Computational Nanoscience
NSE C242 & Phys C203
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Lecture 22: Pop Quiz!

(yes, really)

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Computer Simulation

1) What are the Advantages and Disadvantages of Doing Computer Simulations

a) Advantages

Even when a model is known to a high degree of accuracy, an exact analytical solution of the equations of motion is usually out of question.

Computer simulations can obtain *essentially exact* numerical solutions to the equations of motion for the model of interest, with no approximation.

Generally allow to calculate the most relevant quantities, those that are measured in an experiment, or that are most directly related to our understanding, or that would be too difficult to measure experimentally.

b) Disadvantages

Results are *numbers*, as opposed to elegant equations; thus, one has to make sense out of a set of numbers, i.e. interpret the results.

One has to assess the sensitivity of the results to the system size (finite-size scaling).

The results are usually affected by *statistical errors*, which have to be estimated

Sources of Error

2) Give at least 2 real examples for each of these types of errors common to computer simulation.

a) Systematic Errors

- The finite size of the simulation sample
- A defective random number generator in Monte Carlo simulations
- The finite time-step in Molecular Dynamics simulations
- Round-off errors due to the finite precision of the computer (any numerical calculation suffers from this)
- Sometimes, approximations in the numerical procedure (hopefully, this is never the case!

b) Statistical Errors

- Fluctuations in the average of a given physical observable in a Monte Carlo simulation.
- The error bar associated with a distribution function in a molecular dynamics simulation.
- The variation in temperature

Molecular Dynamics vs. Monte Carlo

3a) What is the difference between the MD and MC approaches?

In MC, non-analytic potentials can be used and the outcome is a random walk through phase space to compute an integral.

In MD, dynamical quantities can be computed, and simple Newtonian equations of motion are solved to move the system.

In Monte Carlo the outcome of each trial move depends on only the preceding trial and not on any other previous ones, whereas in Molecular Dynamics a given snapshot can be traced all the way back to the initial conditions.

3b) Give several examples of simulations where you would choose one over the other, and explain why.

MC: Hard-sphere liquid. Phase transitions.

MD: Vibrational spectra. Diffusion coefficients.

Molecular Dynamics

4a) In molecular dynamics, is it possible to develop an algorithm that accurately predicts the trajectory of all particles at both short and long times? Explain your answer.

No, although the ability to be more accurate in one or the other timescale depends on the choice of integration scheme.

There is no perfect scheme, but the Verlet and Gear-Predictor approaches are most common and tend to do quite well for short range times.

4b) What is the most expensive (computationally) part of a molecular dynamics simulation?

The calculation of forces.
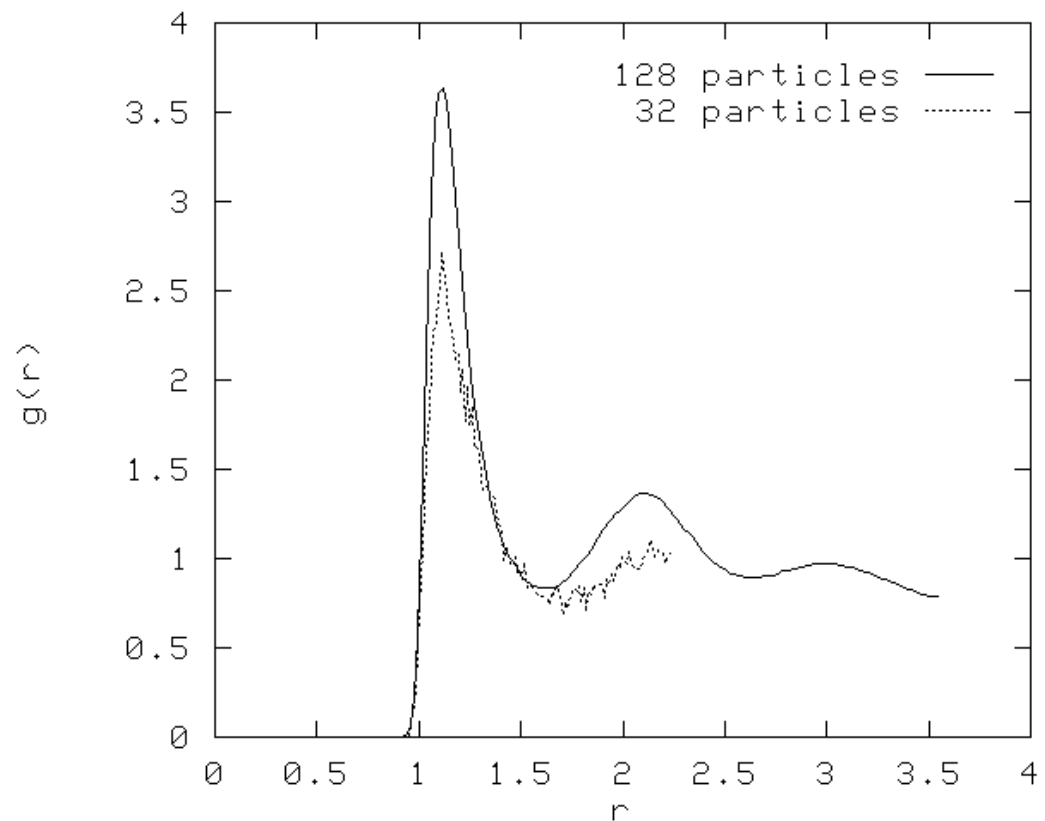
Molecular Dynamics

5) Here is a pair distribution plot for a 32 and 128 particle system interacting via an LJ potential. Is the system a liquid or solid?

a) Liquid or solid, and why?

A little hard to say yet, but it seems that the system is more solid than liquid.

b) Comment on the difference between 32 and 128 particles

A finite size effect is clearly seen.

Monte Carlo

6a) Why is it importance to obey detailed balance? How does the Metropolis algortihm obey detailed balance?

Detailed balance implies that in the absence of external forces, you are properly sampling an equilibrium distribution.

By using a Metropolis approach, you can be sure that the relative amount of time you spend in two distinct states is proportional to the Boltzmann factor (or other relevant probability distribution).

6b) Explain how you might use Monte Carlo methods to look for phase transitions. What problem will you run into? How do finite size effects affect your simulation?

A phase transition is characterized by an order parameter. In a Monte Carlo simulation of a system near a phase transition, the order parameter varies and the fluctuations diverge.

Critical Slowing Down. It takes an infinite amount of time to get statistically uncorrelated configurations.

Finite size effects "smear out" the phase transition.

6c) What is Kinetic Monte Carlo? What is the biggest source of error in a KMC simulation?

In a kinetic Monte Carlo simulation, one hops from one local minima to another at rates that are consistent with transition state theory. In this manner, a sense of "time" is recovered.

The biggest source of error is not choosing properly the transitions that are expected for a given system (incomplete set of processes).

Boundaries

**7a) Tell me everything you know about periodic boundary conditions (PBC).**

With 1000 particles, about 60% of the particles will lie in the vicinity of the wall - need to be able to eliminate surface effects when needed.

In PBC, when a particle crosses a boundary, it re-enters the cell from the opposite side.

Cells are not distinguishable from one another.

Interactions are counted only between the closest N particles (or images).

The potential must be modified (truncated at the boundary).
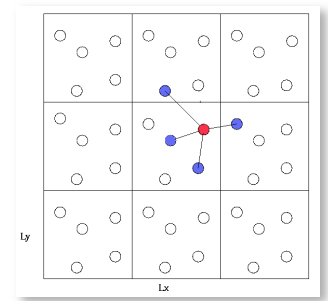
7b) Give at least 2 examples of simulations where you should employ PBC and 2 examples where you should not (or at least need not).

Should: (1) Any liquid or solid of any kind; (2) Nanotubes, nanowires; (3) Surface properties.

Should Not: (1) Properties of an isolated molecule; (2) Reactions between molecules.

Interatomic Potentials

8) Here are the main degrees of freedom in typical classical potentials. As we have learned, not everything can be optimized for all properties. Give at least three physical examples of simulations and state for each case which potential terms are most important to get "right".

Liquid Water: Electrostatics, van der Waals

Solid Silicon: Bonds, Angles

Protein: Bonds, Angles, Dihedrals, Torsions, Electrostatics

Hard Spheres: van der Waals
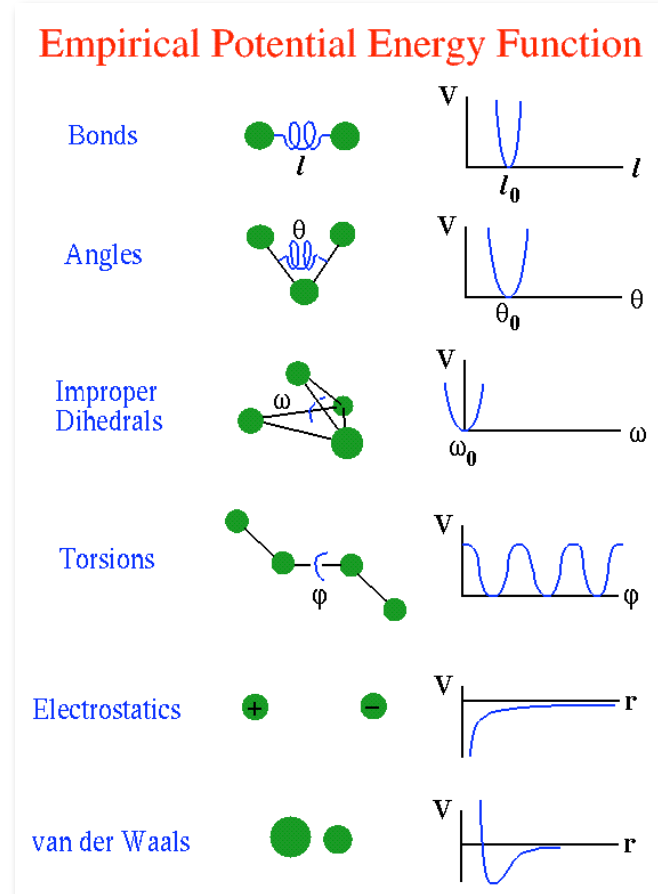
http://cmm.info.nih.gov/intro_simulation/node15.html

Quantum Mechanics

9a) In what situations should we use a quantum mechanical calculation?

When we require information about the electronic structure of the system (ie, specifics about what the electrons are doing and how they are reacting/interacting).

To test the accuracy of a classical potential for anything. To calculate, for example: electronic transport, charge densities, bond breaking, optical properties.

9b) What's a pseudopotential and when do we use it and when do we question its use?

Pseudopotentials are way to "freeze" out the (usually) inactive core electrons. We use it in most quantum mechanical calculations of electronic structure. We avoid using it when the core electrons could be polarized, as in the case of magnetic systems.

9c) Tell me everything that you know about basis sets for representing the electronic wavefuction in a quantum mechanical simulation.

The full electronic wavefunction is usually written as a product of "one-body" functions, for example in a Slater Determinant. The one-body functions, which contain 1 or 2 electrons each (depending on whether spin is explicit) are expanded in some basis set in order to make them amenable to fast computer calculations.

There are many kinds of basis sets, but the most common two choices are gaussians and planewaves.In the limit of a "complete" basis, the same problem with the same theory should give the exact same result, regardless of which basis type is chosen.

Basis Sets

10) What is the difference between a plane wave basis and a gaussian basis?

Gaussian basis sets are local in nature and are thus ideal in molecular calculations, Planewave basis sets satisfy the Bloch condition and are periodic in nature, thus ideal in solid and liquid calculations.

One can use planewaves to simulate molecular properties, but the basis functions will unnecessarily occupy empty parts of the periodic box, making the calculation very inefficient.

Gaussian basis sets can be made "better" by increasing the number of gaussians; however, it is difficult to make this a systematic approach, whereas in planewaves there is only the energy cutoff parameter, which can be systematically increased until convergence is reached.

Gaussian basis sets lead to efficient real-space representation, resulting in numerous 2-center integrals which are fast and efficient to evaluate on a computer.

Plane wave basis sets lead to efficient k-space representation, resulting in fairly straightforward integrals over sines and cosines and then efficient fast fourier transforms.

Quantum Mechanics

11a) Tell me everything you know about the difference between Hartree-Fock and Density Functional Theory.

HF theory is based on a wavefunction expansion, while DFT is based on a density representation. In both cases, single-particle orbitals are solve via a Schrodinger-like equation.

HF includes exchange exactly, but no correlation energy.

DFT includes both exchange and correlation energy, incorrectly but the errors cancel rather well.

HF underbinds and DFT overbinds.

HF overestimates the gap and DFT underestimates the gap.

11b) In DFT there are many functionals. What are the differences between them? How do you know which one to use?

This, as in so many cases in computational nanoscience, depends on what you want to compute and what system you are simulating.

For example, for phonons, LDA is usually very good. For binding energies, a GGA is substantially better. Hybrid, or "exact exchange" functionals perform the best, but are slower and not yet implemented in solid calculations.

Quantum Monte Carlo

12a) What does adding correlation do? What is the leading order effect in the wavefunction?

Correlation is important for bonded systems, binding energies, and many other properties! For isolated atoms, the electrons must stay close to the nucleus and to each other. However, for bonded systems, the electrons have more room to avoid each other while staying close to a nucleus. This means that correlation can have a different effect on different kinds of systems (e.g., atom vs. molecule vs. solid).

Jastrow factor, which depends explicitly on the electron-electron distances (the next term in the Hamiltonian). Allows us to get close to the ground state without using too many parameters.

12b) How is diffusion Monte Carlo different from Hartree-Fock, variational Monte Carlo, and post-Hartree Fock methods?

There is no ansatz for the wave function.

Also, it can recover nearly all of the correlation energy. It scales as N^3 or even better. It does not bias the result based on the variational freedom in the wavefunction. It scales linearly with the number of processors.

Codes

13) We have worked with 8 codes so far in this class. Tell me, briefly, whatever you can about each one:

Average

Lennard-Jones Molecular Dynamics

LAMMPS Molecular Dynamics

Hard-Sphere Monte Carlo

Ising (pronounced *Eye-Sing*) Monte Carlo

Quantum Chemistry (GAMESS)

DFT for Solids (Siesta)

QMC

Last Question

15) How would you simulate the following systems/properties. Please list which code(s), approach(es), and any details you can think of.

a) Mechanical energy transfer rate between two carbon nanotubes.

A classical molecular dynamics simulation should be fine, since electronic effects are unlikely to play a role in the mechanical energy transfer. We choose MD because we will want to study dynamical behavior.

b) Band gap as a function of diameter, crystal growth direction, and surface termination of Si nanowire.

Tight binding may do the trick and would allow for the exploration of many different configurations, although at least several cases should be checked using a more accurate, DFT approach. If the gap is required with quantitative accuracy, one must go beyond DFT, which gives a large underestimate for the gap.

c) Phase transition in liquid Argon.

Classical Monte Carlo, using a simple Lennard-Jones potential for Argon. Simulate the system as a function of temperature and check for finit-size errors.

d) Strength of nanoscale materials with defects.

Depending on the material, we would choose either classical or quantum approach. However, since the system will have a defect, it is safer to go with quantum mechanics since a defect can create charge redistribution and other electronic effects that may not be captured in a classical model. Also, since the strength calculation is static, and requires only a small set of calculations (something, like distance or volume, as a function of total Energy), the slowness of quantum mechanics should be tolerable. Strength also usually implies a material that is "infinite" in at least one dimension, so a planewave code such as VASP would be best.