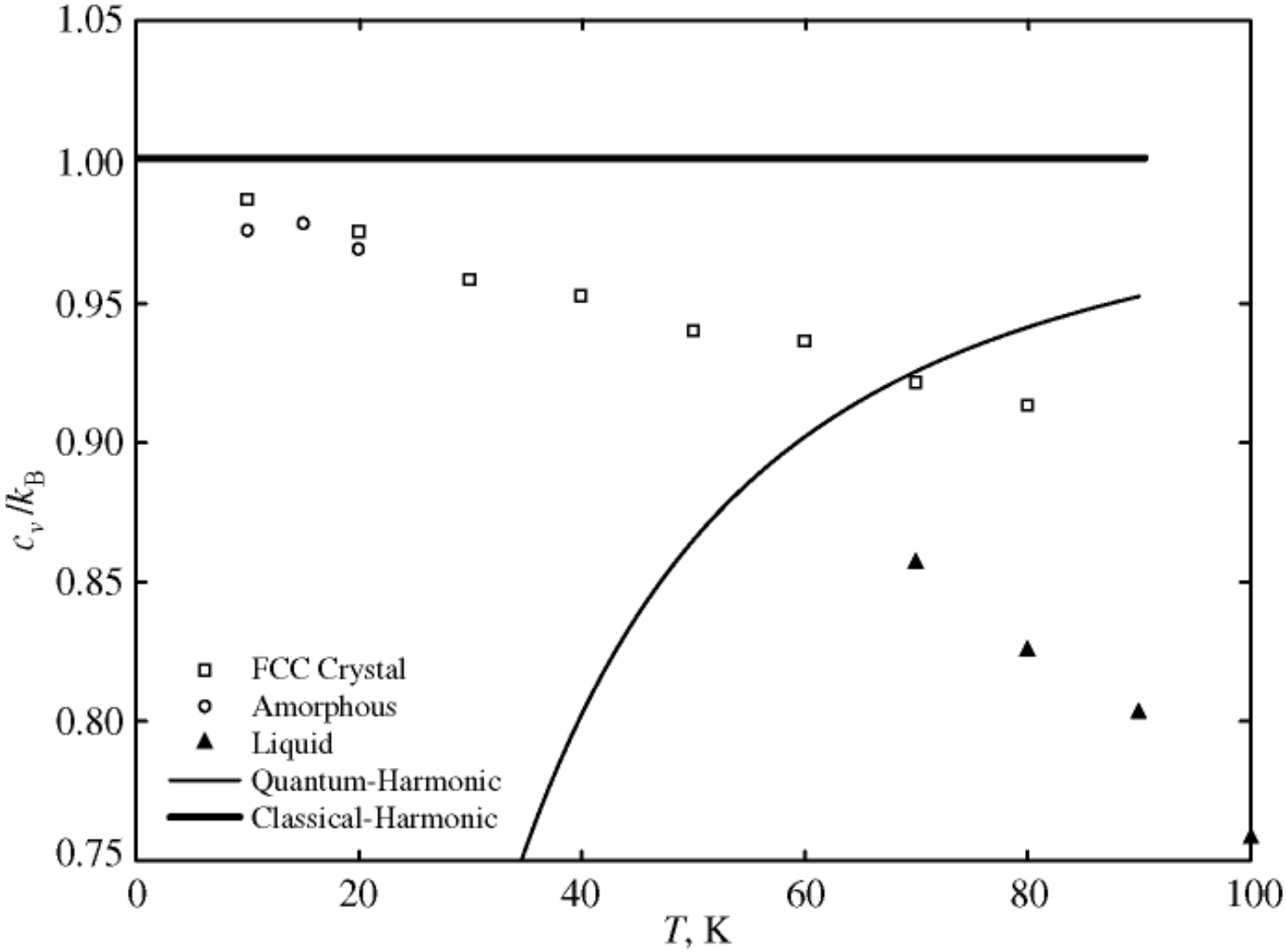
Continuum Modeling

- 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.

Classical vs. Quantum Systems

- In a classical system:
  - Electrons cannot be explicitly modeled (they are quantum entities)
    - Can model metals using MD/MC, but cannot capture electron transport
  - Equipartition of energy (or at least something very close to it)
    - All degrees of freedom in a harmonic system have the same expectation value for their energy, given by $k_B T/2$
    - In a solid, each atom will have $\langle e \rangle = 3k_B T$, so that the expectation value for the total system energy will be $\langle E \rangle = 3Nk_B T$
    - The specific heat will then be $c_v = \partial E / \partial T = 3Nk_B$ = constant
    - Experimental results are completely different!
    - At low temperature, some vibrational modes are "frozen out"
    - Can develop much better models using quantum mechanics (solid state physics course)
    - MD simulations are actually *anharmonic*
  - Vibrational energies are not quantized

Specific Heat in an MD Lennard-Jones system



McGaughey, Ph.D. thesis (2006)

Computer Stuff

- You will be writing code. You must start from scratch (don't use parts of a code from your research group). You will be submitting your code. Don't submit something that doesn't compile and run.
- Options: C++, Fortran. DO NOT USE A MATH PROGRAM.
- Any examples presented in class will be in C++.
- Don't make code any more complicated than it needs to be.
- Add lots of comments (you will forget how/why you did something).
- For analysis, a spreadsheet program (Excel) and a math program (Matlab, Mathematica) will be helpful.

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

What You Should Do Now

- Buy the textbook (see syllabus).
- Establish your computer presence.