1.021, 3.021, 10.333, 22.00 Introduction to Modeling and Simulation - Spring 2010

Part I - Continuum and particle methods: Problem set #1

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Due: Friday, February 26, 2010

Team Building and Team Work: We strongly encourage you to form homework teams of three students. Each team only submits one solution for correction. We expect true team work, that is, one where everybody contributes equally to the result. This is testified by the team members signing at the end of the team copy a written declaration that "the undersigned have equally contributed to the homework". Ideally, each student will first read individually through the homework set and think about solutions. The team then meets and discusses questions, difficulties and solutions, and eventually, meets with the TA or instructor.

Important: Specify all resources you use for your solution (lecture note, book, and web).

The following set of exercises is designed to train you in the basics of atomistic and molecular simulation, focusing on analysis methods, development and application of interatomic potentials and visualization. You will also apply molecular dynamics to study the tensile deformation of a copper nanowire, and generate an animation that visualizes the associated molecular mechanisms. For each exercise, show us how you came to your answer and result. We highly encourage you to make drawings where appropriate. **Note to carefully select the parameters before submitting your job to GenePattern; the default parameters may not have been adapted to the case you are studying.**

Note: In the MD analysis you will use in parts 3-5, the reference length is $l^* = 1$Å =1E-10 m, the reference energy is $E^* = 1$ eV and the reference mass $m^* = 1$ amu. All input and output from the MD code is expressed in these units. To facilitate the solution, calculate the units of temperature and pressure (or equivalently, stress) as well as the time unit in terms of the above given reference units.

1. Calculation of diffusion constant and temperature dependence

Fluorite (CaF_2) is a well known "fast-ion" conductor, which could prove useful in battery technology. The plot below (see Figure 1) provides the mean squared displacement (MSD) of the ionic species in this material from simulations at different temperatures, resulting from a 3D molecular dynamics simulation. The goal of this exercise is to practice the application of the MSD to calculate diffusivities, and to study the dependence of diffusivities on temperature.

(a) Comparing the curves for Ca^{2+} versus the plot for F^-: What is the main difference between these MSD curves? From that difference, what can you say about the motion of Ca^{2+} ions versus F^- ions through the material?

(b) From the plots for F^-, determine the diffusion constant D for the given temperature.

Note: The graph is color online; the MSD curves for F^- go from bottom to top for increasing T.

(c) Plot D as a function of temperature T, and discuss the dependence.

(d) Discuss the temperature dependence and estimate the activation barrier assuming an Arrhenius relationship between D and T:

$$D = D_0 \exp\left(-\frac{E_b}{k_B T}\right) \qquad (1)$$

Explain the meaning of all variables in equation (1).

(e) Based on the analysis carried out in part (d), discuss possible mechanisms for atomic diffusion.

Hint: Consider the physical meaning of E_b. Make a simple drawing to illustrate the meaning of eq. (1) and E_b.

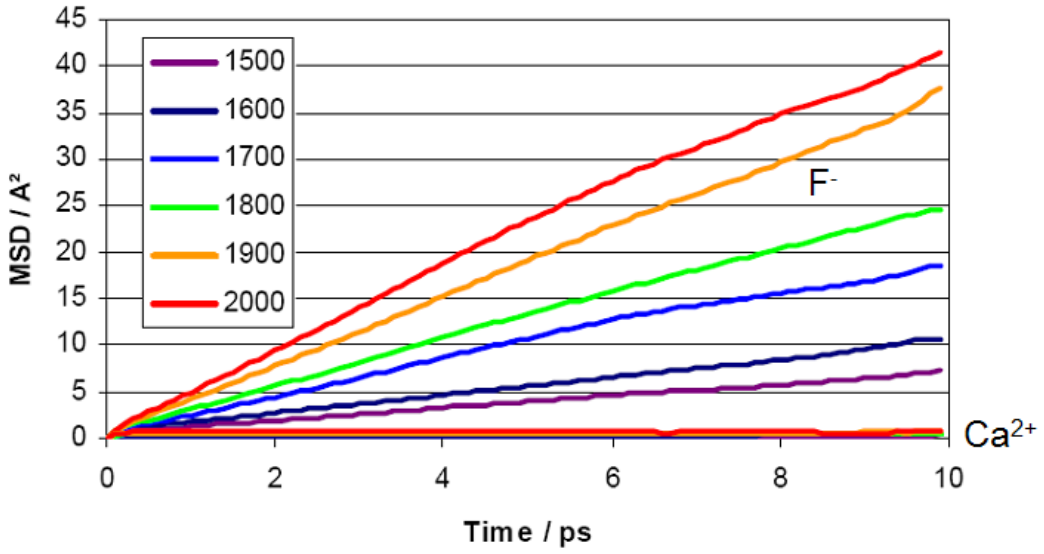

Figure 1: Mean squared displacement function for Ca^{2+} and F^- ions, for different temperatures, resulting from a 3D molecular dynamics simulation (Figure courtesy J. Elliott, Cambridge University).

2. Data analysis and property calculation

Here we are interested in determining structural information of a few atomistic systems, by only considering the atomic coordinates. Please download the five ".xyz" files on Stellar found in the zipped file "Structures.zip". These files are the results of molecular dynamics simulations. This exercise trains you in the analysis of structural material information from molecular dynamics simulation.

File format of ".xyz" files: Each ".xyz" file provides the number of atoms (line one), then a comment line (line two) followed by all of the atoms and their corresponding *x, y*, and *z* coordinates in Angstroms (lines three to the end).

Some of the files provided represent multi-component systems (that is, there are more than one types of atom). However, the actual atom type is not given (e.g. the atoms have been given a generic name "X", "X1", "Y", … or other symbols).

Describe for each of the files:

(a) Phase state (that is, whether the material is a gas, liquid, or a solid)

(b) For the files that are determined to be solid, what is the structure of the material?

(c) Based on your analysis, find one-to-one matches of the files with the following list of materials and explain your reasoning in detail. Each file corresponds to one of the following options:

A. Carbon Nanotube
B. Ni
C. Fe
D. Protein
E. Water

In your solution, provide a detailed description of the approach you use to solve this problem. Include the developed code in your solution. Justify the approach used for the analysis. **Do not use a visual analysis to solve this problem.**

Hint: Develop a code for this analysis, in Matlab, python, C, or any other programming language you are comfortable with.

3. Unit cells and crystallographic orientations, molecular dynamics units

The first step in understanding the relationship between atomistic structure and its elastic properties of solid crystals is to consider the particular crystal structure. Here we focus on single crystals of copper (chemical symbol Cu) composed of a repeating sequence of unit cells defining the crystal structure. The goal of this exercise is to familiarize yourself with atomic crystal structures, units, and how to interpret results from MD simulations in terms of the units.

Copper has a face centered cubic (FCC) lattice, with a lattice constant of a_0 = 3.615 Å. For all lengths in the atomistic model use the length unit of Angstrom (1 Å = 1E-10 m).

(a) Define and draw the atomic coordinates in Å in proper unit cells of a FCC crystal of copper in the [100][010][001] crystal orientation. Indicate characteristic distances between atoms in the drawing.

(b) Calculate the atomic volume and mass density of copper (defined as mass per volume), based on this atomic model of a perfect crystal.

Hint: Consider the mass of a copper atom and calculate how many atoms are included in the unit cell.

(c) How is the lattice constant a_0 related to the nearest neighbor distance of atoms in the copper lattice?

In the MD code you will use for MD simulations, the reference length is l^* = 1Å =1E-10 m, the reference energy is E^* = 1 eV and the reference mass m^* = 1 amu. All input and output from the MD code is expressed in these units.

(d) Calculate the units of temperature and pressure (or equivalently, stress) in terms of the above given reference units.

(e) Convert eV/Å to SI units.

4. Elastic properties of crystals modeled using a LJ pair potential

Pair potentials are one of the simplest potentials used to describe the atomic interaction of crystalline materials (lecture notes for lecture 5). Here we develop a simple 12:6 Lennard-Jones pair potential for FCC copper to fit experimental values of elastic properties of copper as well as copper's lattice constant a_0.

(a) Assuming a 12:6 Lennard-Jones potential (see lecture notes), derive an expression for the equilibrium position between pairs of atoms. This position corresponds to the nearest neighbor distance. Consider only nearest neighbor interactions between atoms.

Express the LJ length parameter σ as a function of the lattice parameter a_0.

(b) Determine an expression for the minimum potential well of the LJ potential, corresponding to the maximum energy stored in each bond.

(c) Develop a Taylor series expansion of the LJ potential, considering up to second order terms, developed around the equilibrium distance between two atoms, denoted by r_0. Denote the second derivative of the potential by the parameter $\varphi'' = k$.

(d) The next step is to determine a set of parameters of the Lennard-Jones (LJ) potential that closely resemble experimental properties of copper.

Determine numerical parameters for σ and ε based on experimental values for the lattice constant and elastic properties of copper. For example, write an expression for the Young's modulus as a function of relevant potential parameters, then determine the unknowns. Consider only nearest neighbor interactions. For elastic properties of copper you may use any appropriate reference (lecture notes, book, web, please specify the reference).

Compare the resulting values with the LJ copper potential reported by Cleri and coworkers (*Phys. Rev. Lett.*, 1997).

Discuss possible disagreement in light of the potential formulation and the potential range.

(e) Now we use the LJ potential developed above and carry out an MD simulation.

Using the web based code (use the module **IMDElastic**), calculate the bulk elastic properties of copper by plotting the virial stress tensor coefficients σ_{11}, σ_{22} and σ_{33}. This module enables you to apply deformation (strain) to a crystal in periodic boundary conditions and measure the stress tensor under increasing deformation.

For the simulation analysis, use:

(i) the LJ potential with the LJ parameters developed above (**note:** Consider only nearest neighbor interactions by choosing a proper cutoff radius, maybe 10 to 20% larger than the nearest neighbor distance), and

(ii) Cleri's potential (larger cutoff radius).

Consider equitriaxial strain loading, that is, the same strain applied to all three directions of the unit cell.

(iii) Calculate the critical strain when the crystal becomes unstable, that is, when the slope of the stress-strain plot approaches zero.

Hint: Consider the "EngPlot.png" that plots the stress in the three spatial directions to solve these problems.

Deformation is measured in strain $\varepsilon_{ii} = \Delta u_i / L_i$ (where Δu_i is the elongation of the crystal in the *i*-th direction with its initial length L_i); the relationship between strain and stress is the bulk modulus, $\sigma_{ii} = K\varepsilon_{ii}$ (since deformation is the same in all three directions, i = 1,2 or 3.

(f) Assuming the LJ potential with nearest neighbor interactions developed above, what is the energy difference between these three atomic configurations:

The red and black lines indicate an equal distance between atoms corresponding to the equilibrium separation. Discuss what implications this may have for modeling such a one-dimensional string of atoms. (Answer this question without carrying out simulations and solely based on on-paper calculations.)

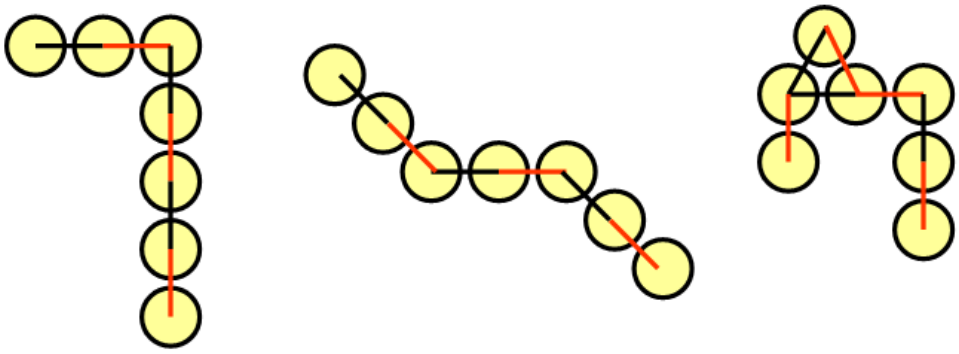

Figure 2: Different atomistic geometries.

5. Deformation of a copper nanowire using an EAM potential

Here we focus on deformation and fracture of copper nanowires. Nanowires could play a critical role in future electronic devices, serving various needs including interconnects, for electronic devices, waveguides or mechanical sensors. Due to the inherently small dimensions, classical, continuum descriptions of the material behavior are questionable and molecular modeling becomes a reliable modeling tool to understand the mechanical properties of these materials.

The goal of this exercise is to model a tensile and compression test of a copper nanowire using molecular dynamics simulation with an EAM potential (see Figure 3 for an example of a "macroscopic" tensile test machine).

Figure 3: Instron tensile test machine, as used for "macroscopic" specimen to measure force versus extension, or stress versus strain. Corresponding tests can also be carried out for nanostructures (e.g. nanowires) by using Atomic Force Microscopes.

Use the web based MD code that uses an EAM potential to model the atomic interactions. As discussed in class, the EAM potential provides a more accurate representation of the chemical bonding in metals than a simple LJ pair potential, and in particular, it can accurate represent the chemical bonding at the surface. This is critical to describe the properties of nanowires, since the surface to volume ratio is particularly large.

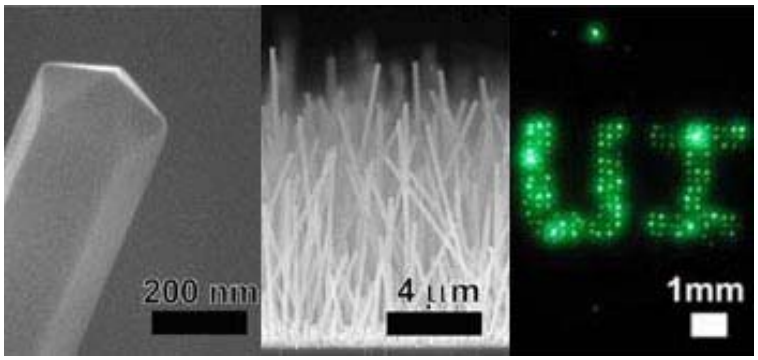

Figure 4: Copper nanowires on different surfaces; each wire is between 70 nanometers and 250 nanometers wide. This figure illustrates a potential application of copper nanowires (note that the specific application is not connected to this problem set). The nanowire arrays could find use in field-emission displays (FED), a new type of display technology that promises to provide brighter, more vivid pictures than existing flat-panel displays. FEDs work in a manner that is similar, in principle, to cathode-ray-tube (CRTs) televisions, but they are only a few millimeters thick and use millions of tiny electron emitters instead of using a single electron gun. In FEDs, the copper nanowires would be used to fire electrons at red, green and blue phosphor particles that are coated on a screen, lighting them up. The nanowires are uniform and have a very pointed tip, and they emit electrons at low voltages, unlike the tungsten filament used in conventional, bulky CRTs, which require many kiloVolts. Source: "*Nanowires Grown for Ultra-Thin Displays*", http://nanoarchitecture.net/article/?c=nano-emissive-displays

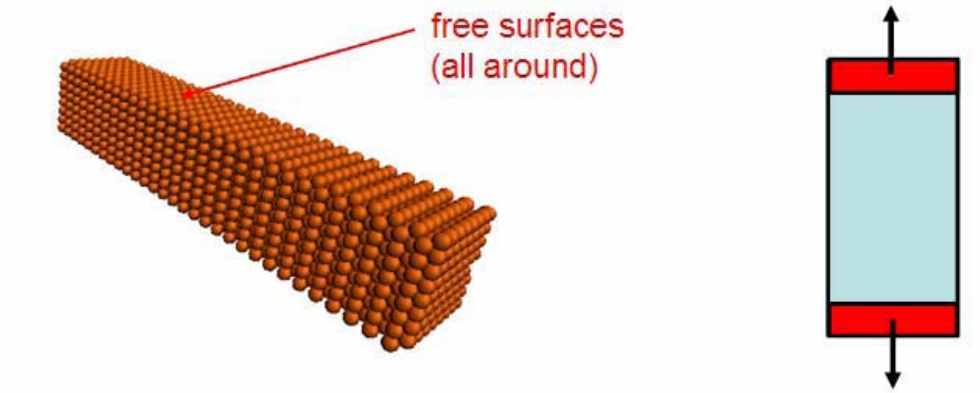

Figure 5: Illustration of boundary conditions.

Here we will use the module **IMDNanowire** (see additional notes posted on Stellar) to carry out a tensile and compressive deformation of a copper nanowire as shown schematically above. Note that this module is based on the IMD code (see original manual at: http://www.itap.physik.uni-stuttgart.de/~imd/); it might be helpful to check the meaning of some of the parameters there.

The crystal orientation for the nanowire is x=[110], y=[1-10] and z=[001]. The dimensions given in x, y and z (in the **IMDNanowire** module) are directly in units of the unit cell, which is in the x and y direction 2.556 Angstrom and in the z-direction 3.615 Angstrom. Thus to get the correct dimensions of 20 x 20 x 130 Angstrom^3 you will need to choose dimensions of 8 x 8 x 36 in GenePattern.

(a) Use the web based program to build and model tensile deformation of a copper nanowire. Choose dimensions of 20 Å and 130 Å.

Run the simulation for 30,000 integration steps, or until you observe significant deformation of the nanowire. Use a displacement rate of 0.02 Å per 20 integration steps at the boundaries (both at lower and upper part).

Note: Apply the load in the *z*-direction, the axial direction of the nanowire.

(b) Take snapshots of the system as it undergoes deformation and include them in your report for this problem set, clearly labeled and clearly explained. The visualizations should be done carefully as they assist you in analyzing the microscopic details of the simulation results.

(c) Discuss the observed deformation mechanisms in detail. What atomic mechanisms are responsible for deformation? Do you see any particularly interesting mechanisms, such as rotation of the end points relative to each other, shear, slip, necking, or others?

Hint: Generate a movie of the deformation process within VMD and watch the simulation results from different angles as the structure undergoes deformation.

(d) Plot the components of the stress tensor as the applied deformation (strain) increases, and clearly indicate what regime of deformation corresponds to which snapshot you have shown in part (b).

(e) Estimate Young's modulus for the nanowire, considering small deformation. Compare with Young's modulus of copper known from macroscopic tensile tests.

Note: For this case, the Young's modulus is defined as the slope of the stress-strain relationship, $\sigma_{33} = E\varepsilon_{33}$ (index 3 here because load is applied in the *z*-direction).

(f) Double the cross-sectional area of the nanowire while keeping the length the same. How does the deformation mechanics and stress-strain response change? Explain the differences, if any.

(g) Describe the deformation mechanics under compression (carry the simulation on until you see significant deformation of the nanowire, using the same deformation rate as above and the same geometry of the nanowire as in part (a) but adapt the parameters for compressive loading). Discuss the results.

Physical constants:

k_B = 1.3806503E-23 J/K
1 eV = 1.60217646E-19 J
1 amu = 1.660538E-27 kg

Notes regarding GenePattern website and MD codes

For this assignment, we use the ITAP IMD code, suitable for modeling metallic systems with the EAM potential or a LJ potential. The ITAP IMD code is made accessible via the GenePattern website at:

http://web.mit.edu/star/molsim/

You will need two modules, **IMDElastic** and **IMDNanowire**.

It is recommended to take a look at the supplementary material provided in recitation – in particular the tutorials that give details about how to run the various codes. If necessary, you may find additional information regarding the ITAP IMD code at the website:

http://www.itap.physik.uni-stuttgart.de/~imd/

including instructions and a manual.

Visualization: You may use the program "vmd" (download at http://www.ks.uiuc.edu/Research/vmd/) to visualize the resulting ".xyz" files. "vmd" is available free of charge. You can directly access a file that contains a series of snapshots, for easy visualization of a movie with VMD. Consider the file "VMDMovie.xyz" that appears as output in GenePattern.

The GenePattern website also produces .png files that you can view immediately in your web browser. However, it is recommended to use VMD for the final report and analysis of the results.