

MatSci 331 Homework 3

Molecular Dynamics: Integrators, equilibrium, phonons, diffusion

Due February 11, 2013 at the beginning of class.
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In this homework, you will write/modify some code to perform molecular dynamics simulations using a Lennard-Jones potential. You will write an integration scheme, experiment with energy conservation and time step size, calculate the temperature and study the rate of equilibration, and calculate vibrational spectra.

Included in this HW distribution are some MATLAB scripts which serve as a template. You are welcome to use these or write your own code. You can use the scripts you wrote for HW 2, but you may want to use some tricks to speed up your force calculation routine - see the tricks employed in the distribution to speed up force calculations for periodic boundary conditions. See Chapter 4 of Frenkel and Smit for further discussion of these tricks. If you wish to be more sophisticated, you might consider employing a Verlet or cell list described in Appendix F. It is not necessary to use a Verlet or cell list to do this HW.

You will need to use a continuous form of the LJ potential,

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

For these calculations, use a fcc crystal for the initial atom positions, as in HW 2. Set the initial atomic velocities to have random directions with a specified total kinetic energy. See the example code for details.

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 Preliminaries

1. Show that the total energy of the system is a conserved quantity by taking the time derivative. The total energy is,

$$E_{\text{total}}(t) = \sum_{\ell=1}^N \frac{1}{2} m \vec{v}_{\ell}(t) \cdot \vec{v}_{\ell}(t) + V(\vec{r}_1(t), \dots, \vec{r}_N(t)) \quad (2)$$

2. Assuming equipartition, express the instantaneous temperature $k_b T_{\text{instantaneous}}(t)$ in terms of the kinetic energy of the atoms.
3. Time-reversibility of an integration algorithm is a pre-requisite for energy conservation at long times. Show that the Verlet algorithm is time-reversible, i.e. the atom positions exactly retrace their paths when integrating backward in time. Starting from the original Verlet expression for $r(t + \Delta t)$, show that the expression for $r(t - \Delta t)$ obtained by changing the sign on Δt retraces the trajectory.
4. Using a similar approach, show that the Euler method (a Taylor expansion for $r(t + \Delta t)$ about $r(t)$) is not time-reversible, i.e. flipping the sign on Δt takes the system along a different pathway.

2 Verlet integration

1. Write some code to advance the atom positions and velocities through a time step Δt . Use one of the Verlet variations discussed in class. The distribution scripts are set up for utilizing the original Verlet method.
2. Write another piece of code that calculates the total kinetic energy and the temperature.
3. Test your integration scheme by calculating the total energy, Eq. 2. Be careful to evaluate the potential energy V and kinetic energy at the same time, rather than at times that differ by Δt .
4. Run your MD code for 1000 steps using a timestep of $\Delta t = 0.01$. Use a computational cell consisting of a 2x2x2 replication of the cubic fcc unit cell with the T=0 minimum energy lattice constant for $r_c = 1.3$ that you worked out in previous homework (cubic primitive lattice constant is $2^{\frac{1}{2}} 2^{\frac{1}{6}} = 4^{\frac{1}{3}}$). Set the initial velocities with an initial temperature of $k_b T = 0.2$, a temperature below the melting point of the crystal.

To check your code, plot the time evolution of the temperature $k_b T_{\text{instantaneous}}(t)$. It should start at your specified initial temperature of 0.2. If it doesn't, there may be a problem with your temperature calculation code.

5. Plot the time-dependence of the total energy deviation, $E_{\text{total}}(t) - E_{\text{total}}(t_0)$. As a check on your code, it should get smaller with decreasing step size. To make some sense out of the magnitude of this deviation, convert this energy to an (approximate) temperature and compare to the current temperature, i.e.

$$k_b T_{\text{deviation}}(t) = \frac{1}{3N} [E_{\text{total}}(t) - E_{\text{total}}(t_0)] \quad (3)$$

Acceptable levels of deviation result in energy drifts much less than the temperature. Make a plot for the case of time steps of 0.01, 0.02, 0.04 and 0.06.

3 Approach to equilibrium

1. The simulation starts out of equilibrium, i.e. the atom positions are in a high symmetry state and the random initial velocities do not necessarily give the equilibrium vibrational populations. Before doing statistical sampling, equilibrium should be established.

Using an acceptable time step (as determined in the previous section), plot the time evolution of $k_b T_{\text{instantaneous}}(t)$. How much time is required for the temperature to reach a state where the average value and average variance does not significantly change with time? Roughly how many atomic vibrations? (Note that the fastest features in $k_b T_{\text{instantaneous}}(t)$ correspond approximately to the timescale for one atomic vibration). Here, the equilibrium value is the value of the time average after equilibrium has been reached.

2. What is the equilibrium value of the temperature, i.e. the time average of $k_b T_{\text{instantaneous}}(t)$ after equilibrium has been achieved? Why is it different than your specified initial temperature? Hint: What is the heat capacity of a classical crystal and how are the initial atom positions anomalous?
3. Plot $k_b T_{\text{instantaneous}}(t)$ for computational cells consisting of 2x2x2 and 3x3x3 periodic copies of the fcc cubic primitive cell. How do the magnitude of instantaneous temperature fluctuations compare? Why is there a difference?

4 Vibrational spectrum

1. First, sketch the qualitative dispersion relation $\omega(k)$ that you expect for a 1D chain of atoms with 1 atom in the primitive cell. Is the spectrum continuous or discrete? For additional background, see e.g. Kittel's book, Introduction to Solid State Physics for a review.
2. The vibrational spectrum can be determined from the Fourier transform of the ve-

locity autocorrelation function,

$$P(\omega) = \frac{1}{3N} \sum_{\ell=1}^N \sum_{\alpha=\{x,y,z\}} |\tilde{v}_{\ell}^{\alpha}(\omega)|^2 \quad (4)$$

$$= \frac{1}{3N} \sum_{\ell=1}^N \sum_{\alpha=\{x,y,z\}} \tilde{v}_{\ell}^{\alpha}(\omega) \tilde{v}_{\ell}^{\alpha}(-\omega) \quad (5)$$

$$= 2\tau \int_0^{\tau} dt e^{i\omega t} \langle \vec{v}(0) \cdot \vec{v}(t) \rangle \quad (6)$$

where

$$\tilde{v}_{\ell}^{\alpha}(\omega) = \int_0^{\tau} dt' e^{i\omega t'} v_{\ell}^{\alpha}(t') \quad (7)$$

Calculate $P(\omega)$ using Eq. 4 and make a plot for a 2x2x2 computational cell. Is this consistent with your sketch?

3. Make the same plot for the 1x1x1 cell and 3x3x3 cell. Explain how the spectrum changes as you change the size of the computational cell and how it connects to the dispersion relation that you sketched. Hint: Think about the impact of periodic boundary conditions on the allowed k-vectors.
4. How does the amplitude of the peaks relate to the vibrational density of states $\rho(\omega)$? Will there necessarily be a peak in your calculated $P(\omega)$ for each vibrational mode of the system if the system is out of equilibrium?

5 Quantum nuclear effects

Despite the purely classical MD approach utilized here, it is possible in some cases to calculate the free energy incorporating some quantum nuclear effects. Unless $k_b T \gg \hbar \omega_{\max}$ where ω_{\max} is the maximum vibration frequency, quantum vibration effects play a role. For the temperature considered previously ($k_b T = 0.2$), is the purely classical approach valid? Use parameters for Argon: Lennard Jones parameters are $\epsilon = 167 \times 10^{-16}$ ergs and $\sigma = 3.4 \times 10^{-8}$ cm.

6 Diffusion coefficient

1. Calculate and plot the time dependence of the mean-squared displacement of the atoms,

$$\langle |\vec{r}(t) - \vec{r}(t=0)|^2 \rangle = \frac{1}{N} \sum_{\ell} |\vec{r}_{\ell}(t) - \vec{r}_{\ell}(t=0)|^2 \quad (8)$$

Do this for $L=M=N=3$ at two different initial temperatures, $k_b T = 0.2$ and $k_b T = 4$. Run your calculations for about 20 time units; be sure to use a time step that constrains energy drift magnitudes to a small fraction of the temperature. What is the qualitative difference between these two cases?

2. Estimate (roughly) the diffusion coefficient for the higher temperature case. Using the numerical values of ϵ and σ given above for Argon, how does this diffusion coefficient compare with the $0.0016 \text{ mm}^2/\text{s}$ diffusion coefficient observed for water?
3. How would you expect $P(\omega)$ (from problem 4) to distinguish between a solid and liquid? Make and compare plots at initial temperatures $k_b T = 0.2$ and $k_b T = 4$.
4. Show analytically how the diffusion coefficient relates to $P(\omega)$.

7 Nose-Hoover dynamics (optional)

The Nose-Hoover thermostat is among the most common NVT thermostats:

1. $\dot{v}(t) = f_{\text{potential}}(t)/m - \xi(t)v(t)$
2. $f^{NH}(t) \equiv f_{\text{potential}}(t) - m\xi(t)v(t)$
3. $\dot{\xi}(t) = \frac{1}{Mk_B T_{\text{target}}} (k_B T_{\text{instantaneous}}(t) - k_B T_{\text{target}})$

Implement the Nose-Hoover thermostat by using the following Verlet-based integration scheme:

1. Compute $f(t) \equiv f^{NH}(\{r_j(t)\}, \{v_j(t)\})$
2. $r(t + \Delta t) = r(t) + v(t)\Delta t + f(t)\frac{(\Delta t)^2}{2m}$
3. $v(t + \Delta t/2) = v(t) + f(t)\frac{\Delta t}{2m}$
4. $\dot{\xi}(t + \Delta t) = \dot{\xi}(t) + \frac{\Delta t}{T_{\text{target}} M} [T_{\text{instantaneous}}(\{v_j(t + \frac{\Delta t}{2})\}) - T_{\text{target}}]$
5. $\xi(t + \Delta t) = \xi(t) + \frac{\Delta t}{2} [\dot{\xi}(t) + \dot{\xi}(t + \Delta t)]$
6. Compute $f(t + \Delta t) \equiv f^{NH}(\{r_j(t + \Delta t)\}, \{v_j(t + \Delta t/2)\})$
7. $v(t + \Delta t) = v(t + \Delta t/2) + f(t + \Delta t)\frac{\Delta t}{2m}$
8. Increment t ; Goto (1)

You will need to choose a value of \tilde{M} that minimizes the equilibration time at the start of the calculation. As an initial guess, try \tilde{M} to be around 1 for LJ units. Also note that steps 1 through 3 need to be performed for all atoms to compute $T_{\text{instantaneous}}(\{v_j(t + \frac{\Delta t}{2})\})$ used in step 4.

Set the $T_{\text{target}} = 1.0$ and make a plot of $T_{\text{instantaneous}}(t)$. Does it fluctuate around the desired temperature? Experiment with the effect of \tilde{M} on the equilibration time.

8 Visualization (optional)

Graphical visualization can be a good tool to gain insight into your simulations or to help find a problem with them. There are a variety of freely-available visualization tools that can run on your windows, mac, or linux computer. One of these is VMD:

<http://www.ks.uiuc.edu/Research/vmd/>

VMD can take as input the xyz file format described here:

http://en.wikipedia.org/wiki/XYZ_file_format

You can concatenate multiple xyz files together to make a movie in VMD. VMD does not incorporate periodic boundary conditions in a straightforward fashion, but can display some periodic copies of the computational cell if you explicitly include periodic copies of atom positions in the xyz file.