1 Equation of State

The goal of this exercise is to study the properties of the Monte Carlo simulation of a classical Lennard-Jones liquid for different temperatures and densities.

1.1 Directory Structure

Files for this exercise are stored in the main directory ex1/. All data files are stored in the 'data' directory with the exact location depending on the density. There are several directories named 'length_XXX' that store the data for different box side lengths (and therefore different densities). All graphs are stored in the 'plots' directory

1.2 Energy vs Density

To begin the main 'metropolis' program was ran for several different densities by changing the side length of the box, storing the data each time in a separate directory.

We wanted to estimate the thermal expansivity at zero pressure with the data given. In order to do this we wanted to first visualise how the energy varies with density. This was done for each temperature (plots can be found in the relevant directories) and a few of theses plots are shown below.
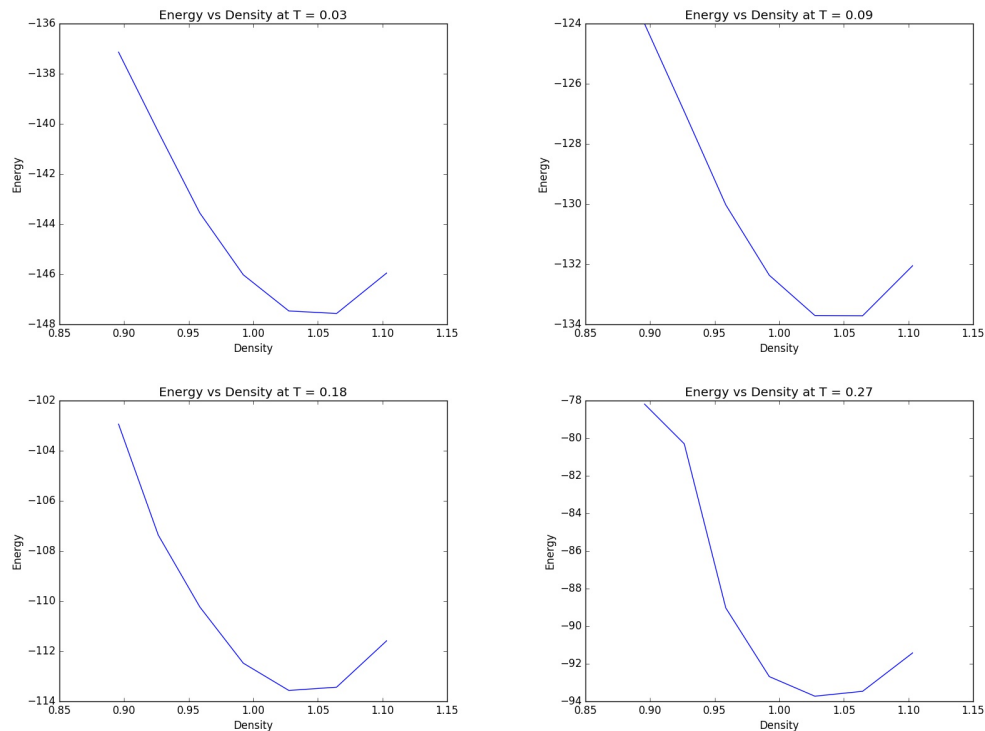

Figure 1: Relationship between energy and density for different temperatures

Although only a few points were taken for the previous plots, a general pattern can be seen in the parabolic shape of these graphs.

We are interested in the zero pressure point for this system. We know that pressure has the same units as $\frac{energy}{volume}$. Therefore, in order to get zero pressure we are interested in where the graph of energy vs volume has a slope zero. This is exactly the same point as where the slope of a graph of energy vs density goes to zero because for a mass $m = 1$ we just have that the graphs would have an flipped shape. Therefore, in order to calculate the thermal expansivity we wanted to find out how the minimum of the energy density graphs shifts with temperature. This was done using the program 'thermal_exp.py' which calculates the density at the minimum of the curve for each temperature and then uses the formula

$$\alpha_{therm} = \frac{1}{\rho}\frac{\Delta\rho}{\Delta T}$$

To calculate the thermal expansivity α_{therm}. In the simulation this was found to be given as

$$\alpha_{therm} = 1.178$$

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In order to test this we were able to use the program 'thermal_exp.py' to plot the volume vs temperature to see that the volume changes in a constant manner with the temperature at constant pressure, in agreement with Charles' Law.
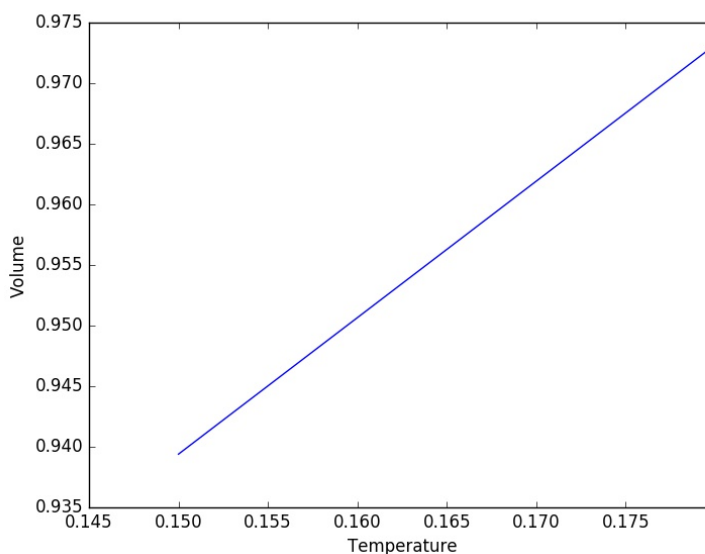

Figure 2: Relationship between volume and temperature for constant pressure

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1.3 Heat Capacity

In this section the goal is to study the properties of the heat capacity and compare results with what's expected from the Dulong-Petit Law.

Once the main program is ran, it records the temperatures and corresponding energies for each density ran for. If we are to look at the point of zero pressure it is very difficult to get enough data points with different temperatures for accurate conclusions to be drawn. Therefore, what was done was that the energy was plotted vs temperature to see what kind of relationship exist.
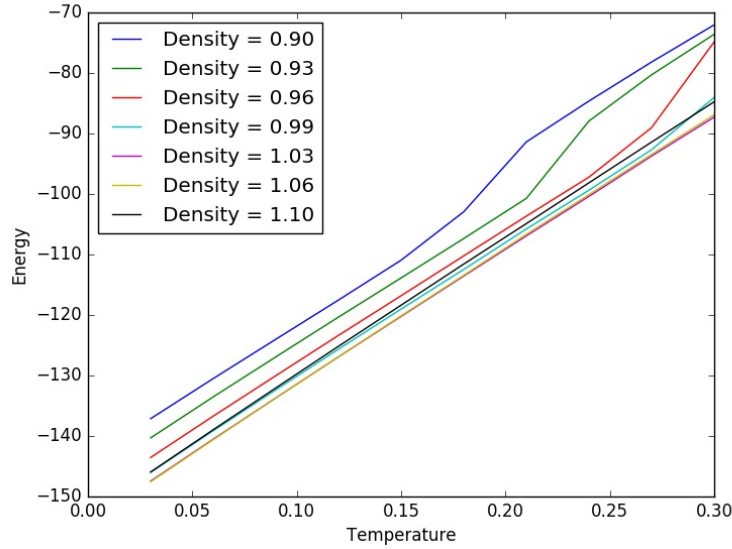

Figure 3: Relationship between energy and temperature for varying densities

For low temperatures (and thus low energies) the slope of the energy vs temperature curves look very similar for all densities. If we look back to *Figure 1* we can see that the zero pressure point occurs at the minimum energy in each case. Therefore we will take the heat capacity for zero pressure to be the slope of the above curves for low temperatures/energies because the slope appears to be constant for low temperatures. Therefore the heat capacity was taken to be an average of the slope for each density. Here the heap capacity has no units as the temperature. In all cases the number of particles was 80, therefore the average heat capacity per particle for the system was found to be

$$c_p = 3.11$$

However, the important part of this analysis is not the absolute value but the relationship with temperature. Because it is hard to calculate the heat capacity accurately at each temperature as we would only be using two points to calculate the slope, a more qualitative approach was taken. From the above plot it's clear that the slope of the graph is relatively unchanged for low temperatures in particular. This is equivalent to having a constant heat capacity, which is exactly what is expected from Dulong-Petit.

2 Pair Distribution Function

The goal of this exercise is to study the pair distribution and how it relates to the density and temperature of the system.

2.1 Directory Structure

The directory structure is the same as before but in the main directory ex2/. Again all data files are stores in the 'data' directory with the exact location depending on the density for which the simulation was ran for. There are several directories named 'length_XXX' that store the data for different box side lengths (and therefore different densities). All graphs are stored in the 'plots' directory

2.2 Pair Distribution

Here we want to plot the pair distribution function for the highest and lowest density, 1.1 and 0.9 in our case, for different temperatures. The program 'pair_dist.py' takes the pair distributions for each temperature, given the density and plots the results. Below are graphs for the high and low density.
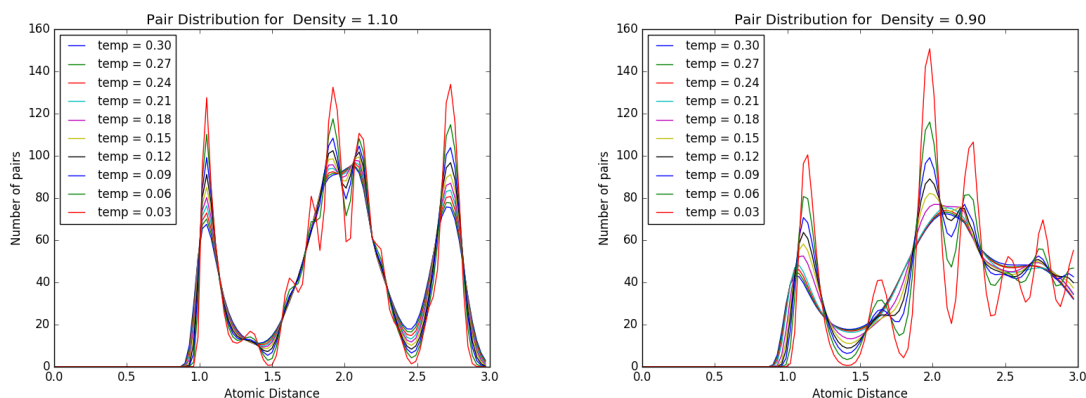

Figure 4: Pair distribution for high and low density limits used

There are a few things that can be noticed here. Firstly there are noticeable patterns in the atomic distances between particles. Although the pair distribution curves vary with temperature and density, the position of the largest spikes appear to be focused around the same distances. For low temperatures in particular the atoms appear to be quite confined to having a separation of roughly 1, 2 and 2.75. This suggests that there is an underlying structure the 80 particle system has..

Lowering the density causes the separation between atoms to become more 'relaxed' with the atoms being more evenly distributed for lower densities. This is what we would expect because decreasing the density causes the structure to become more liquid.

Changing the temperature had quite an interesting effect on the pair distribution curves. As can be seen above, decreasing the temperatures increases the number of 'spikes' in the curve meaning the particles become more restricted to having certain atomic separations. This is because for lower temperature the atoms have less energy and thus less freedom to move. In the low temperature limit used the structure exhibits the properties of a solid with particles confined to certain atomic distances. In the high temperature

limit however, the structure exhibits properties more like a liquid where the atoms are much more free to move. It is also important to note that this structural change with temperature appears to have a larger effect for lower densities. This may be because at lower densities there is less restriction on the positions of the particles and so the it requires less energy to form a liquid structure.