24-623/12-623 2017 HW#4

Total points: 50
Assigned: October 11, 2017.
Due: October 26, 2017, midnight to Canvas. Please use the Canvas discussion board to ask questions of the instructor, the course assistant, or the other students.

1. (10 points) To perform MD simulations in the NVT ensemble using the Nose-Hoover thermostat, the following equations of motion are used:

$$\begin{aligned}
\dot{\mathbf{r}}_i &= \mathbf{v}_i \\
\dot{\mathbf{v}}_i &= \mathbf{F}_i/m_i - \eta\mathbf{v}_i \\
\dot{\eta} &= \frac{1}{\tau_T^2}\left(\frac{T}{T_{set}} - 1\right).
\end{aligned}$$

Use Taylor series to prove that the implementation for the velocity Verlet algorithm is:

$$\begin{aligned}
&1.\, \mathbf{v}_i(t+\Delta t/2) = \mathbf{v}_i(t) + [\mathbf{F}_i(t)/m_i - \eta(t)\mathbf{v}_i(t)]\Delta t/2 \\
&2.\, \mathbf{r}_i(t+\Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t+\Delta t/2)\Delta t \\
&3.\, \eta(t+\Delta t) = \eta(t) + \frac{\Delta t}{\tau_T^2}\left[\frac{T(t)}{T_{set}} - 1\right] \\
&4.\, \mathbf{v}_i(t+\Delta t) = \frac{\mathbf{v}_i(t+\Delta t/2) + \mathbf{F}_i(t+\Delta t)\Delta t/(2m_i)}{1+\eta(t+\Delta t)\Delta t/2}.
\end{aligned}$$

2. (25 points) Modify your MD code so that it controls temperature using the Nose-Hoover scheme discussed in class and summarized in the file NVT.pdf on Blackboard. Perform your simulations using the 256-atom liquid LJ system provided in HW#3. Use a thermostat time constant of 0.05. Make sure that your system has equilibrated before extracting data.

(a) Plot the average pressure as a function of density, ρ, for 950 kg/m$^3 < \rho < 1{,}150$ kg/m^3 at an argon temperature of 100 K. Estimate the density that gives zero pressure. Compare to your result from HW#3. Explain how you determined when your system is equilibrated.

(b) The thermodynamic temperature in the NVT ensemble is given by

$$\langle T\rangle = \left[\frac{\langle (E - \langle E\rangle)^2\rangle}{3(N-1)k_{\mathrm{B}}c_v}\right]^{1/2}.$$

Using a dimensionless box size of 7.4, run a sufficiently long simulation so that $\bar{T} = 100$ K and assume that $\langle T\rangle = 100$ K. Use the energy fluctuations to find the heat capacity. Report the result in J/kg-K for argon. Note that $3c_v$ is the heat capacity per atom. Explain what you did using words, plots, tables, etc. Just giving the answer is not sufficient.

3. (15 points) Read this paper: L. Hu and A. J. H. McGaughey, "Energy accommodation between noble gases and carbon nanotubes." *Journal of Physical Chemistry C* **117**, 18804-18808 (2013), available at http://ntpl.me.cmu.edu/pubs/.

Pretend that you are reviewing this paper for *Journal of Physical Chemistry C*. Prepare a typed 1-2 page review where you describe: (a) the objective(s), (b) the important conclusion(s), and (c) concerns you have with the MD simulations and/or data analysis. Based on your review, comment on whether or not the paper is suitable for publication and what changes you want the authors to make in a revised version.