

# Monte Carlo Simulations of a Lennard-Jones System

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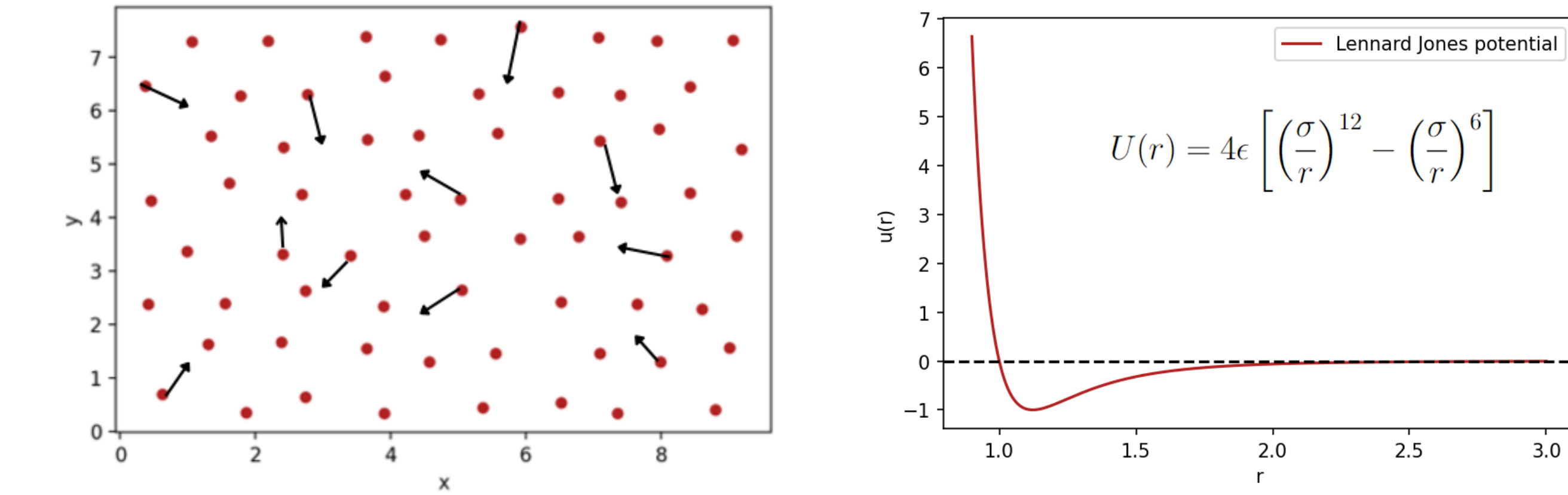
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## Introduction

Given our understanding of the interaction between two particles, we want to extend it and understand the behavior of an interacting system of many particles and extract thermodynamic information regarding its phases, potential energy, pressure, and more. One approach to do this is by solving the equations of motion of each particle (accounting for forces due to all other particles) and combining the results, which is known as *molecular dynamics*. However, this method requires substantial computational resources, and thus alternative approaches may be explored. Here, we implement a statistical mechanical approach of averaging over multiple microstates of the system, chosen from the Boltzmann probability distribution, and thus calculating the relevant thermodynamic quantities. Figure 1(a) below shows a snapshot of the system of interacting particles.



(a) System of many particles with pairwise inter-particle interactions, interacting using the Lennard-Jones potential. In this project, we use 64 particles for all our analysis. (b) Mathematical expression and plot of the Lennard-Jones potential. There is a clear optimum inter-particle distance, making it the lowest energy configuration, and thus be most stable at that distance.

Figure 1. (a) General snapshot of the modeled system of particles and (b) The Lennard-Jones Potential

As shown by Figure 1(b) above, a realistic potential to model the interaction between a pair of particles was proposed by British physicist John Lennard-Jones in 1931, which is motivated by the following two features:

1. It is weakly attractive at long distances (Van der Waals forces)
2. It is strongly repulsive at very short distances (Pauli exclusion or electrostatic repulsion)

Considering these two empirical deductions, the Lennard-Jones potential is thus given by Figure 1(b). Here,  $r$  is the inter-particle distance,  $\epsilon$  is the depth of the potential well, and  $\sigma$  is the 'safe' distance at which the potential stops acting. Calculated pairwise and summed up to compute the total potential energy of our system of particles.

## The Radial Distribution Function (RDF)

The RDF  $g(r)$  is a measure of the correlation of particles' positions due to the inter-particle interactions. It gives us a measure of the probability of finding a particle between a distance  $r + dr$  and  $r$  from any given particle. Additionally,  $g(r)$  is also the ratio of the local to the global density of particles. Due to these properties, the RDF of a system helps us to distinguish between various thermodynamic phases of the system, and calculate the values of thermodynamic quantities like pressure and potential energy.

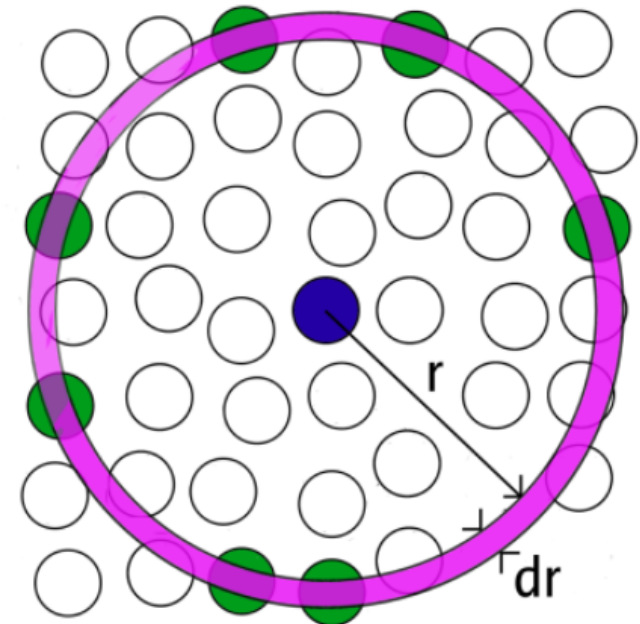


Figure 2. Schematic image to understand the concept of RDF.  $g(r)$  gives us measure of the probability of finding a particle in the purple shell.

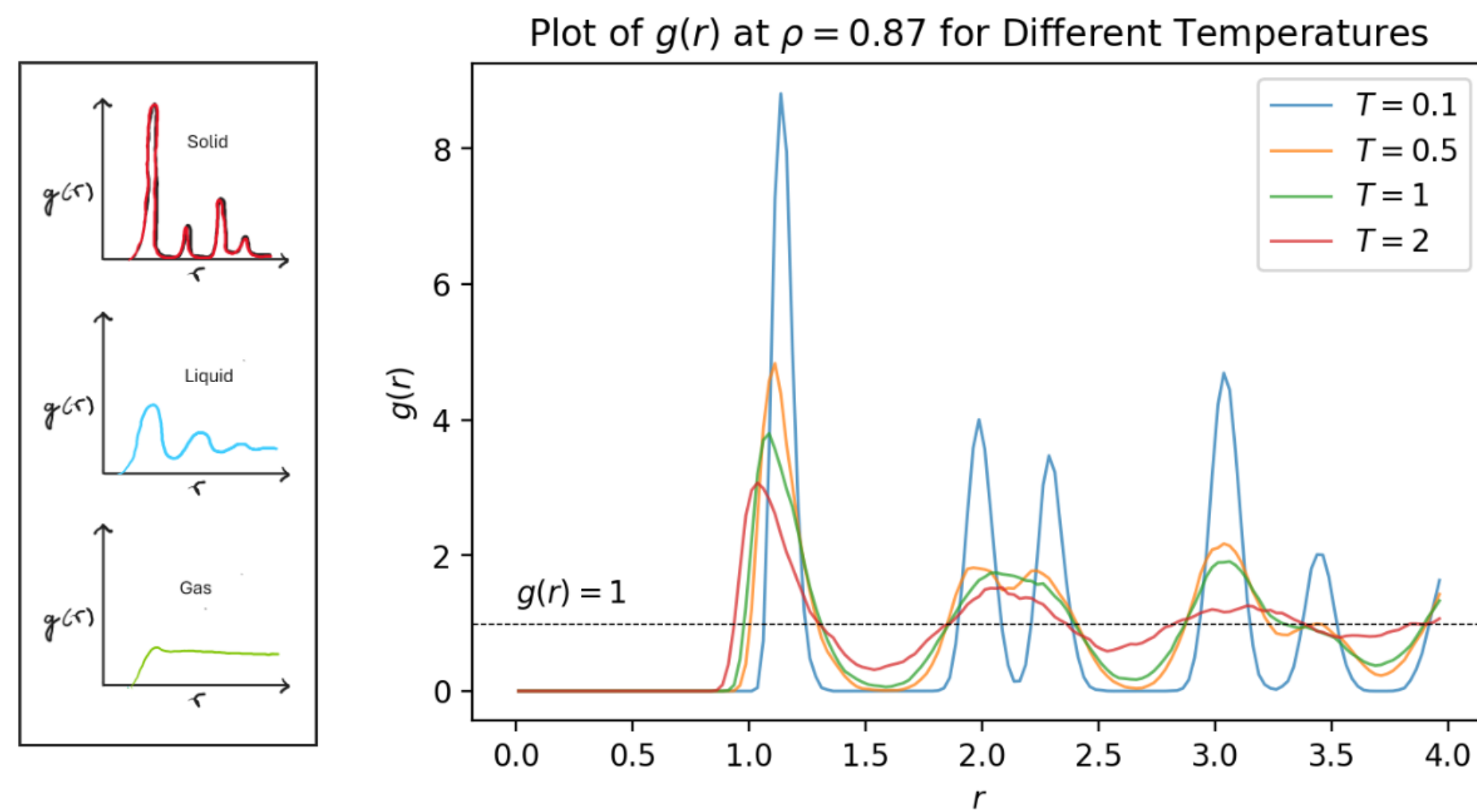


Figure 3. The computed radial distribution function for  $\rho = 0.87$  and  $T = 0.1, 0.5, 1, 2$ . Temperature is measured in units of  $\epsilon/k$ , and  $\rho$  is the number density of the system. We can see three distinct kinds of behaviors of the RDF in the above graph. The blue curve has the sharpest, most localized peaks, signifying a very high regularity. This is at the lowest temperature and thus represents the solid phase. The orange and green curves show slightly more spread out and blunt peaks, signifying a decrease in the regularity of the arrangement of particles at slightly higher temperatures, representing the liquid phase. Finally, the red curve shows extremely blunt and spread-out peaks at a substantially higher temperature, and  $g(r) \rightarrow 1$  as  $r \rightarrow \infty$ , representing the gaseous phase. The schematic curves on the left show us the ideal RDF curves for all three phases, and we verify on the right that our system shows all three behaviors at different temperatures.

## Monte Carlo (MC) Methods

We average over all the microstates of our system to compute the required thermodynamic quantities. However, a large chunk of these microstates do not contribute significantly to the average, and thus it is more efficient to choose microstates randomly from the Boltzmann distribution and only average over those microstates. Ergodicity is assumed: given enough time, the system will eventually enter every microstate. Thus, we implement a particular kind of Monte Carlo method, known as the *Metropolis Algorithm*, to update the positions of all particles in a single MC sweep. The exact algorithmic steps used are as follows -

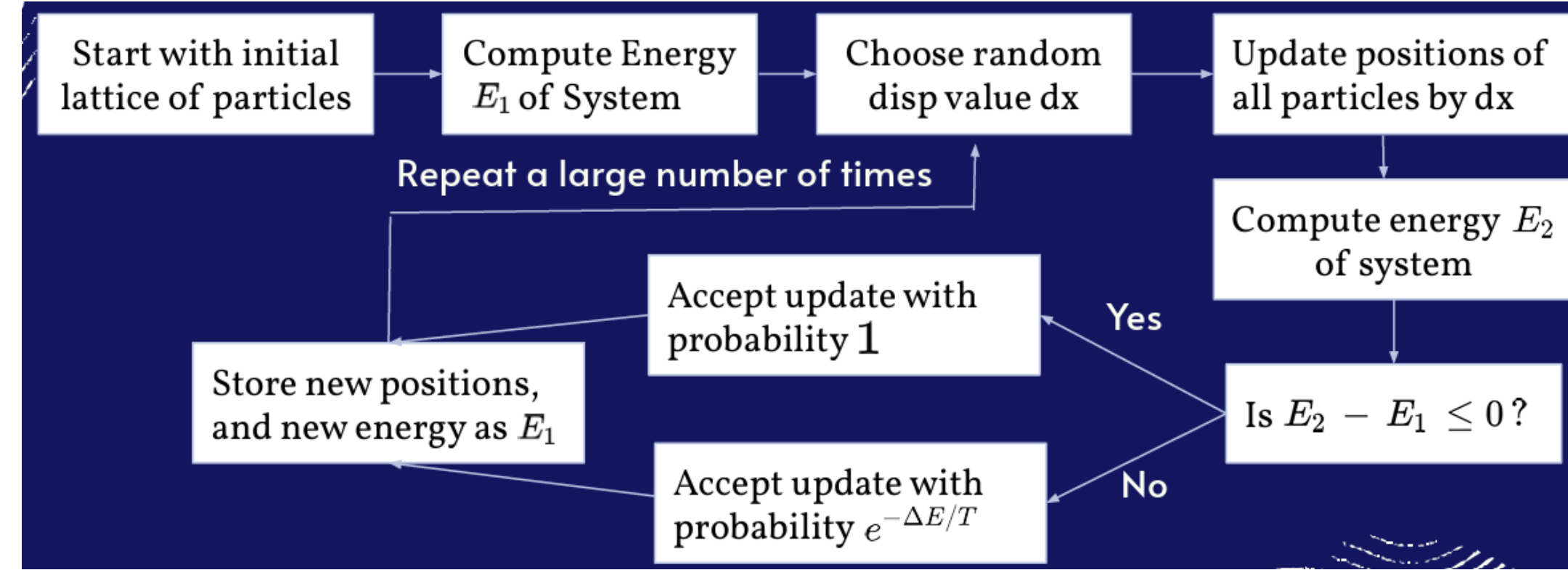


Figure 4. Metropolis Algorithm used to sample microstates from the Boltzmann distribution and update the positions of all particles in every MC sweep. Starting with a randomly disturbed triangular lattice, we simulated 10,000 Monte Carlo sweeps for the system.

## Computing Thermodynamic Quantities

We used the radial distribution function to compute the potential energy and pressure.

Mean potential energy per particle ( $U/N$ ) and mean pressure per particle ( $P/N$ ):

$$\frac{U}{N} = \frac{\rho}{2} \int g(r) u(r) dr^d \quad (1)$$

$$\frac{PV}{NT} = 1 - \frac{\rho}{2Td} \int g(r) \frac{du(r)}{dr} dr^d \quad (2)$$

$V$ : volume,  $T$ : temperature,  $\rho$ : number density,  $g(r)$ : radial distribution function,  $u(r)$ : Lennard-Jones potential between two particles,  $d$ : no. of dimensions

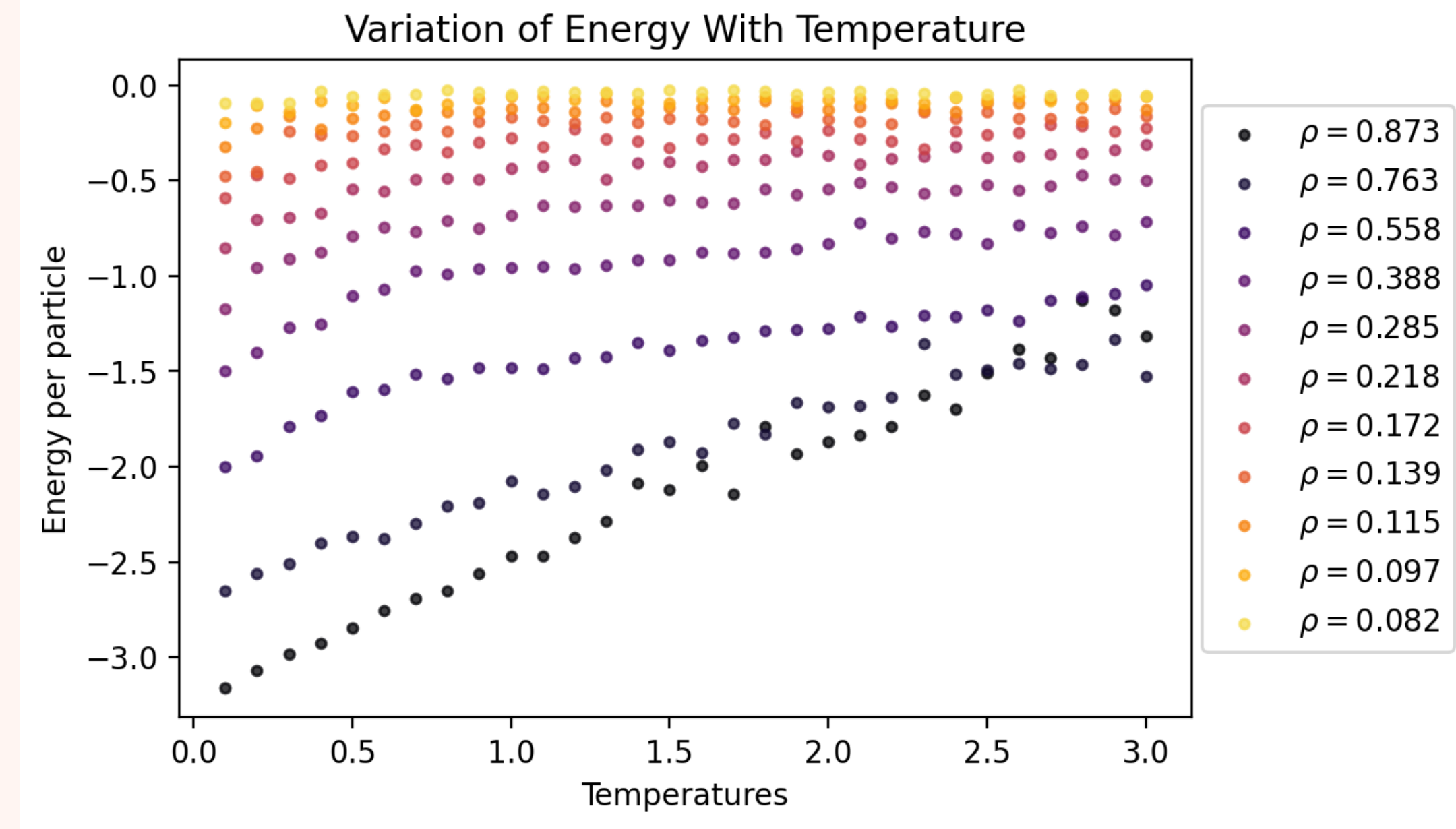


Figure 5.  $U/N$  vs  $T$  for various densities.  $U$  decreases as temperature increases and density decreases, which is the expected trend since the lower density conditions correspond to weaker interactions.

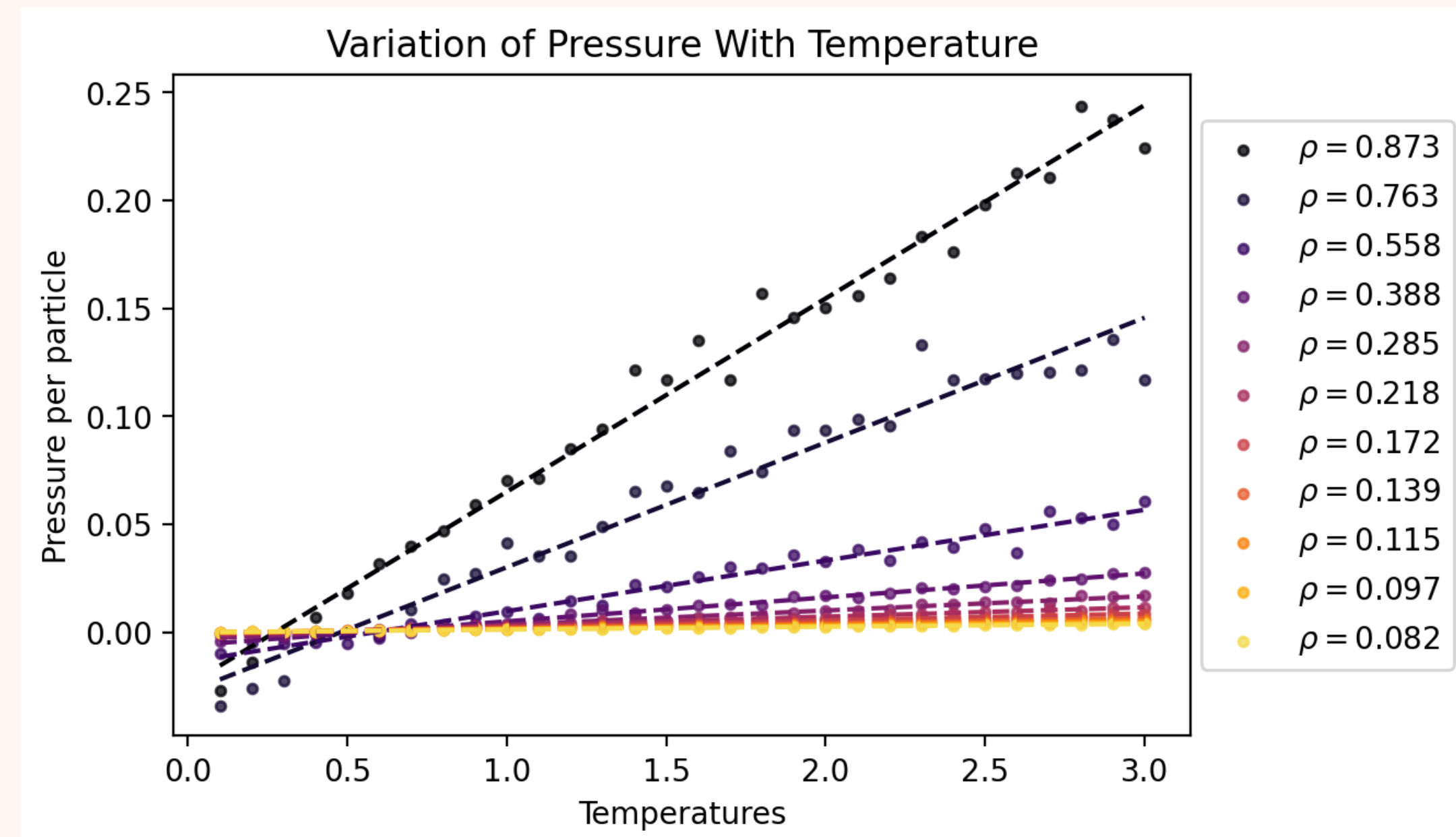


Figure 6.  $P/N$  vs  $T$  for various densities.  $P$  increases linearly with temperature, and the slope of this graph increases as density increases.

## Exploring Connections to Van der Waals Equation of State

The *Van der Waals* equation is an equation of state that extends the ideal gas equation by assuming that each particle occupies a volume  $b$  and experiences some interaction with other particles, the strength of which is characterized by the parameter  $a$ . Thus, we investigate if our Lennard-Jones system can display Van der Waal gas-like behavior, and if yes, we also attempt to find the relevant density regimes.

$$(P + a\rho^2) \left( \frac{1}{\rho} - b \right) = T \Rightarrow \frac{P}{N} = \frac{T}{N \left( \frac{1}{\rho} - b \right)} - \frac{a}{N\rho^2} \quad (3)$$

$P$ : pressure,  $T$ : temperature,  $\rho$ : number density,  $a$  and  $b$ : Van der Waals constants. This tells us that at a given density, the graph of pressure against temperature should be a straight line. If the graph of  $P$  against  $T$  has slope  $m_{PT}$  and y-intercept  $c_{PT}$ , then we have

$$\frac{1}{m_{PT}} = \frac{N}{\rho} - Nb, \quad c_{PT} = -\frac{a}{N\rho^2} \quad (4)$$

We observe that for  $\rho = 1/b$ ,  $m_{PT}$  is undefined. We call this density the critical density  $\rho_c$ .

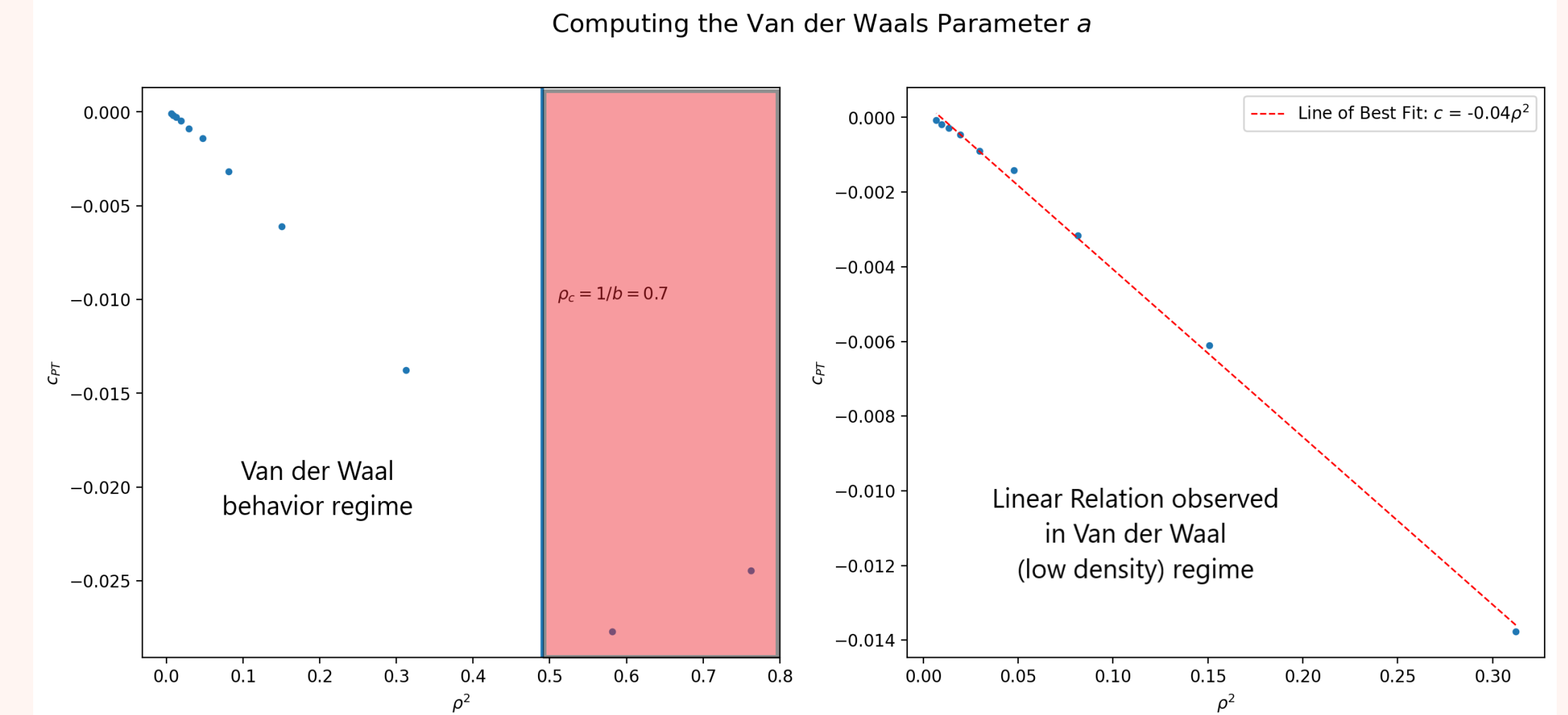


Figure 7. Plot of  $c_{PT}$  against  $\rho^2$ . The graph on the right shows only the linear part of the graph on the left, and the slope of this graph is used to calculate  $a$ .

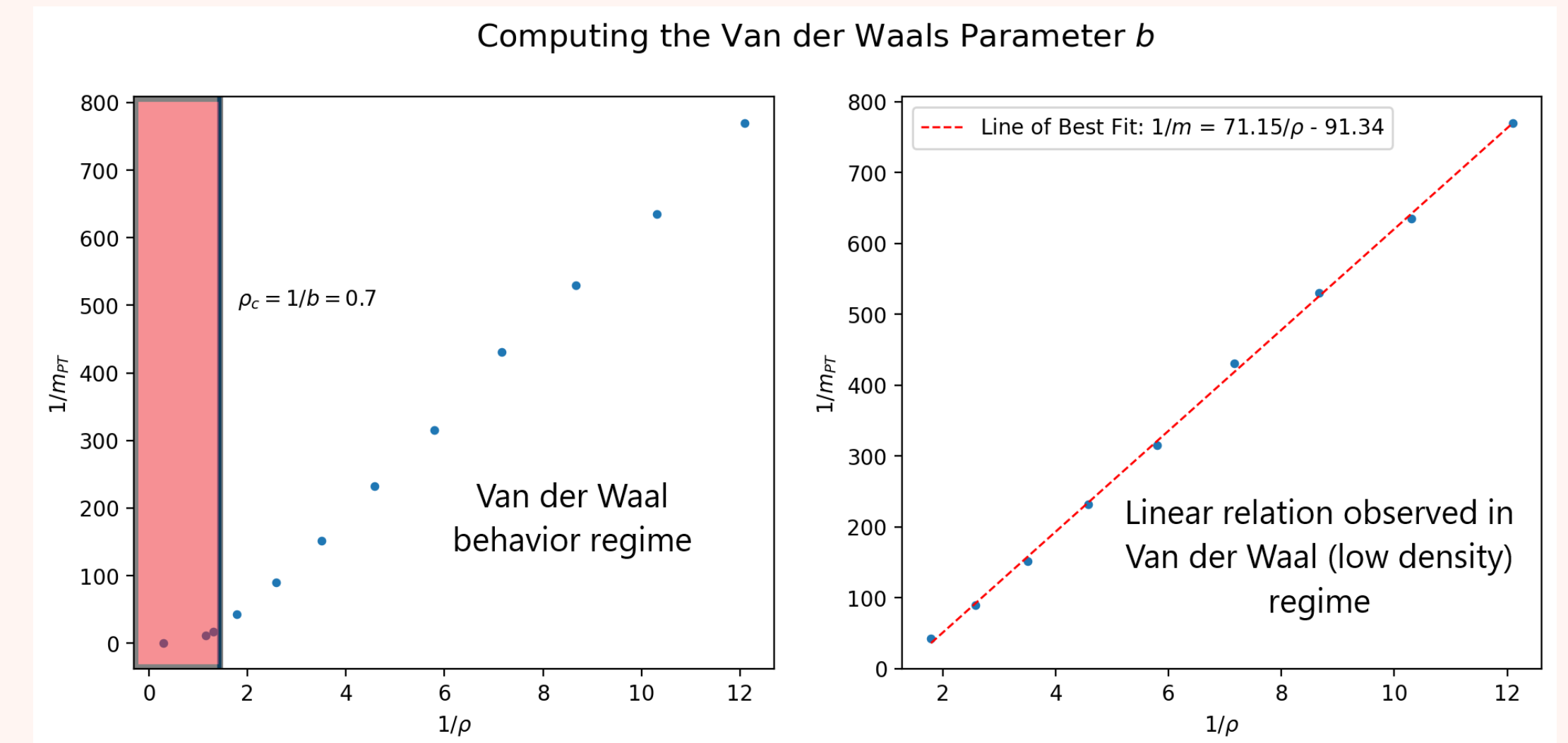


Figure 8. Plot of  $1/m_{PT}$  against  $1/\rho$ . The graph on the right shows only the linear part of the graph on the left, and the y-intercept of this graph is used to calculate  $b$ .

$$a = 2.87 \pm 0.36, \quad b = 1.43 \pm 0.09, \quad \rho_c = 1/b = 0.70 \pm 0.09 \quad (5)$$

The vertical lines in the plots are plotted at this value of  $\rho_c$ , and we see that the Van der Waals equation of state seems to be valid for densities lower than  $\rho_c$ . Physically, we can explain this by observing that  $\rho_c$  is the value of the density at which the system is solid, and the Van der Waals equation of state only describes a fluid. The error bounds have been obtained from linear regression, and thus bear scope for a much more detailed analysis.

## Future Work

We computed the chemical potential ( $\mu$ ) of the system using the **Widom test-particle** insertion method, and its variation with temperature for a few density values.

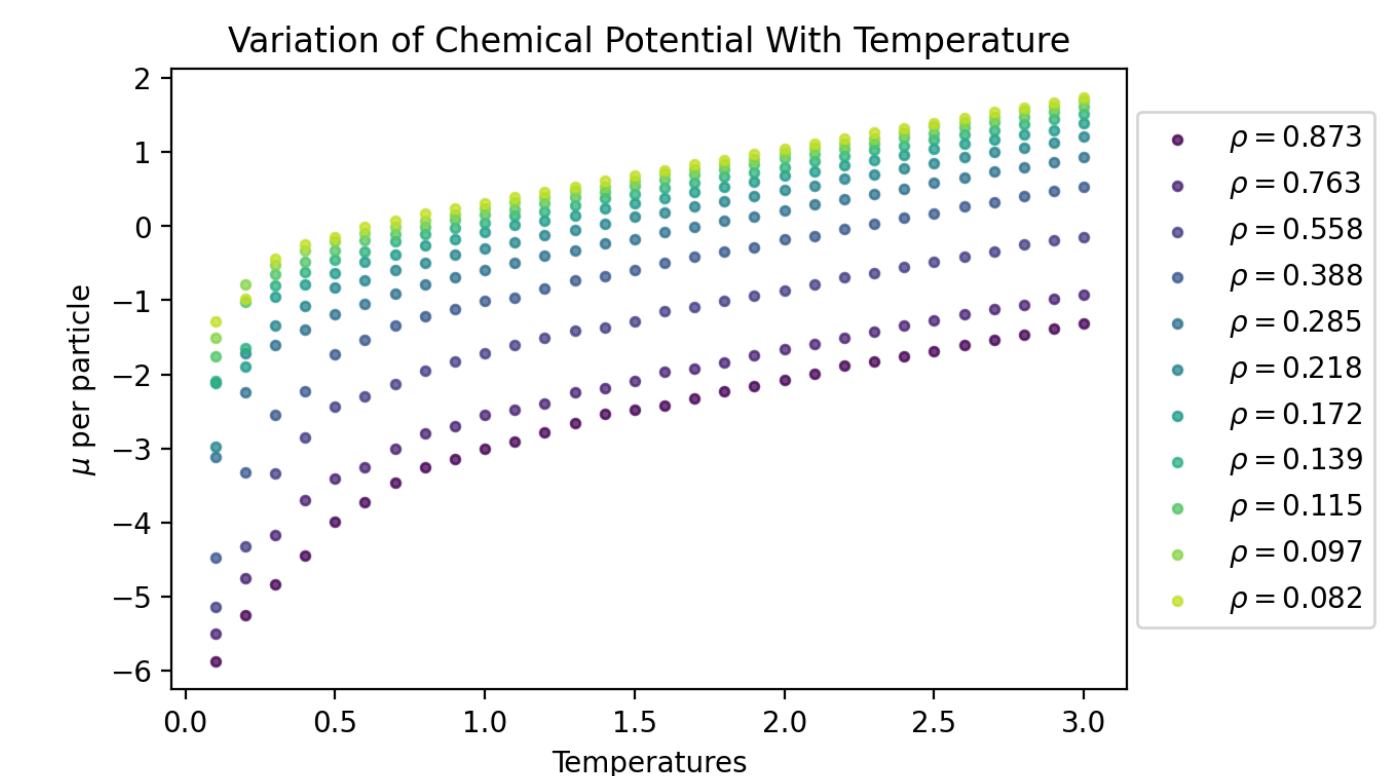


Figure 9. Plot of the chemical potential against temperature for various densities.

For a few densities and temperatures,  $\mu$  is positive, while usually  $\mu$  is negative for a gas. We aim to work on understanding this behaviour. This project was as part of the coursework for the Statistical Mechanics course taught by Prof. Bikram Phookun in Monsoon 2023.

## References

- [1] Tobochnik Gould and Christian. An introduction to computer simulation methods applications to physical system. 2016.