24-623/12-623 2015 HW#4

Total points: 50
Assigned: October 14, 2015.
Due: October 29, 2015, 8 PM to Blackboard. Please use the Blackboard discussion board to ask questions of the instructor 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:

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

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 $< \rho <$ 1150 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

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

Run a sufficiently long simulation so that $\bar{T} = \langle T\rangle = 100$ K, then 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 the paper: L. Hu and A. J. H. McGaughey, "Energy accommodation between noble gases and carbon nanotubes." *Journal of Physical Chemistry C* **117** (2013) 18804-18808, available at http://ntpl.me.cmu.edu/pubs/.

Pretend that you are reviewing this paper for *Journal of Chemical Physics C*. Prepare a 1-2 page review where you describe: (a) the objective(s), (b) the important conclusions, (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.