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Assignment: 3 (Isobaric-Isothermal Lennard Jones Fluid)

Introduction

This Assignment involved a Monte Carlo simulation of a Lennard-Jones fluid at constant Temperature and constant Applied Pressure. Initially, NVT ensemble methods were used and after getting the equilibrium configuration, NPT ensemble methods were used on the same configuration at different constant applied pressures where the initial Volume fraction was the same for all of them. After further equilibration, a sampling of states was done to obtain average measurable quantities like average Chemical Potential, average Volume Fraction and average Energy. All of these quantities were then plotted against the pressure.

Simulation parameters

- Number of Particles, $N_{part} = 10$
- Cubic Box Length, $L = 5$
- Initial Volume fraction, $\varphi = 33.33\%$
- Boltzmann constant times Temperature, $K_b T = 2$
- Radius of particles, $\sigma = 1$
- Lennard Jones $\epsilon = 1$
- Potential Cutoff at $3 \times \sigma$.

- Planck's constant, $h = 1$
- Particle mass, $m = 1$
- Thermal wavelength, $\Lambda = \frac{h}{\sqrt{2\pi m K_b T}} = 0.2821$
- Number of Iterations, 2000 for equilibration at constant volume, 8000 for equilibration at constant pressure, and 2000 further for sampling.
- Maximum particle displacement, ± 0.05
- Maximum logarithmic Volume change. ± 0.025
- Pressure values = 5, 10, 15, \dots , 295

Plots

0.1 NVT Equilibration step

Energy of System versus Iteration count data are plotted here.

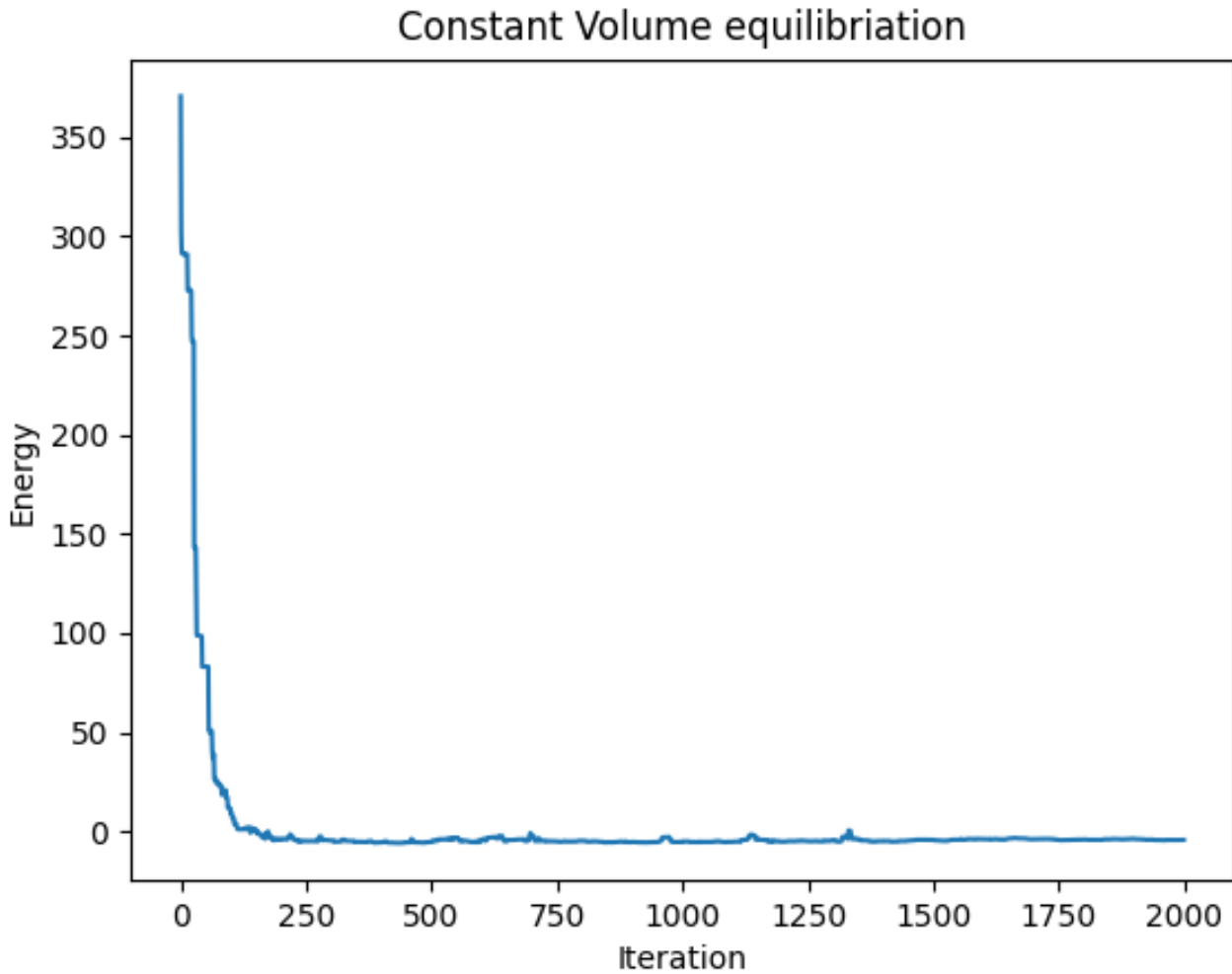


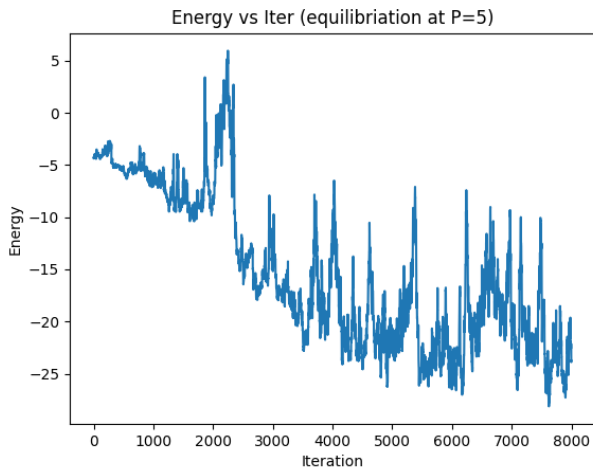
Figure 1: Energy vs Iteration

Remarks

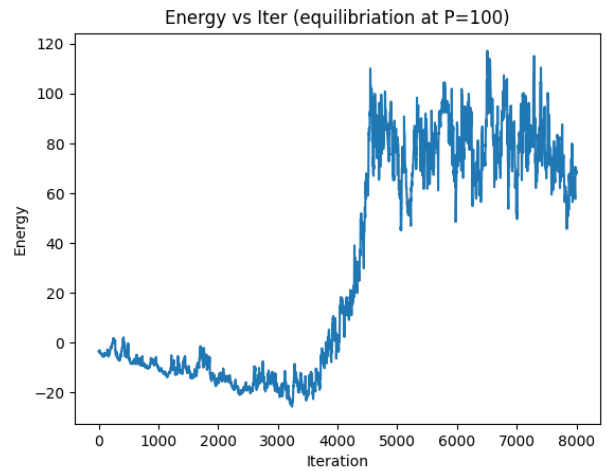
The initial configuration was made by uniform randomly packing the particles inside the box. As can be seen, after 1500 iterations the configuration has stabilized to the configuration corresponding to the ambient temperature, i.e. $K_b T = 2$.

0.2 NPT Equilibration step

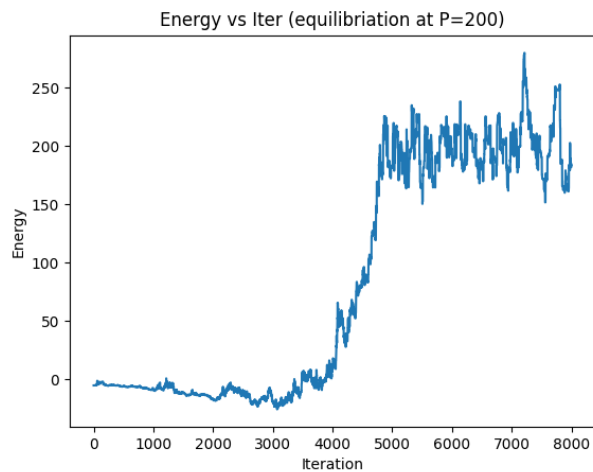
0.2.1 Energy vs Iterations



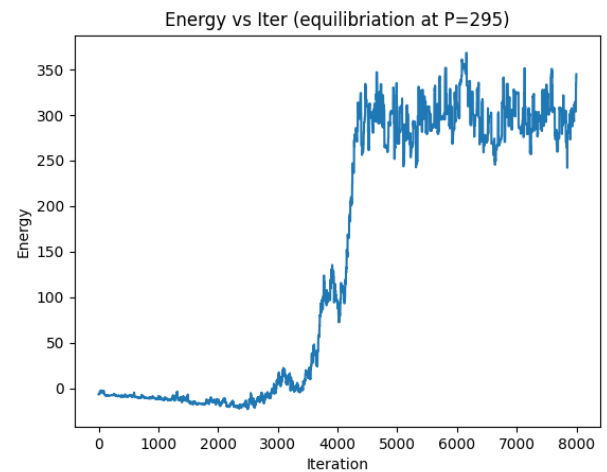
(a) $P = 5$



(b) $P = 100$



(c) $P = 200$



(d) $P = 295$

Figure 2: Energy vs Iterations

Remarks : All of these ensembles at different applied Pressures are initially the same previous NVT ensemble. As can be seen, the equilibrium average Energies of all these NPT ensembles, at different applied pressures, are different. Equilibrium average Energy can be seen to be increasing with the increasing applied Pressure. Refer to Figure 3

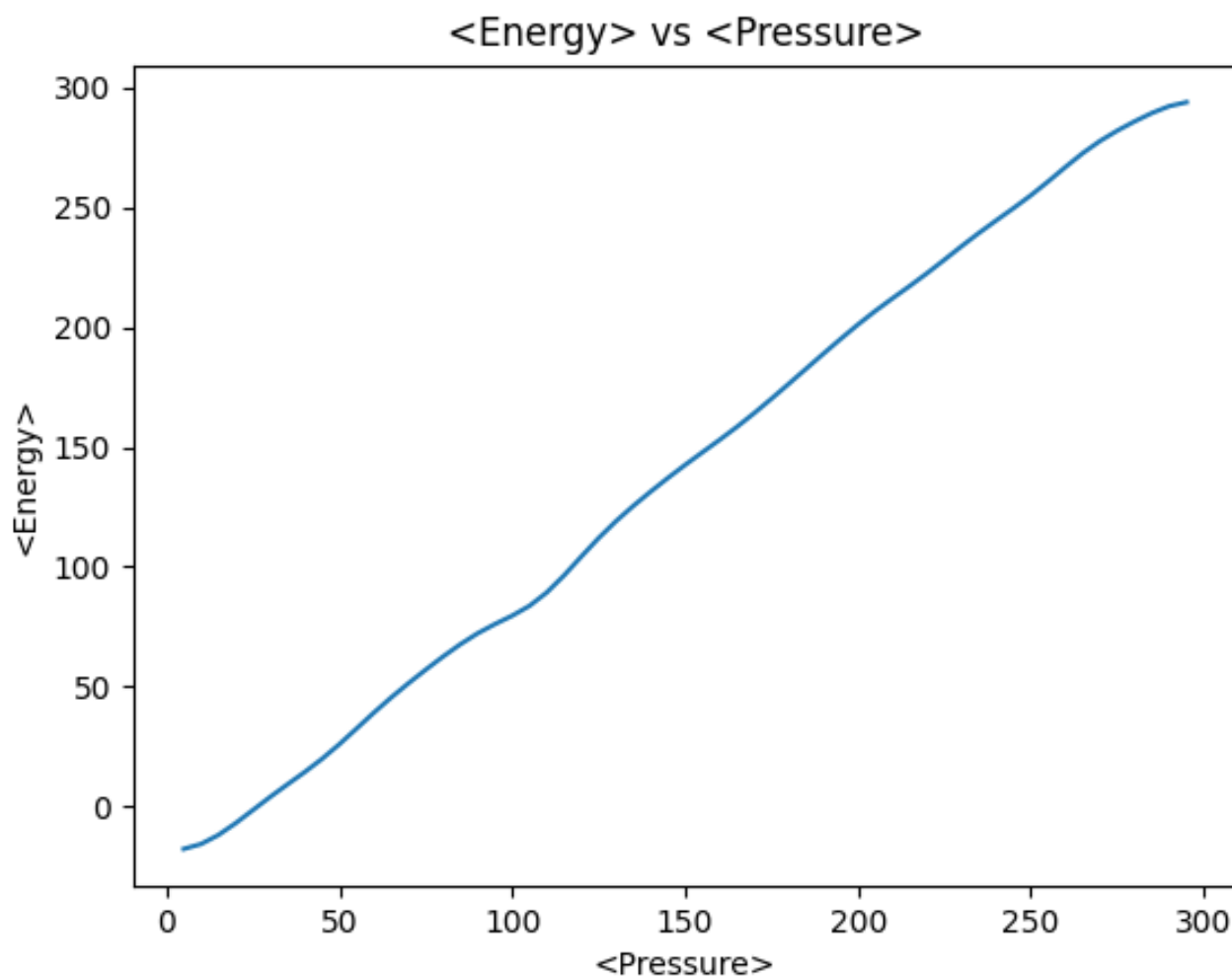
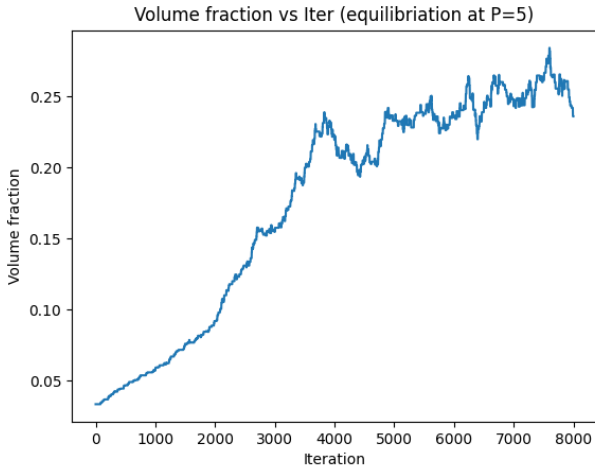


Figure 3: <Potential Energy> vs <Pressure>

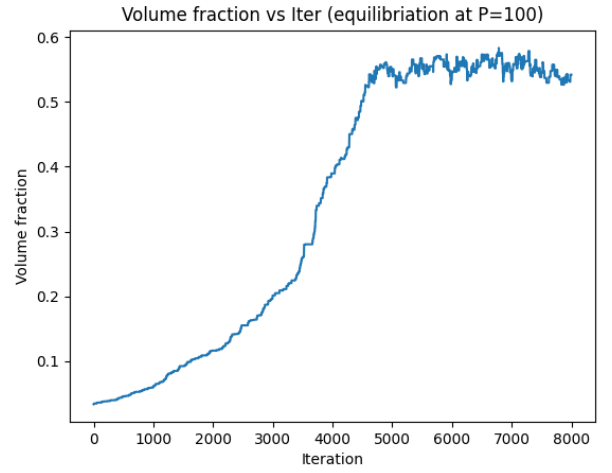
Note : Applied Pressure is equal to the average virial pressure values.

Remark : The relation between Applied Pressure and Average Potential Energy appears to be linear in nature with a positive slope throughout the seen variation.

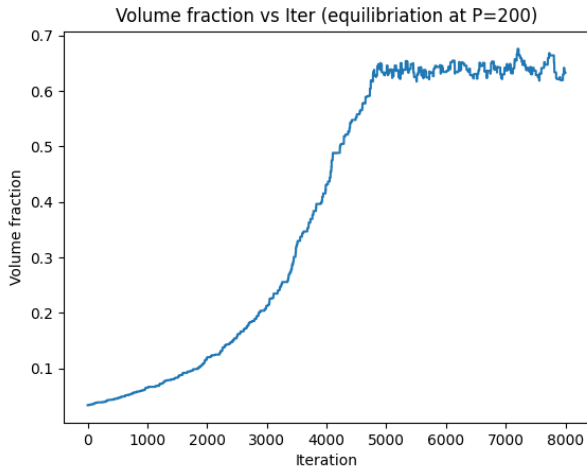
0.2.2 Volume Fraction vs Iteration



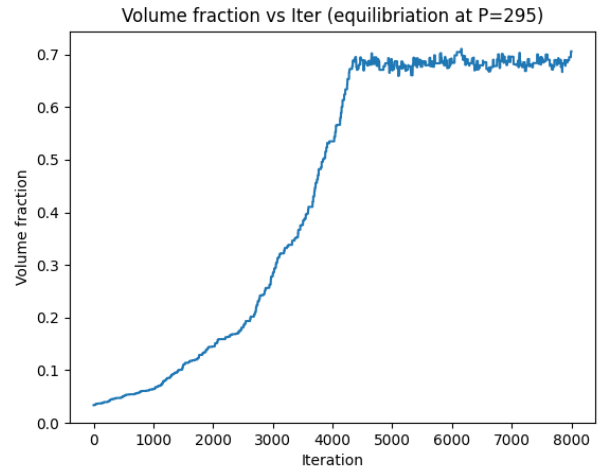
(a) $P = 5$



(b) $P = 100$



(c) $P = 200$



(d) $P = 295$

Figure 4: Volume Fraction vs Iterations

Remarks : All of these NPT ensembles start from the configuration with the same volume fraction, i.e. $\varphi = 33\%$. As can be seen, the Equilibrium average volume fraction increases with the increasing applied pressure. This is expected for a compressible fluid. Refer to Figure 5.

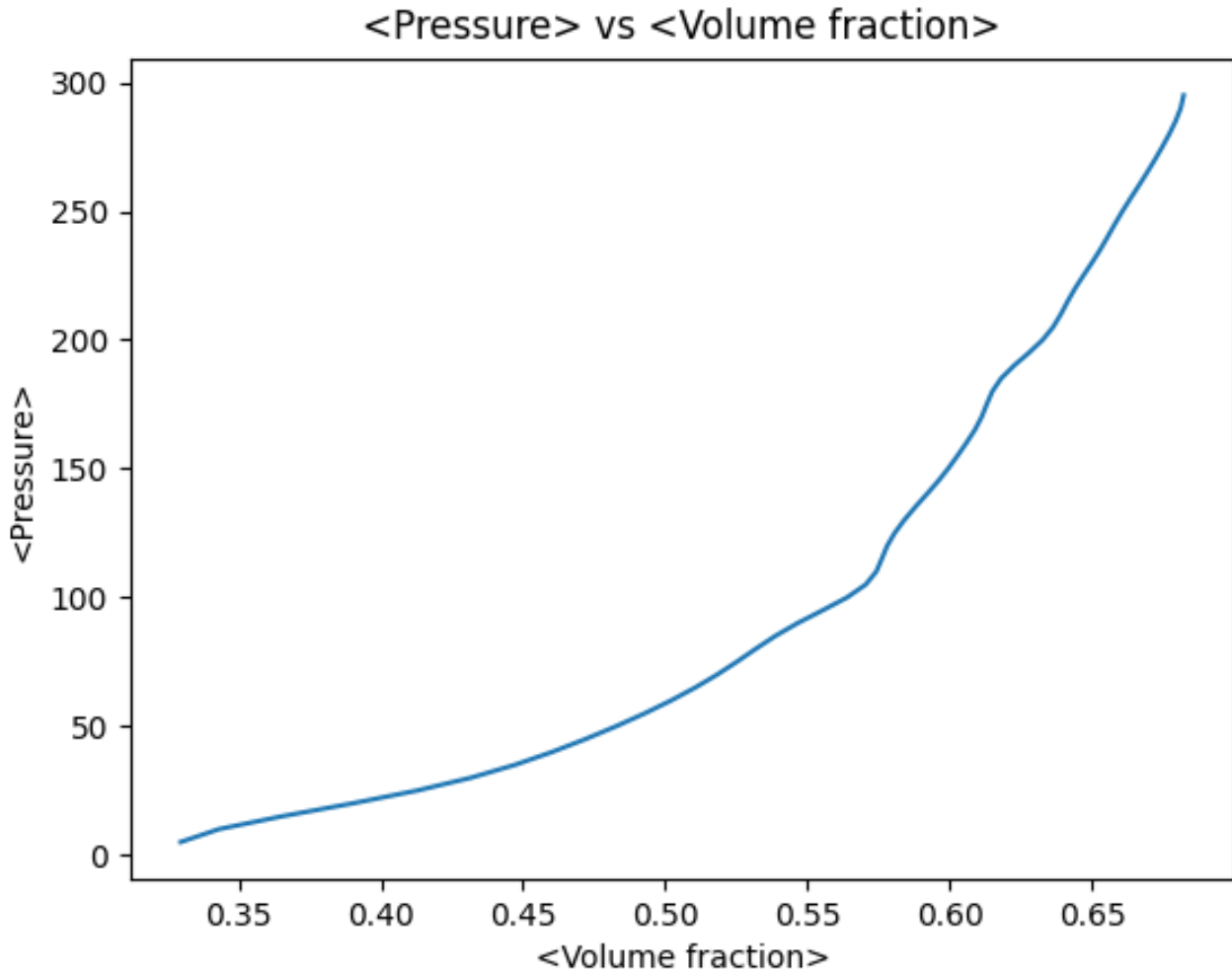


Figure 5: <Pressure> vs <Volume Fraction>

Remarks : The mean Volume fraction appears to be increasing with increasing pressure, but the relation appears to be linear in nature for small values of mean Volume fraction. This is because at low density, the potential between particles nearly vanishes, and so the fluid mimics the behaviour of an ideal gas for which volume fraction varies linearly with applied pressure. As the volume fraction increases further due to increasing applied pressure, at high applied pressure, the inter-particle potential becomes significant, and the behaviour deviates from ideal gas behaviour and tends to the incompressibility regime.

0.3 Potential Energy vs Volume Fraction

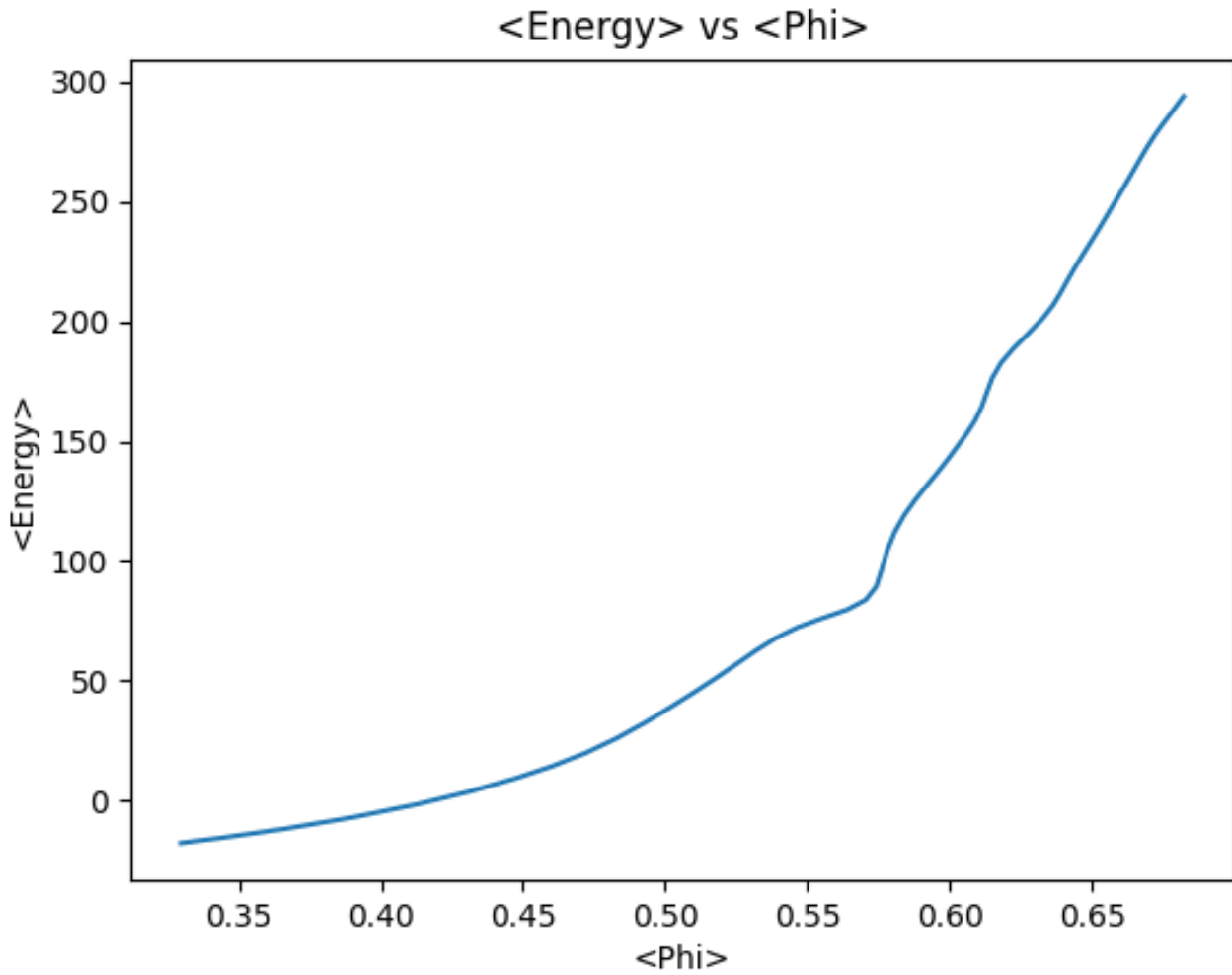


Figure 6: $\langle \text{Potential Energy} \rangle$ vs $\langle \text{Volume Fraction} \rangle$

Remarks : The relation between mean Potential Energy and mean Volume fraction resembles that of relation between applied pressure and mean volume fraction. This can be attributed to the observation that mean potential energy increases linearly with applied pressure.

0.4 Chemical Potential vs Applied Pressure

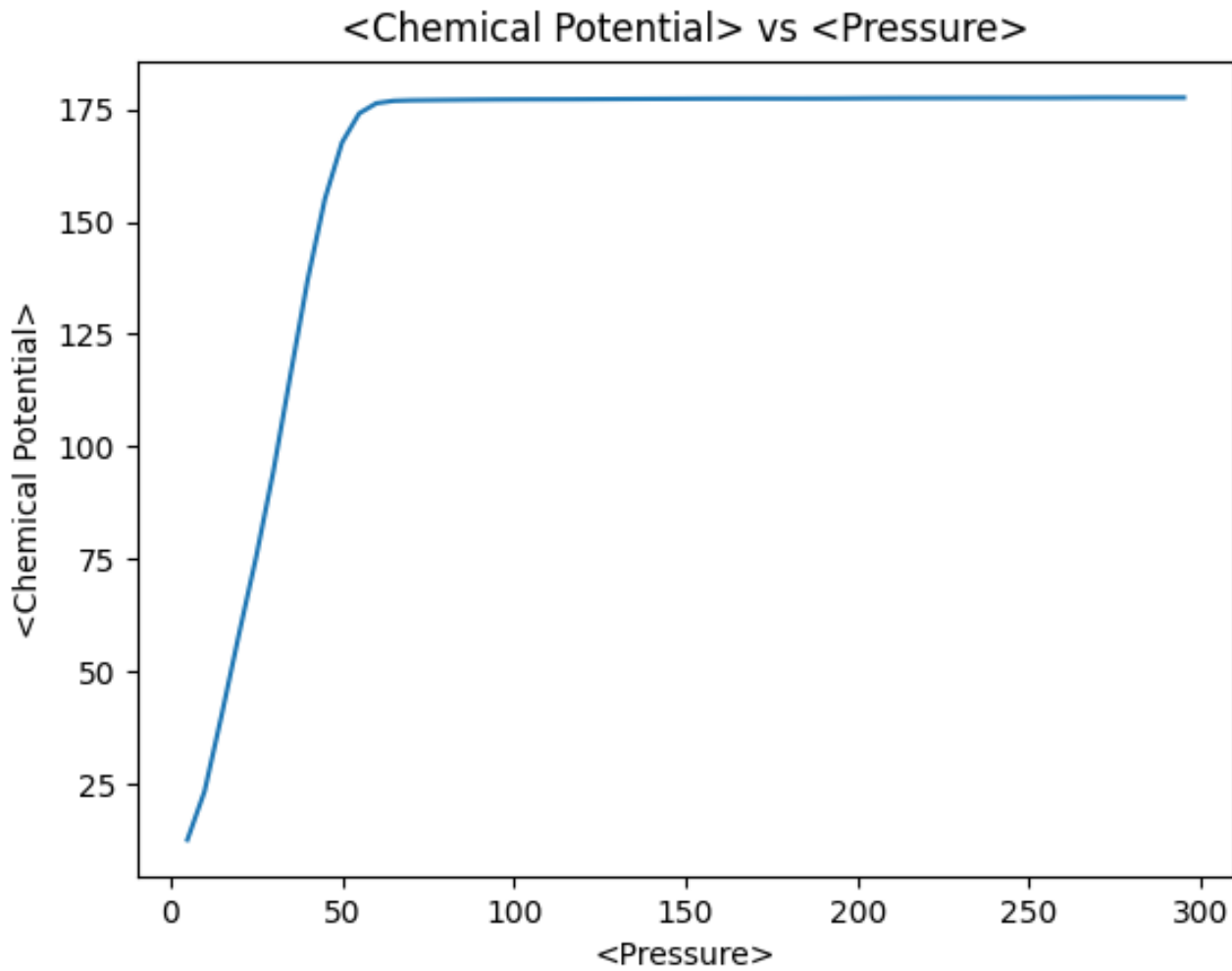


Figure 7: <Chemical Potential> vs <Pressure>

Remarks : For small values of pressure, the relation appears to be nearly linear with a positive slope. But around $P = 50 - 75$, there seems to be a discontinuity in relation. At the same pressure values, as can be seen in Figure 5, the applied pressure and mean Volume fraction relation starts deviating from the linear nature, and the inter-particle interactions start becoming significant. This thus appears to be a phase change.

0.5 Chemical Potential vs Volume Fraction

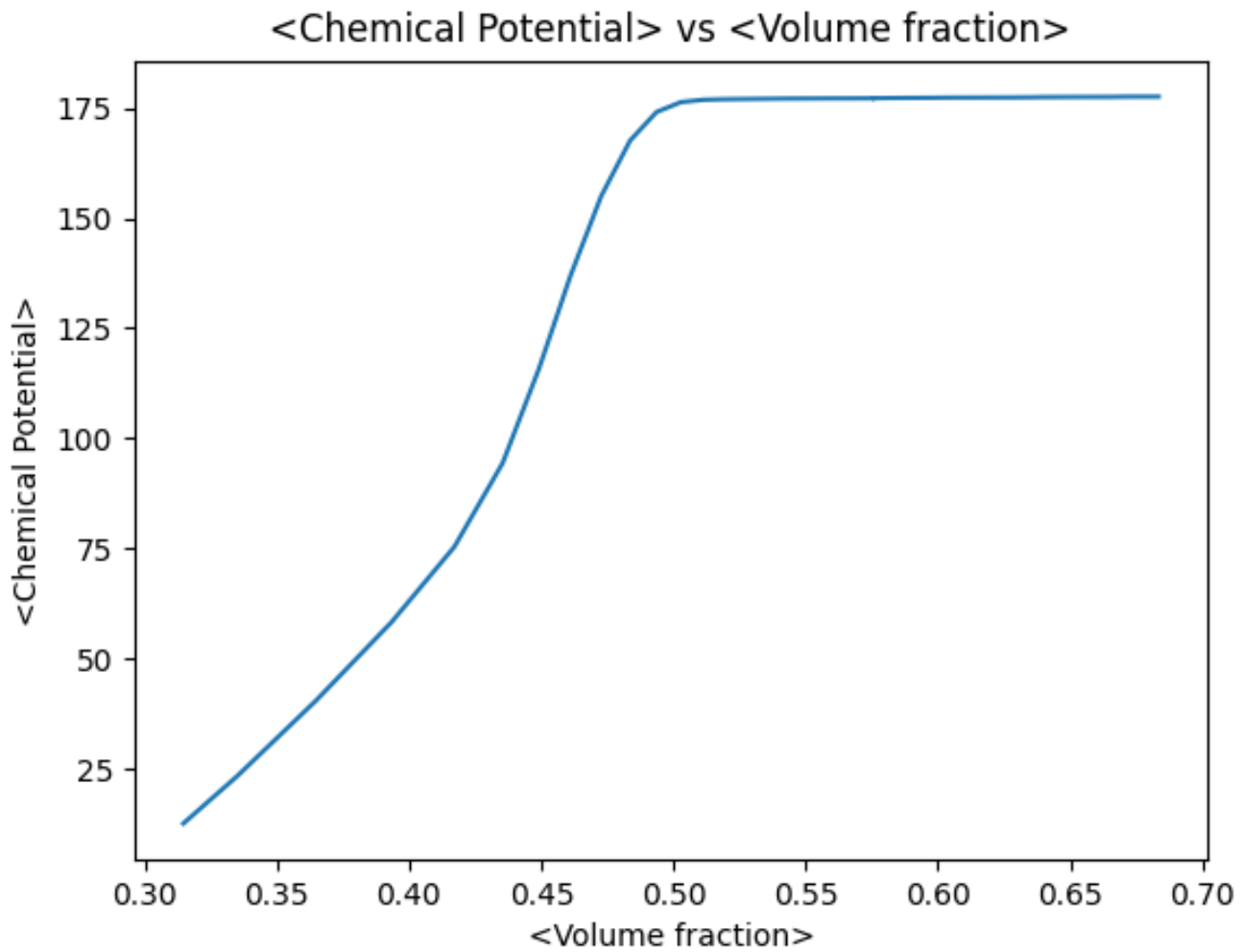


Figure 8: <Chemical Potential> vs <Volume Fraction>

Remarks : Throughout the variation, the mean chemical potential increases with the mean volume fraction. For low values of volume fraction, the linear nature of the relation is apparent, then as volume fraction increases, linearity is lost, and after that, a discontinuity is seen, which happens to be the same point of discontinuity as described in the remark of Figure 7.

Code

For the code, visit [here](#)

For plots at all specified temperature values, click [here](#)