22.53 Homework Problems

Problem 1

Use the molecular dynamics code `moldyn_sim.f` to carry out the following three simulation studies:

a. System equilibration at a low temperature (in the solid state) without temperature rescaling. Verify equipartition, demonstrate reversibility, and check energy conservation by varying the size of Δt.

b. Study a solid at several temperatures, plot U, P, $\langle \Delta^2 \mathbf{r} \rangle$, $g(r)$. Compare the $g(r)$ results with that of an ideal fcc lattice. What happens at high temperatures (does the solid melt)?

c. Determine the thermal expansion coefficient at approximately zero pressure for argon and compare your result with experiment.

Write up each study as a brief "lab report" with the following sections:

- Statement of the problem (with specification of parameter values)
- Results (in the form of figures or tables)
- Brief Discussions (what the results mean and what does one learn from this study)

Problem 2

Draw the flow chart for the MD simulation code `moldyn_sim.f`. Describe the function of each subroutine in the code.

Problem 3

Plot the Lennard-Jones potential and the corresponding radial force $F(r) = -dV(r)/dr$ in the same figure using the values for Argon, $\epsilon = 120$K and $\sigma = 3.405$A. Discuss all parts of the potential and the force to which you can give physical meaning.

Problem 4

Calculate and plot the cohesive energy curves (variation of potential energy at 0K with volume) for the three crystal structures, fcc, bcc, and simple cubic. For each structure, how does one determine the equilibrium volume? Discuss the relative stability of these structures. Calculate and plot the variation of pressure with volume for the three structures. Discuss the physical significance of your results.

Problem 5

Calculate and plot the radial distribution function $g(r)$ for the three structures in Problem 4 at the respective equilibrium volumes. Tabulate the distances between an atom and its nearest, 2nd, 3rd, 4th and 5th neighbors, along with the total number of neighbors at each distance.

Problem 6

Compare $g(r)$ for a solid, liquid, and gas plotted on the same graph. Calculate and plot the mean squared displacement as a function of time for the same three systems. Express your results in both dimensionless units and physical units of length and time. Discuss any significant characteristic features in your results.

Repeat the calculation for a glass which you can prepare by taking a well equilibrated liquid and quenching it (taking away the kinetic energy in a few time steps). Do you have any problems with crystallization? If so, discuss what one can do to avoid crystallization or promote it.

Problem 7

Develop a Monte Carlo simulation code by modifying the Haile (L-J) code. Write a subroutine called METRO which moves the particles by Metropolis sampling, so that in the Main Loop instead of moving the system forward one time step after another, you are sampling a new system configuration one after another. By saving the configurations thus generated, you can then calculate system properties by averaging over the sampled configurations instead of averaging over the trajectories.

Problem 8

Devise your own simulation runs to demonstrate that your Monte Carlo code is working properly. In particular, carry out runs under the same conditions for which you have made MD runs with Haile (L-J) in order to compare (and discuss) the MC and MD results for energy, pressure, $g(r)$, and MSD. In the case of MSD, do you expect the two simulations to give comparable results? In comparing time-dependent results, how do you determne the equivalence between an MD time step and an MC configuration step?

Problem 9

What can you say about the efficiency (computation time to carry out one time step or one configuration move) of MD and MC relative to each other? Formulate and then carry out a number of timing tests to demonstrate in a quantitative way the relative efficiency that is expected on general considerations.

Problem 10

Write a brief essay (no more than just a few pages, don't worry about complete sentences or any writing etiquette, could even be an extended outline with explanatory phrases in appropriate places) describing the basic ideas underlying each of the following methods of describing interatomic interactions as used in atomistic simulations:

- pair potentials
- empirical many-body potentials
- tight-binding approximation
- first-principles method

In each case, give a specific example to illustrate what you want to discuss as well give general comments on relative effectiveness (robustness and limitations) and computational simplicity in comparing the particular method under discussion with the others in the list above . You can be as specific as you like, and be sure to give explicit acknowledgments (at least citations) if you are quoting results from published work.

Note: The idea of this problem is the following. Imagine you are preparing to give a seminar talk on interatomic potential functions for use in atomistic simulations. You would like to give a broad survey of the current status as well as show off your understanding of the complications in implementing a particular method – in other words, you know when to use which method. The essay is the outline you would follow in giving your talk. Assume the audience knows the Haile code well but not much else beyond that.

Problem 11

Give a brief outline of the general ideas behind the harmonic methods discussing the following issues:

- On which assumptions are these methods based?
- How are the free energies calculated? (quantum mechanical and classical)
- When are harmonic methods expected to provide a reasonable description?
- When are harmonic methods expected to fail? Why?

Problem 12

We have seen several different variations of harmonic methods for the calculation of free energies. Two examples are the Local Harmonic (LH) and the Quasi-Harmonic (QH) methods. What is the difference between them?

Another variation is the Purely Harmonic (PH) method. The approach is essentially equal to the Quasi-Harmonic method. However, there is 1 fundamental difference between them. What is this difference? (Hint: consider the equilibrium configurations.)

Problem 13

We consider a perfectly crystalline solid which is characterized by the potential energy function U(a), where a is the lattice parameter of the crystal. No external stresses are applied.

What is the condition for mechanical equilibrium at $T = 0$K?

How does this condition change for $T > 0$K?

How can we determine the thermal expansion of the crystal within the harmonic approximation? Which harmonic method (QH, LH, PH) would you use?

Problem 14

The program `QHA.F` is a code (to be provided in class - see the TA) which computes free energies of the Lennard Jones fcc copper crystal as a function of temperature and density using the LH method. In order to prepare an executable program, the file `QHA.F` should be compiled with the additional routine ZHPEV.F which performs diagonalization of the Dynamical Matrix. To do this use the command:

```
f77 -o qha qha.f zhpev.f
```

This command will create an executable with the name qha. On running, the program will ask for the number of atoms in the periodic cell, the reduced density and the real temperature. The LJ parameters for copper are $\epsilon = 0.167$ eV and $\sigma = 2.3151$ A. The cutoff is set at 2.3273σ. On output the program returns the free energy, entropy and internal energy (both Quantum mechanical and Classical) of the harmonic system for that particular reduced density. All output quantities are in reduced units.

Using `QHA.F`, find the equilibrium lattice parameter (in A) at $T = 300$K for the cell with 256 atoms. Present plots of free energies, entropies and internal energies as a function of the lattice parameter. Give a discussion of the results (including differences between classical and quantum mechanical data).

Repeat this procedure for $T = 700$K and $T = 1100$K.

Compare your equilibrium lattice parameters with those obtained by S. Foiles in his paper on the harmonic methods (Fig. 1). What are the differences and similarities and how would you interpret them?

While determining the lattice parameter at $T = 1100$K, you should have noticed a stability problem. What happens to the eigenvalues of the Dynamical Matrix? Give a physical interpretation of this instability.

Term Project

As part of the assignment in this subject each student is asked to do a term project and submit a report at the end of the term.

The idea is to report an independent study, formulated and carried out during the term, in the form of a journal paper (length and format requirements to follow the *Physical Review Letters* or *Scripta Metallurgica* - further details will be given in class). The subject should be an atomistic simulation study involving either molecular dynamics or Monte Carlo, using a courseware code that you have modified, or a code which you will develop on your own. Other than this, the choice of topic is yours. You are encouraged to discuss your topic selection with the instructors as early as possible.

October 2 - A one paragraph statement (up to a page) describing your topic, the approach you intend to follow, the simulation code you will use, and the key result you are seeking is due. Include a key reference or two, if your project is closely based on published work.

November 20 - A brief progress report (one or two pages) stating your project goal(s), results obtained, and results still needed for completio= n is due.

December 15, 5 PM - Final term project is due. Do not expect any extension. If you absolutely cannot finish, the only recourse is an Incomplete which is generally NOT recommended.