

MatSci 331 Homework 4

Molecular Dynamics and Monte Carlo: Stress, heat capacity, quantum nuclear effects, and simulated annealing

Due Thursday Feb. 21 at 5pm in Durand 110.

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In this homework, you will build on your previous MD code using a Lennard-Jones potential and introduce a Monte Carlo function for your code that utilizes your LJ energy calculation functions from earlier homeworks.

Like the last HW, you will need to use a continuous form of the potential,

$$\phi(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] - 4\epsilon \left[\left(\frac{\sigma}{r_c}\right)^{12} - \left(\frac{\sigma}{r_c}\right)^6 \right], & r < r_c \\ 0, & r \geq r_c \end{cases} \quad (1)$$

In this HW, we use Lennard-Jones units given by energy ϵ , length σ , and the atom mass m . For example, units of time are $m^{\frac{1}{2}}\sigma\epsilon^{-\frac{1}{2}}$.

1 Stress

Whether using empirical potentials like LJ or quantum methods like DFT, knowing the stress in your computational cell is important for every calculation that you do. Small changes in computational cell strain can produce phenomenally large stresses in your computational cell (more than 10,000 atmospheres!).

The pressure in your computational cell is,

$$p^{instantaneous}(t) = \frac{Nk_bT^{instantaneous}(t)}{V} + \frac{1}{3V} \sum_{\ell, m > \ell} \vec{r}_{\ell m}(t) \cdot \vec{f}_{\ell m}(t) \quad (2)$$

Here, $f_{\ell m}$ is the force on atom ℓ due to atom m .

1. Write a subroutine that calculates the stress. You might consider putting the potential energy portion of the stress calculation in your energy and force calculation routine for efficiency. Run a MD simulation with your LJ potential with $r_c = 1.3$ and minimum energy lattice constant that you used in the last HW (cubic conventional

cell lattice constant is $2^{\frac{1}{2}}2^{\frac{1}{6}} = 4^{\frac{1}{3}}$). To get a sense for the magnitude of this stress in a typical covalent or ionic material, take $\epsilon = 1$ eV, $\sigma = 2\text{\AA}$, and take $T=300$ K. Remember that T in LJ units is given by kT/ϵ . Calculate the stress in GPa = 10^9 Pascals (1 Pa is the SI unit of pressure, J/m³). 1 atmosphere is approximately 10^5 Pascals.

2. Calculate the stress and adjust the computational cell lattice vector so that the stress oscillates around zero at equilibrium - be sure to let the system equilibrate. What is the lattice constant of your fcc crystal that gives average zero stress for a 3x3x3 fcc lattice computational cell?
3. Now increase the temperature using an initial $T = 3000K$. How much does the pressure change upon this temperature change at the minimum energy lattice constant? What is the lattice constant of your fcc crystal that gives average zero stress at this temperature.
4. Now decrease the length of the lattice constant by 5% from the minimum energy lattice constant and calculate the average stress at $T=300$ K. How do the magnitudes of the kinetic and potential parts of the stress compare? Would it be reasonable to ignore the kinetic part of the pressure at high pressures when calculating the enthalpy as we discussed in class?

With periodic boundary conditions, average pressures (time-average of instantaneous pressure) of a few tenths of a GPa or less can typically be considered to be approximately "zero" or atmospheric. Perhaps even 1 GPa can be considered zero in some systems. While these are very large by everyday standards, the difference in strain between these pressures and zero is typically *assumed* to be of little consequence. It's a good idea to look at the pressure at the start of your calculations, whether they are DFT-based or otherwise.

2 Heat capacity from MD thermal fluctuations

The time-dependent fluctuations of MD simulations are very rich in information, as we discussed in the context of the Kubo relations for transport properties. Another quantity that can be determined from fluctuation magnitudes is the heat capacity. In the micro-canonical ensemble (constant energy), the variations in temperature can be shown to obey the relation (see, e.g. Allen and Tildesley or Pearson, et al, Physical Review A **32**, 3030 (1985).),

$$\frac{\langle T(t)^2 \rangle - \langle T(t) \rangle^2}{\langle T(t) \rangle^2} = \frac{2}{3N} \left(1 - \frac{3k_B}{2c_v} \right) \quad (3)$$

where c_v is the heat capacity per atom at constant volume.

1. Calculate the heat capacity of 2x2x2 LJ crystal with initial $T=0.2$. Omit the equilibration period, and see if you can converge your result to within 10%. How long to you need to run (in LJ time units) to get around 10% accuracy? Getting this level of convergence may require more run time than you expect. How does your result compare with the classical heat capacity of a perfect harmonic crystal ($c_v = 3k_B$)? You might consider using Matlab's var function.
2. Think about what approximations you are making in this calculation: Are you assuming a perfectly harmonic crystal? Are you assuming quantum nuclear effects are negligible?
3. Now set your initial $T=4.0$ and calculate the heat capacity in the liquid state. Use a 3x3x3 computational cell. This one may require some extra run time. How does it compare with the crystal case?

3 Free energy, heat capacity, and quantum vibrations (15 bonus points)

For a system in vibrational equilibrium, the vibrational spectrum can be determined from the Fourier transform of the velocity autocorrelation function,

$$\rho(\omega) = \frac{m}{k_b \langle T \rangle} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \vec{v}(t) \cdot \vec{v}(0) \rangle \quad (4)$$

Recall that vibrational equilibrium is required because only then does each mode have the same amount of energy, namely $k_b T$.

1. By integrating over omega, show that this function is normalized to 3.

The free energy (Helmholtz energy) within the quasi-harmonic approximation is given by,

$$F = E(\{r_\ell\}_{min}) + \int_{-\infty}^{\infty} d\omega \rho(\omega) \left[\frac{1}{2} \hbar \omega + k_b T \ln \left(1 - e^{-\beta \hbar \omega} \right) \right] \quad (5)$$

Here, $\{r_{min}\}$ is the minimum energy configuration obtained, e.g. via steepest descent.

This free energy assumes each vibrational state of the system is a quantum harmonic oscillator. This approximation can break down at high temperatures or in liquids, but it might be generally expected to be ok.

To see the impact of quantum nuclear effects, calculate the heat capacity of your LJ system using the quasiharmonic approximation. The heat capacity of a single quantum harmonic oscillator is (see, e.g. a statistical mechanics text),

$$c_v^{HO}(\omega, T) = k_b \left(\frac{\hbar\omega}{2k_bT} \right)^2 \frac{1}{\sinh^2 \left(\frac{\hbar\omega}{2k_bT} \right)} \quad (6)$$

So the heat capacity for your MD system is (per atom),

$$c_v(\omega, T) = k_b \int_{-\infty}^{\infty} d\omega \rho(\omega) \left(\frac{\hbar\omega}{2k_bT} \right)^2 \frac{1}{\sinh^2 \left(\frac{\hbar\omega}{2k_bT} \right)} \quad (7)$$

Note that T defined above can be chosen to be a different value from the T of your MD simulation used to find $\rho(\omega)$.

2. First, determine $c_v(\omega, T)$ in the limit $T \rightarrow \infty$. Plug in the above expression for $\rho(\omega)$ and calculate the heat capacity. Is this what you expect within the harmonic approximation? (Think about the harmonic crystal heat capacity.)
3. Now calculate the heat capacity of your crystal with the MD and HO temperatures set to be the same. Use a density of states calculated from a 2x2x2 crystal and LJ parameters for a typical covalent material of $\epsilon = 1$ eV and $\sigma = 2 \times 10^{-8}$ cm with atomic mass 28 atomic mass units. For the harmonic oscillator temperature, consider 300 K. The density of states you calculated in the last HW, but this time you need to be more careful about the normalization. For the purpose of this HW, a (quick and crude) simplistic approach to get the desired normalization of 3 is to multiply your $\rho(\omega)$ from HW 3 by the appropriate scaling factor that gives a normalization of 3.
4. How different is the quantum quasiharmonic heat capacity from the classical value?

4 Monte Carlo generation of ensemble averages

In this section, you will produce a Metropolis Monte Carlo code like the one described in class. You can also consult Chapter 3 of Frenkel and Smit for some example codes. Note that the Frenkel and Smit algorithms are in 1D rather than 3D. You can utilize the Matlab rand function for random number generation in the interval [0,1].

For random configuration changes, move one atom at a time, i.e.,

$$r_{new}^{\alpha} = r_{old}^{\alpha} + \Delta \times (\text{rand} - 0.5) \quad (8)$$

where $\alpha = x, y, z$ and δ is initially 0.1 in LJ units. Be sure to use a different random displacement for each of the x , y , and z components, otherwise you are displacing atoms only along a line rather than a volume. Also, be sure to make your displacements reversible

to satisfy detailed balance, i.e. you must be able to displace atoms and return to the same configuration with the same probability.

You can re-use your energy evaluation function that your MD code uses. Since you are moving only one atom at a time, your MC code can potentially be considerably sped up by writing an energy evaluation function that calculates the change in energy due only to the movement of one atom. However, I suggest using your existing energy evaluation function initially. It is sufficiently fast to do this HW.

1. Start with a 2x2x2 fcc computational cell with LJ parameters described above. Take the temperature $k_bT = 0.1$. Note that this is different from the initial k_bT that you set in your MD simulations. Run the calculation for 10,000 steps. Calculate the fraction of rejected steps and plot the potential energy as a function of step number. Note there is an equilibration period at the start of the simulation, as in MD.
2. To check your code, you can compare to a MD simulation. Run MD with the same cell size, but set initial $k_bT = 0.2$ to achieve an equilibrated $k_bT=0.1$. Plot the potential energy versus time and compare with the potential energy from MC. Are the average values the same? Are the magnitudes of the fluctuations the same?
3. Experiment with the δ for atomic displacements. This parameter controls the fraction of rejected configurations. Too many rejects is inefficient, and too few means the atoms could be sampling the relevant phase space more rapidly with larger steps. Aim for a rejection ratio of around 50%. This is a very rough number, not necessarily optimum for this problem. What value of δ gives a reject ratio of around 50%?

5 Heat capacity from MC

The canonical ensemble energy fluctuations of potential energy (here we will refer to potential energy as ϕ) can be related to the heat capacity of the system,

$$\langle \phi^2 \rangle - \langle \phi \rangle^2 = N k_b T^2 (c_v - \frac{3}{2} k_b) \quad (9)$$

1. Calculate the heat capacity from the potential energy fluctuations for the 2x2x2 LJ crystal at $k_bT = 0.1$. Be sure to omit the equilibration period. Explore the convergence of your heat capacity as a function of the number of MC steps. How many MC steps do you need to take to get a result converged to within around 10%?
2. How does your heat capacity compare to the value calculated from MD?

6 Monte Carlo and the quest for the global minimum

In this problem, you will explore the use of simulated annealing to search for the global minimum of Lennard-Jones systems.

We know that Lennard-Jones favors close packed structures zero pressure conditions, but the lowest energy structures can differ from close packed when the volume of the system is constrained to be a value that differs from the zero stress volume. For example, imagine placing a LJ crystal under tension by placing positive strain on the computational cell. Tension raises the energy of the crystal by pulling neighbor atoms up onto the attractive part of the interatomic potential. Beyond a critical strain, one might expect to find *lower* energy configurations that include, e.g. dislocations, vacancies, amorphous regions, other crystal structures, or voids that cause the system to be less homogeneous. In the limit of very large strain, keeping the number of atoms fixed, we might expect the system to form a nanoparticle surrounded by vacuum. Determining the shape of the lowest energy state of the system (nanoparticle face areas, etc.) is a global minimization problem.

1. First, increase the lattice vector length of your computational cell by 10% and use a $L=M=N=3$ cell with fcc atom initial positions. For the initial simulated annealing schedule, make your temperature ramp linearly from $k_bT = 2$ to 0 over 2000 MC steps. Be sure to use a random atom movement length that gives a reasonable acceptance ratio. Is the final state energy lower than your initial state fcc energy? What does this mean about the configuration of atoms at the end of the simulation - how does it compare with the initial configuration?
2. By varying your annealing schedule, number of MC steps, random atom movement length, try to find the lowest energy structure that you can. For full credit, try at least one other annealing schedule that gives lower final energy than the one above.
3. One of the challenges with low symmetry systems is figuring out how to characterize the states observed. Is your system amorphous but homogeneous? Full of vacancies or voids? Partial dislocations? A picture can be worth 1000 words here - you can try using VMD (VMD info in the previous HW).
4. A method for determining the atomic transport during your annealing process is to look at $\langle \Delta r^2 \rangle$ as a function of the number of MC steps. You calculated this in your last HW and can reuse your code. You want your annealing schedule to have sufficient parameters that the atoms move outside of their local potential minima. Make a plot - are the atoms moving out of their local minima during the anneal? Remember that $\langle \Delta r^2 \rangle$ in this case has nothing to do with the diffusion coefficient, as it did in MD.
5. A radial distribution function (RDF) is a good way to characterize the spatial distribution of atoms in crystals and amorphous states alike. RDFs are chock full of information (see Allen and Tildesley) like the coordination number and will provide some information about whether the system is amorphous or not. See Frenkel and Smit for an example RDF code. Plotting an RDF is not required for this HW, but you might get some insights if you have the time to implement the RDF calculation.

Other methods include making histograms of atomic coordination, or making an image with atoms color-coded according to atomic coordination. The latter is particularly useful for dislocations within a largely perfect crystal.

6. Now, increase your computational cell lattice constant to twice the minimum energy fcc value and anneal again. Initially, the total energy will be zero because the atoms do not interact. When MC annealing, the atoms will do random walks until they find each other and coalesce. Eventually, one might expect a cluster to form. Find optimal values for the δ and annealing temperature schedule for the initial stages of this problem. Make a plot of energy versus MC steps. You may not get very far with this problem if you're using Matlab. Do what you can.

7 LJ Anneal-Fest 2013 (optional)

By experimenting with annealing schedules and code speedups, find the lowest energy structure that you can for the higher density volume case above. Email a Powerpoint slide containing the annealing schedule, plot of total energy versus MC step, and an image, RDF, or other form of characterization. A VMD movie of the MC process would also be insightful. We will show your slides and annealing details in class!