

Analysis of melting and phase transformation in terms of evolution of kinetic and potential energies

MSE 6270: Introduction to Atomistic Simulations
Homework #4

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1 Question 1

Using the provided experimental value of molar volume of solid Ar at the melting temperature and 1 atm pressure of $V_m = 24.6 \frac{cm^3}{mole}$, we can directly compute the lattice parameter a as follows:

$$a = \sqrt[3]{4 \frac{V_m}{Av}} = 5.467 \text{ \AA} \quad (1)$$

where $Av = 6.022 \times 10^{23}$ is Avogardo's constant, and an implicit unit conversion is performed in the above equation from cm to \AA .

2 Question 2

Before simulating melting, the system was first equilibrated by simulating a short time duration using velocity distribution and pressure control. This was done to ensure that the initial velocity is set to zero for the specified temperature. A Berendsen barostat was used with $P = 0.00100 \text{ GPa}$ (1 atm) with $\beta = 0.10 \frac{1}{GPa}$. A very small timestep was chosen in order to ensure the initial velocities are accurate, and the system was simulated for 1 ps with 100,000 timesteps. By observing the total energy fluctuations during the simulations, it was ensured that equilibrium was reached as indicated by a reduction of fluctuations in total energy (to the order of 0.001 fluctuations in line with thermodynamic properties and effects of the cut-off radius). The temperature fluctuations also diminished, but remained at 3-4% of the equilibrium temperature.

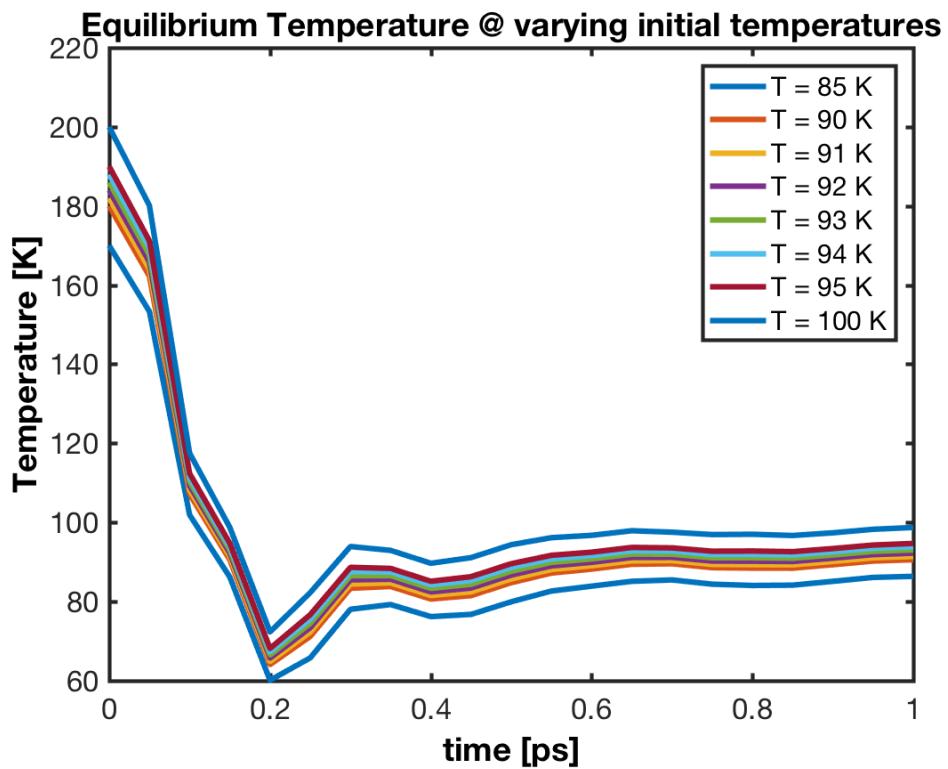


Figure 1: Temperature of each corresponding system with different initial temperatures during the 1ps equilibration simulation. The temperature is first nearly doubled in the first few iterations, and quickly returns to oscillations around an equilibrium temperature. Here, the temperature at each timestep is calculated $T = \sum_{i=1}^{N_{atoms}} \frac{2E_{kinetic}}{3Nk_b}$ where k_b is Boltzmann's constant, and $N = 1372$ is the total number of atoms in the system.

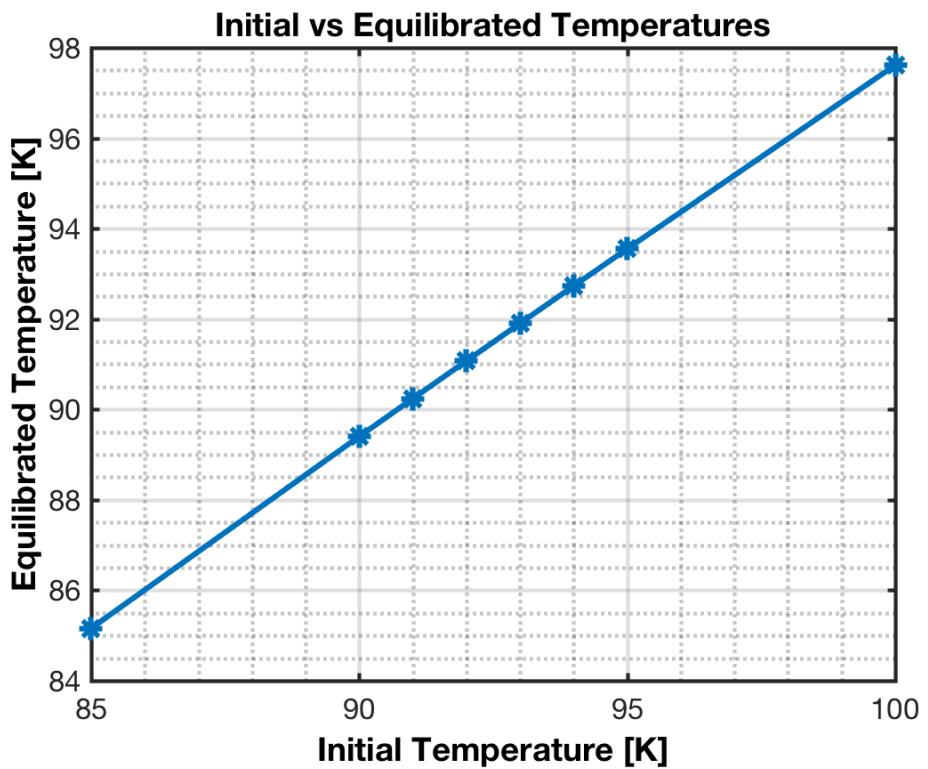


Figure 2: The initial (specified) temperature is compared with the trajectory-averaged temperature after the 1 ps equilibration. In all instances simulated, the equilibrated temperature is lower than the specified initial temperature. Furthermore, the size of the difference increases at increasing temperatures. At specified $T=85$ K, the equilibrated temperature is nearly $T=85$ K, however at specified $T=100$ K, the equilibrated temperature is $T= 97.5$ K.

The final configuration of the equilibrated system after 1 ps was stored and used as a starting point for the longer heating/melting simulation. In addition to using a Berendsen barostat with $P = 0.00010 \text{ GPa}$ (1 atm) with $\beta = 0.10 \text{ GPa}$, a Berendsen thermostat was used to enforce the temperature of the system with $\tau = 2 \text{ ps}$. A timestep inline with the cutoff distance was chosen to be $\Delta t = 0.0010 \text{ ps}$, and 100,000 steps were calculated to simulation 100 ps of time.

Visual analysis of the initial and final configurations below and above the melting point shows a clear distinction of melting. Up to $T=91 \text{ K}$ melting did not occur, and at $T=92 \text{ K}$ a clear indication of melting was signified by the absence of any previously observed crystal structure or long-range order of the final atomic configurations.

The crystal structure is clearly visible even after simulating for 100 ps for the two simulations below $T = 92 \text{ K}$. However at $T = 92 \text{ K}$ the initial crystal structure is no longer present after 100 ps of heating, and no long-range order can be detected in the final atomic configuration. This suggests that melting of an Ar crystal at 1 atm pressure occurs at $T = 92 \text{ K}$, which is in disagreement with the phase diagram provided in the homework statement. This is likely due to the small size of the system and free boundary conditions, which changes the energy landscape. The simulation is heating a nanoparticle in vacuum. (Figure 3 below).

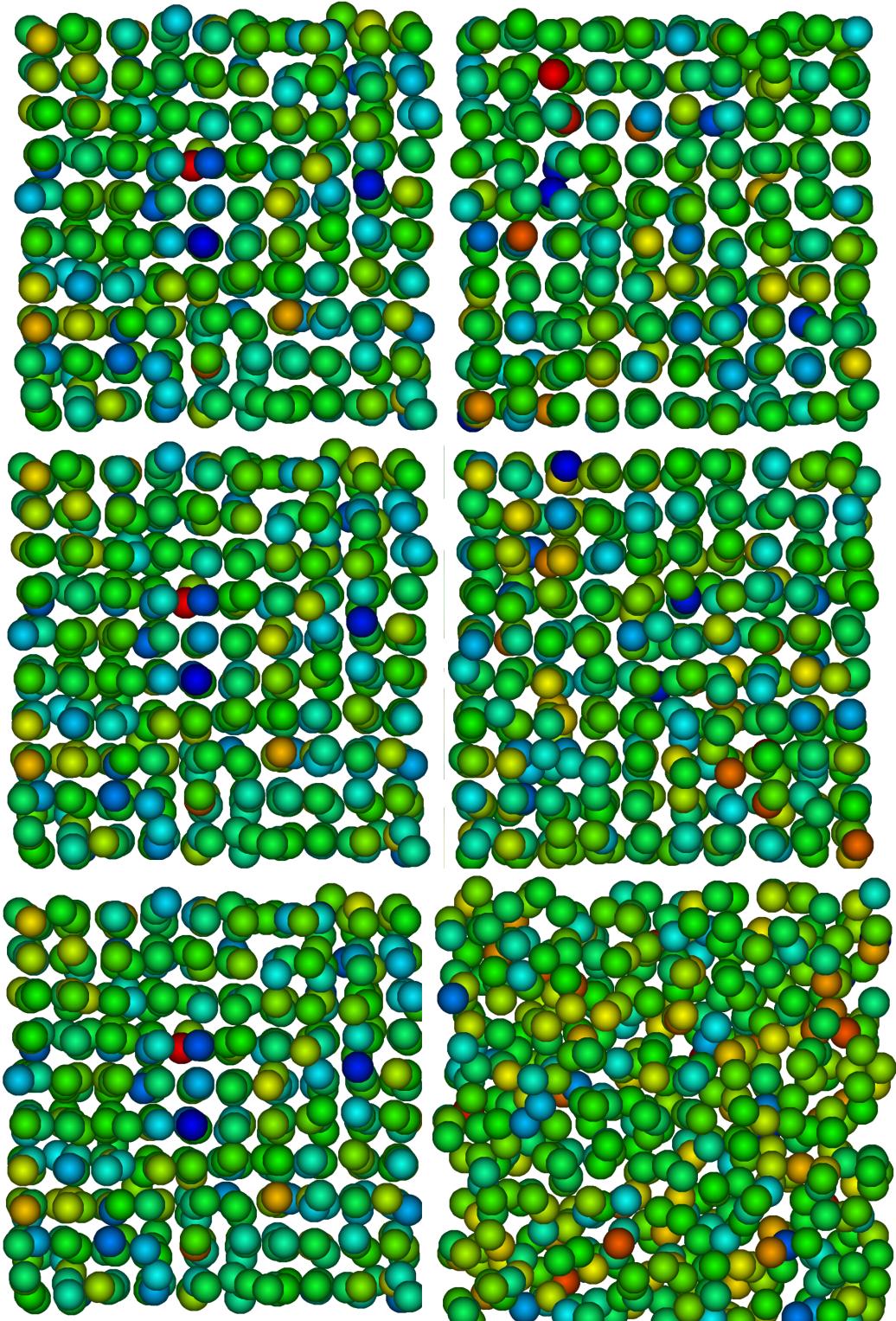


Figure 3: Left: initial atomic configuration at $t=0$ ps. Right: final atomic configuration at $t=100$ ps. Views are of the x-y plane of the simulation face. Simulation was first equilibrated using a Berendsen barostat, and then advanced in time using both a thermostat and barostat. Top row: $T = 90$ K, middle row $T = 91$ K, bottom row $T = 92$ K. (Colors correspond to the x-velocity of each atom).

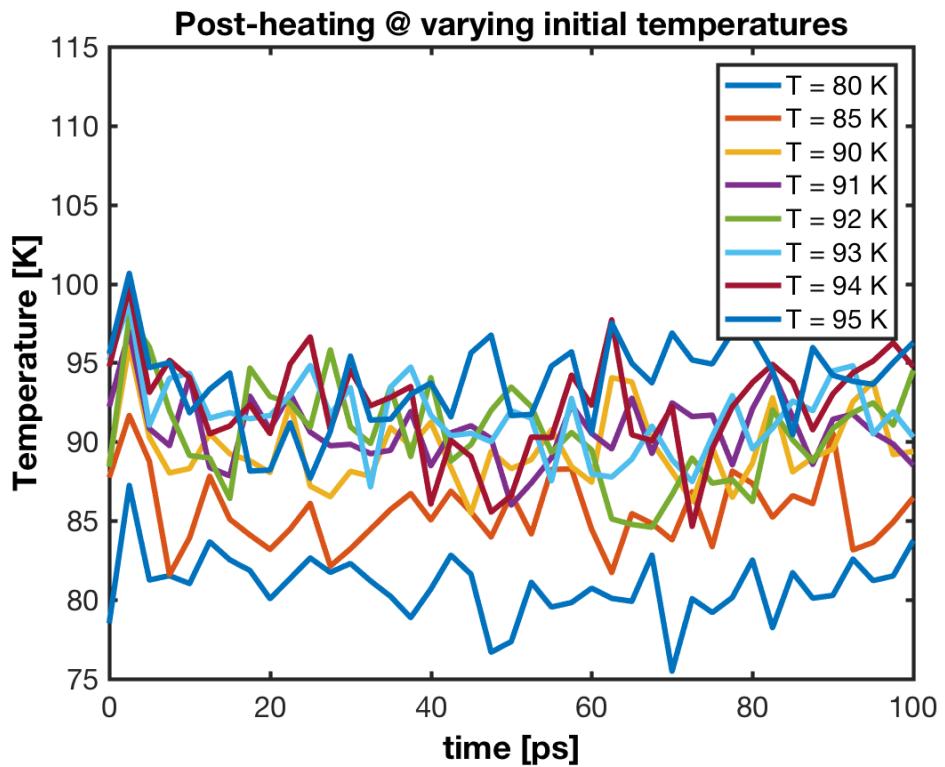


Figure 4: The temperature was tracked throughout the heating/melting simulation using the same relation for temperature as before, $T = \sum_{i=1}^{N_{atoms}} \frac{2E_{kinetic}}{3Nk_b}$ where k_b is Boltzmann's constant, and $N = 500$ is the total number of atoms in the system. Using this plot style it is difficult to determine a trend between initial and final temperatures around the melting point. However there is clear intersection of lines, suggesting a nonlinear trend. The following figure illustrated this better.

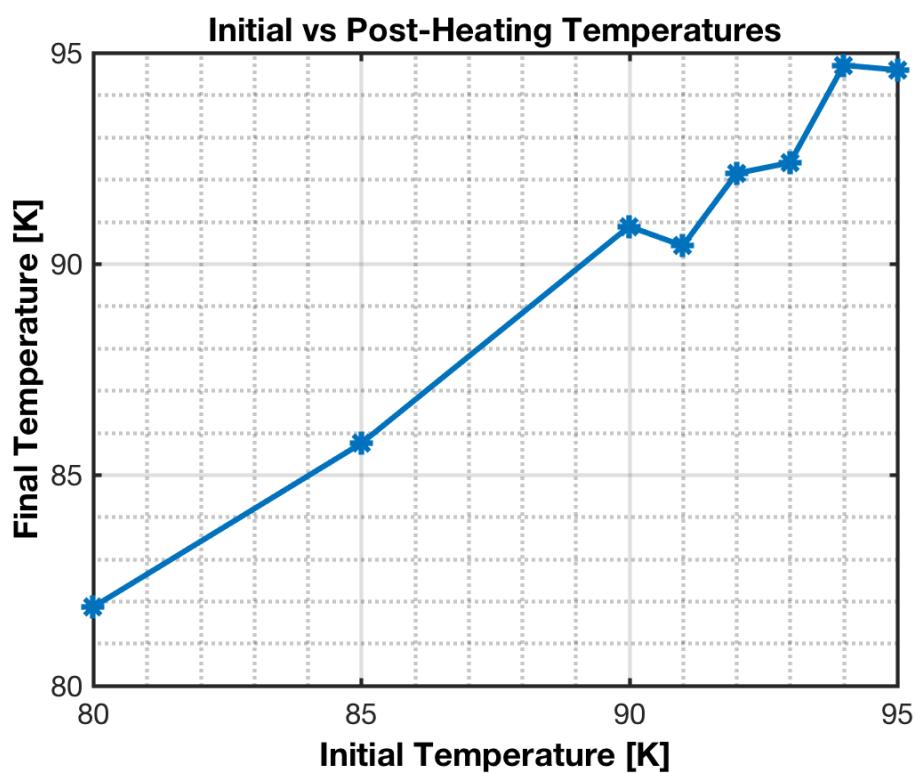


Figure 5: The initial (after 1 ps equilibration) temperature is compared with the trajectory-average temperature after the 100 ps heating/melting simulation. There appears a clear jump from $T=91$ K to $T=92$ K at which point melting occurred, and the data follows a new linear trend with a different slope.

3 Question 3

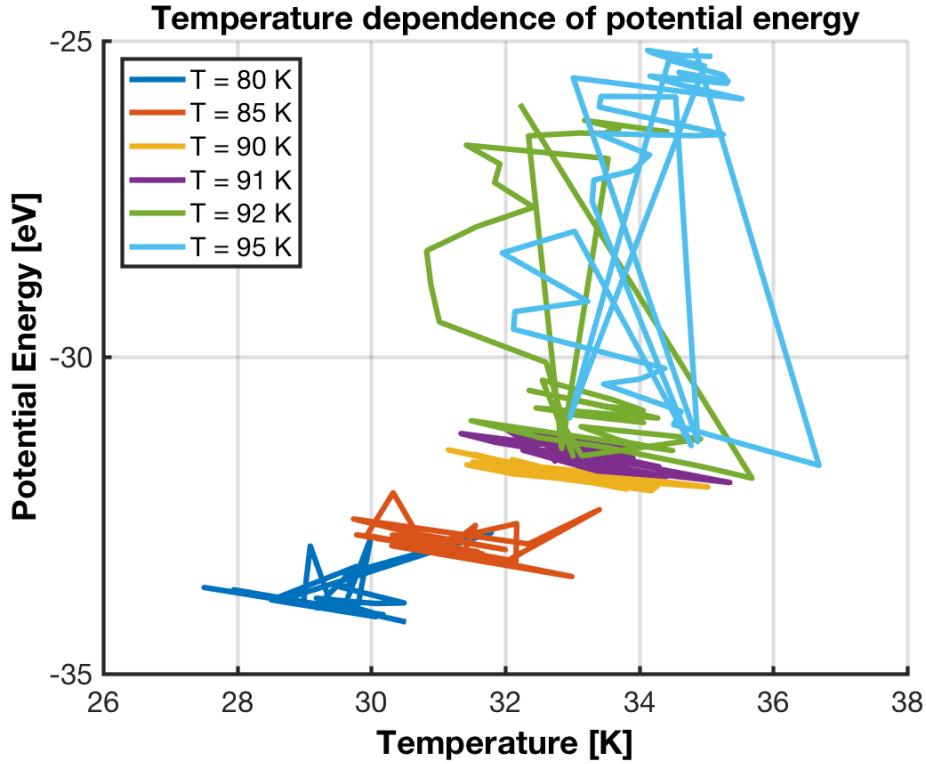


Figure 6: It is (roughly) possible to determine the temperature of the solid-liquid transition from this dependence. When the crystal is heated to sub-melting temperature, the potential energy vs temperature plot remains "compact" meaning that the curve does trace a noticeable area. When the crystal is heating up to and beyond its melting point, the potential energy vs temperature curve traces a more pronounced area. Furthermore, since the change in potential energy is equal to the work done by the system, it is clear from the plot that more work has occurred (melting). Integrating the areas of the traced curves of this plot is equivalent to the integral of work over time, which is power.

4 Question 4

The Maxwell-Boltzmann distribution defines the distribution of speeds for a gas at a certain temperature. From this distribution functions, the most probable speeds, the average speed, and the root-mean-square speed can all be derived. The Maxwell-Boltzmann distribution in terms of the scalar quantity speed c can be written as:

$$f(c) = 4\pi c^2 \left(\frac{m}{2\pi k_b T} \right)^{3/2} e^{-\frac{mc^2}{2k_b T}} \quad (2)$$

To visualize the distribution of velocities in our simulated system, a histogram is constructed with certain ranges of speeds "binned" into one value. Using 50 bins has shown to provide a detailed histogram. To get better statistics of the velocity distribution, data over multiple timesteps was considered in the histogram.

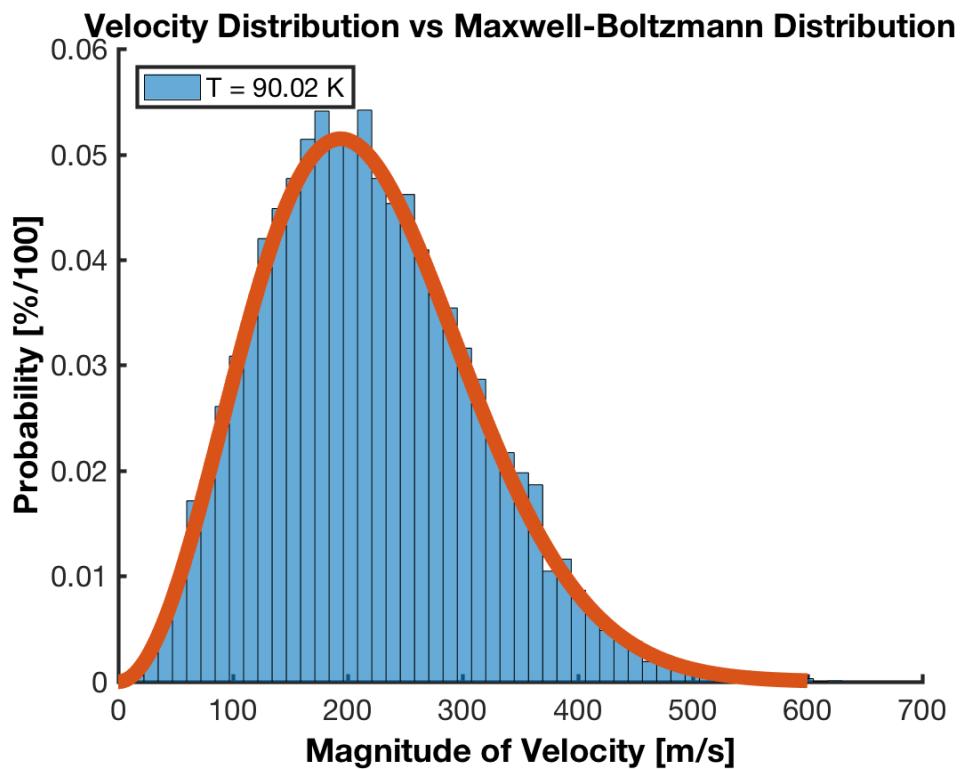


Figure 7: Comparing the velocity distribution of the simulation initially set to $T=92$ K, equilibrated to $T=89.5$ K, and final temperate of $T=91$ K. There is a close agreement between the distribution of speeds observed in the simulation and predicted by the Maxwell-Botlzmann distribution, which is surprising because the MB distribution is typically used to describe gases not solids or liquids.

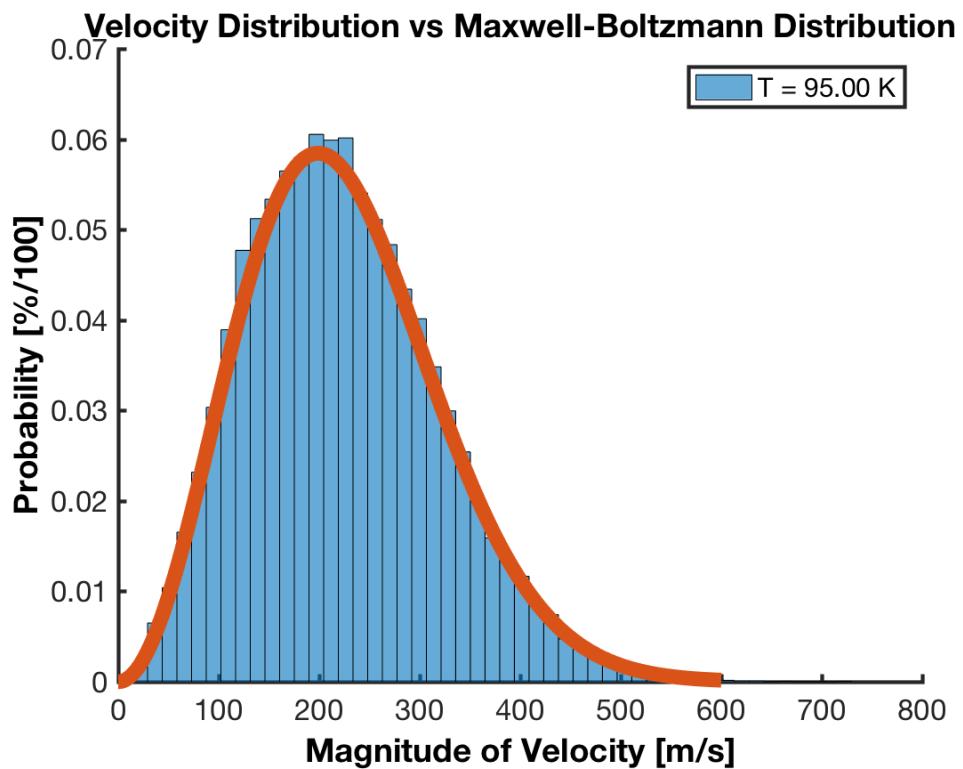


Figure 8: Comparing the velocity distribution of the simulation initially set to $T=95$ K, equilibrated to $T=93.5$ K, and final temperate of $T=94.75$ K. There is a close agreement between the distribution of speeds observed in the simulation and predicted by the Maxwell-Botlzmann distribution, which is surprising because the MB distribution is typically used to describe gases not solids or liquids.

5 Question 5

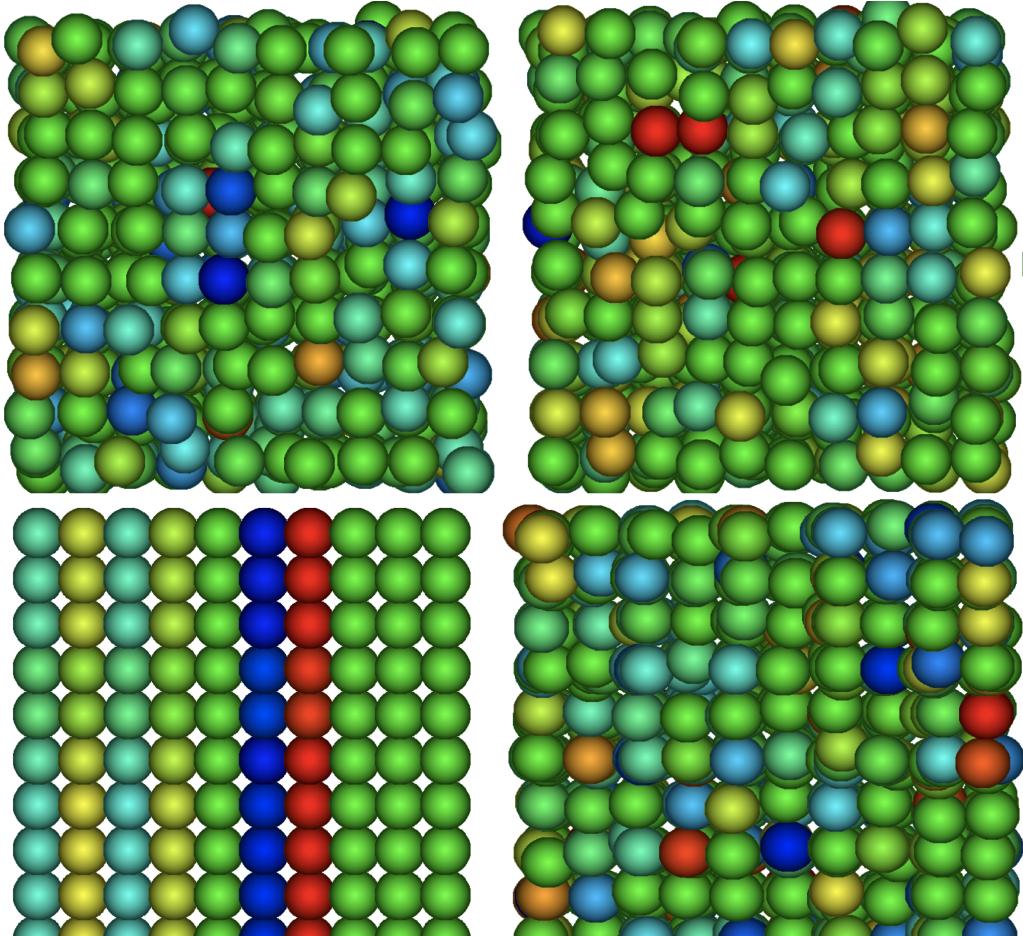


Figure 9: Top row shows the simulation from question 2 at $T = 91$ K with (left) initial and (right) final configurations. Bottom row shows the simulation from the previous HW#3Q6 with $T = 91$ K with (left) initial and (right) final configurations. Neither systems seem to be melted at $T = 91$ K, however the system with studied in this HW#4 shows a greater degree of disorder because the simulation was first equilibrated before simulation.

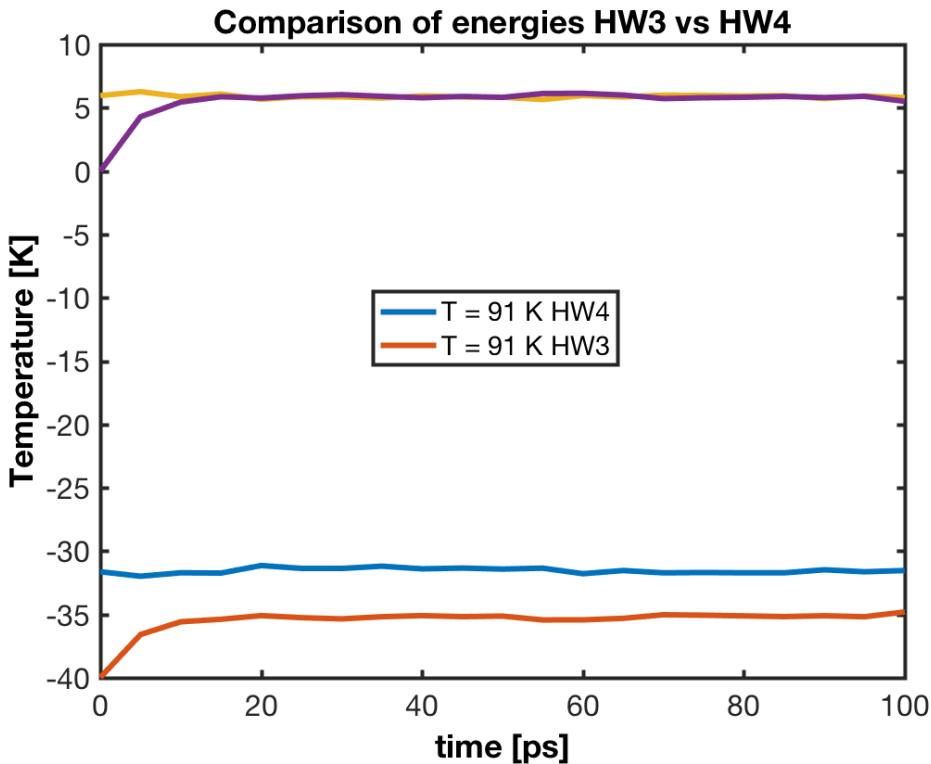


Figure 10: (Disregard the Y-Axis label, it should read Energy [eV]). Bottom two lines in the negative energies are the potential energies, with the more negative line equilibrating to -35 eV corresponding to the old system in HW#3 Q6 with free boundary conditions. The kinetic energies both equilibrate to +5eV. The magnitude of the potential energy in HW3 is ~ 3 eV bigger than in systems studied here. This is likely a feature of simulation size, as a smaller system with less particles will over-represent the long-range order of the potential (the cutoff has more effect with few particles compared to having many particles), resulting in a larger kinetic energy than observed in bigger systems.

6 References

1. The argon melting curve to very high pressures. C-S. Zha, R. Boehler, D. A. Young, M. Ross. *The Journal of Chemical Physics* 85, 1034 (1986)
2. Extended and accurate determination of the melting curves of argon, helium ice (H_2O), and hydrogen (H_2). F. Datchu, P. Laubeyre, R. LeToullec. *Physical Review B* 61, 6535 (2000)

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