Molecular Dynamics Vision

Solid-Liquid Phase Transition

Introduction

One of the most interesting behaviours of materials is their phase change. The physical properties of an element or a compound change dramatically during a phase change. For instance, ice melts at 273.15K and 1 atmospheric pressure and its changes from a giant covalent structure to an irregular one bound by hydrogen bonding. Chemical potential of water is the same in the melting point, but the derivatives of chemical potential with respective to temperature at constant pressure (which is equal to minus entropy) are different for solid and liquid phases.

Over the years, a lot of theoretical and experimental studies have been carried out by scientists to study the properties of different materials when they undergo a phase change. The invention of computer has made simulation of different materials in different states possible. With the findings in solid-liquid and liquid-vapour equilibrium, the nature and structure of particles undergoing phase changes are better understood.

With molecular dynamics simulation, one can observe the structure and arrangement of particles in both phases and the change of structure during phase transitions. This module studies the phase behaviour of Lennard-Jones (LJ) fluid from a solid state to a liquid state. Thermodynamic properties will be discussed.

Setup of Simulations

In this study, Molecular Dynamics Vision program is used to simulate the solid-liquid phase of LJ particles. Parameters of argon are used. The mass (m), size (σ) and LJ parameter (ε) for Ar are 39.948 amu, 3.405×10^{-10} m and 1.6544×10^{-21} J, respectively.

The particles are put in the simulation box with a fixed number density of 0.95 in reduced unit. This corresponds to a real mass density of 1596 kg m^{-3}. The density is highly than that of water in room temperature and pressure. The LJ particles in this state should be either solid or liquid. From the phase diagram of Argon (Fig. 1), the gas phase cannot be reached at this density, no matter how high the temperature we set.

The simulations are carried out with temperatures ranging from 70 K to 250 K and the conditions are shown in Table 1. The data points of simulation of LJ particles are shown in Figure 1 as well and they cut the solid liquid phase boundary.
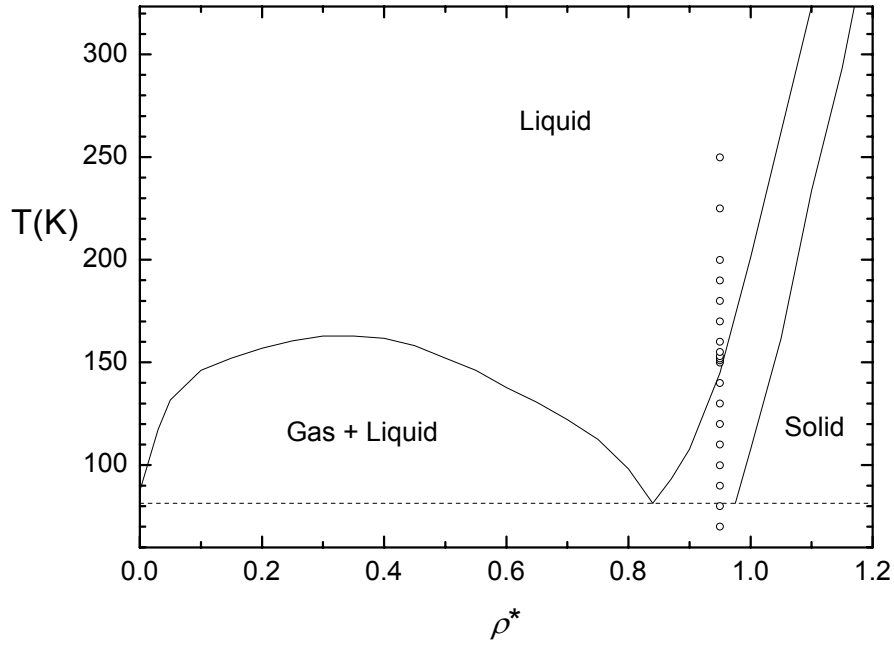
Figure 1. Phase diagram of Lennard-Jones (argon) particles. The circles are points of simulation setup conditions in this study.

Table 1. Setup parameters.

ρ^*	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95
T(K)	70	80	90	100	110	120	130	140	150	151	152
ρ^*	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95		
T(K)	153	155	160	170	180	190	200	225	250		

The simulations are carried out in a constant temperature (NVT) ensemble and temperature is kept constant during the simulation by means of a temperature rescaling in every time step. The time step of the simulation is 1×10^{-14} s. The potential cutoff is 2.5 σ for all conditions. In each data set, the system is run from a regular lattice structure to equilibrium. After that, 1000 steps of simulations are carried out and thermodynamic data are recorded during the simulation.

Results and Discussions

The values of potential energy and pressure of the system are recorded in every step of simulation. The frequency of points simulated are high for the region of 150 K ≤ T ≤ 160 K because the phase change occurs at that region and it is necessary to simulate more points in order to get an accurate value of phase transition temperature. The average values are shown in Table 2 in real units. The error bars are obtained by standard deviation of the values in every time step. Kinetic energy of the system is maintained constant because it is related to the temperature of the system. In a NVT ensemble simulation, temperature is maintained constant and is KE. Potential energy of the system increases with temperature because when temperature increases, particles can sample higher energy configurations.

Pressure of the system increases with temperature and it can be explained by the kinetic theory as well. When a system heats up, the particles gain more energy and move vigorously. This enhances the chance of collision and thus the pressure of the system increases. For a system in a temperature below 80 K, a negative pressure is recorded. This means the interactions among particles are attractive in the system, as the value of pressure in the program is calculated by measuring average force acting on the particles per unit area. One exception to this phenomenon is the phase change of ice to water. When water freezes, pressure increases because the density of ice is lower than water and the packing of ice crystal requires more space. If the volume of the box is fixed, the competition for space will generate a large pressure.

Table 2. Results of simulations of LJ particles in a reduced density of 0.95. Values of temperature, kinetic energy, potential energy, pressure and compression factor are shown.

T (K)	K.E. (kJ mol^{-1})	P.E. (kJ mol^{-1})	P ($\times 10^6$ Pa)	Z
70	0.873 ± 0.004	-7.30 ± 0.03	-46.5 ± 7.7	-2.00
80	0.998 ± 0.006	-7.19 ± 0.04	-18.4 ± 9.5	-0.693
90	1.122 ± 0.006	-7.10 ± 0.05	4.71 ± 10	0.157
100	1.247 ± 0.007	-6.99 ± 0.05	33.4 ± 12	1.00
110	1.372 ± 0.009	-6.89 ± 0.07	58.1 ± 15	1.59
120	1.497 ± 0.009	-6.78 ± 0.06	86.3 ± 14	2.16
130	1.621 ± 0.010	-6.66 ± 0.07	115 ± 16	2.67
140	1.746 ± 0.010	-6.54 ± 0.09	145 ± 20	3.12
150	1.871 ± 0.012	-6.45 ± 0.09	168 ± 19	3.37
151	1.883 ± 0.012	-6.41 ± 0.07	175 ± 16	3.48
152	1.896 ± 0.014	-5.87 ± 0.09	295 ± 20	5.85
153	1.908 ± 0.014	-5.86 ± 0.08	300 ± 17	5.90
155	1.933 ± 0.013	-5.84 ± 0.07	303 ± 15	5.88
160	1.995 ± 0.013	-5.78 ± 0.08	319 ± 17	6.00
170	2.120 ± 0.017	-5.69 ± 0.11	341 ± 23	6.05
180	2.245 ± 0.016	-5.58 ± 0.09	366 ± 20	6.12
190	2.369 ± 0.017	-5.51 ± 0.09	384 ± 19	6.08
200	2.494 ± 0.018	-5.42 ± 0.11	406 ± 23	6.11
225	2.806 ± 0.023	-5.16 ± 0.12	468 ± 26	6.26
250	3.118 ± 0.022	-4.96 ± 0.10	518 ± 22	6.23

Compression factor (Z) of the system is used to determined whether a system obeys ideal gas law and is given by the formula

$$Z = \frac{PV}{NkT}$$

When a gas obeys ideal gas law, the compression factor equals 1. Compression factors of the system at different temperature are shown in Table 2 and the trend is plotted in Figure 2. From the result, compressibility of LJ fluids increase with temperature and it means the deviation from ideality increases. At a temperature of 100 K, the compression factor equals 1. But it does not imply that the system in that condition behaves ideally because the density of the system is high and interaction forces among particles exist. This violates the principle of an ideal gas. It can be seen from Fig. 2 that the compressibility of solid and liquid phases are not the same. Compression

factor for solid increases with temperature, but for liquid, it is nearly constant. The constant value means pressure in a liquid system increases linearly with temperature.
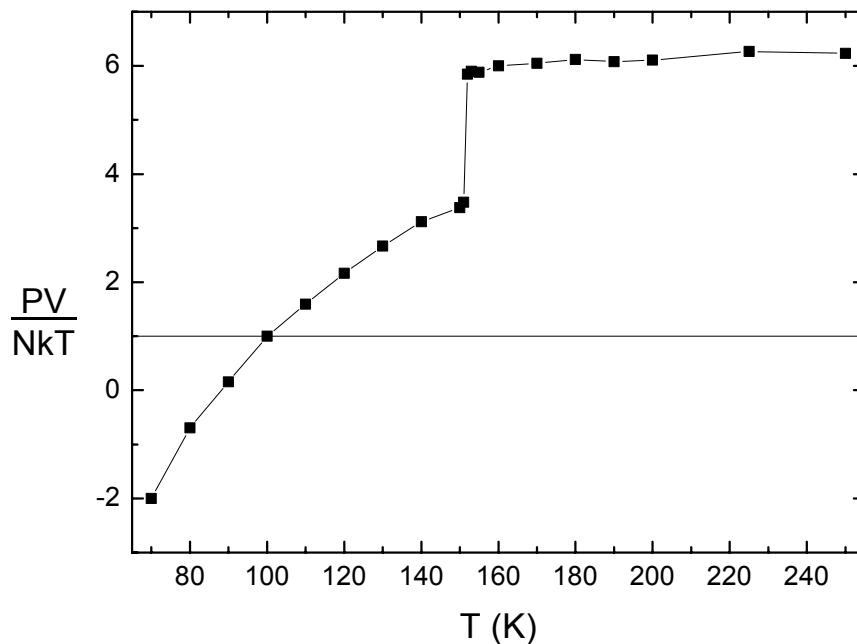

Figure 2. Compression factor of LJ particles as a function of temperature.

The data of potential energy of the system is plotted against temperature in Figure 3. It can be seen that the function is linear at both high and low temperature regions. The two regions are broken at a temperature of 151 K and it corresponds to a change of phase between liquid and solid. This transition temperature agrees with the phase boundary in Figure 1. The values of temperature dependent pressure of the LJ system are plotted in Figure 4.

From Figure 3, the discontinuity in the potential energy versus temperature function is an evidence of the first order phase transition. First order phase transition occurs for solid-liquid, vapour-liquid and solid-vapour phase transitions. Other solid-solid or glass transitions are second order phase transition and they are characterised by a discontinuity in the first derivative of the energy versus temperature curve.

The structure of the particles in different state can be studied by the help of pair distribution functions. Figure 5 shows the pair distribution functions of the LJ system at a reduced density of 0.95 and temperature of 70, 151 and 200 K respectively. The pair distribution function approaches the unity value for the highest temperature system (200 K), which means the particles are distributed homogeneously inside the box and it shows a typical liquid structure. For the graph of the lowest temperature (70 K), however, 4 peaks with 2 of them sharper than the case of liquid are observed. Also the value of function at the end point has a value smaller than 1. This implies the particles are more localized and they are arranged in a more regular manner. As a result, the system resembles a crystalline structure.
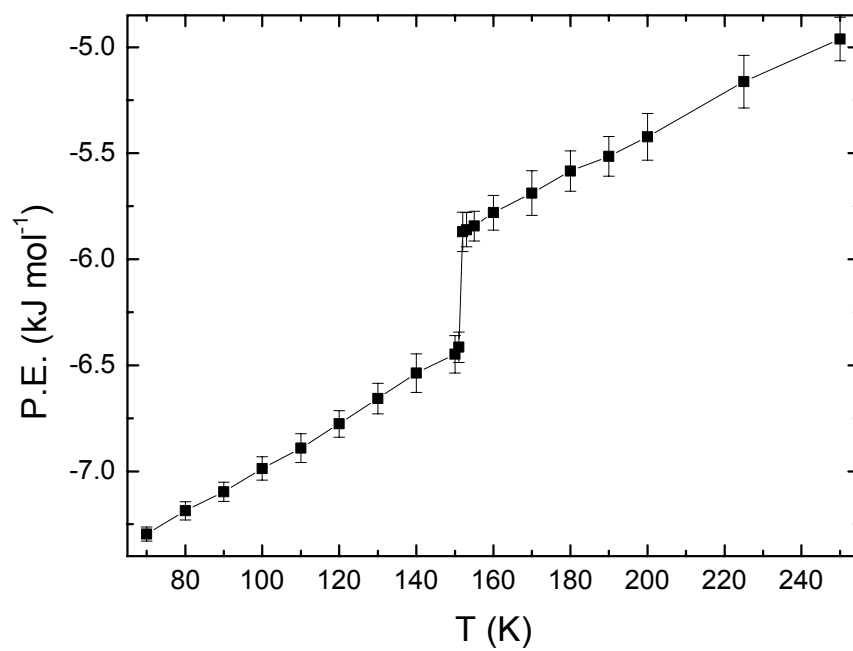
Figure 3. Potential energy of a LJ system as a function of temperature. The steep slope region of the graph is the temperature where there is a phase change.
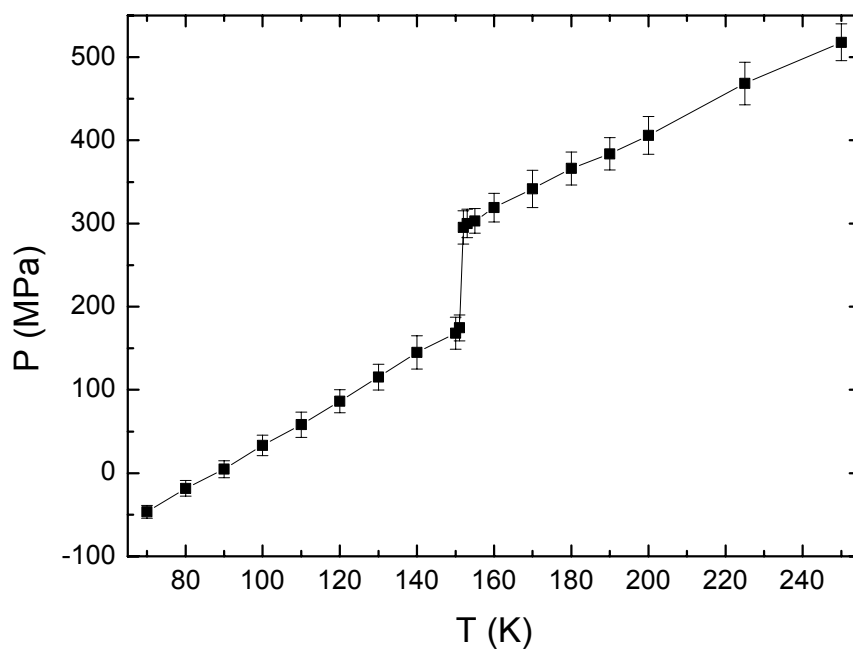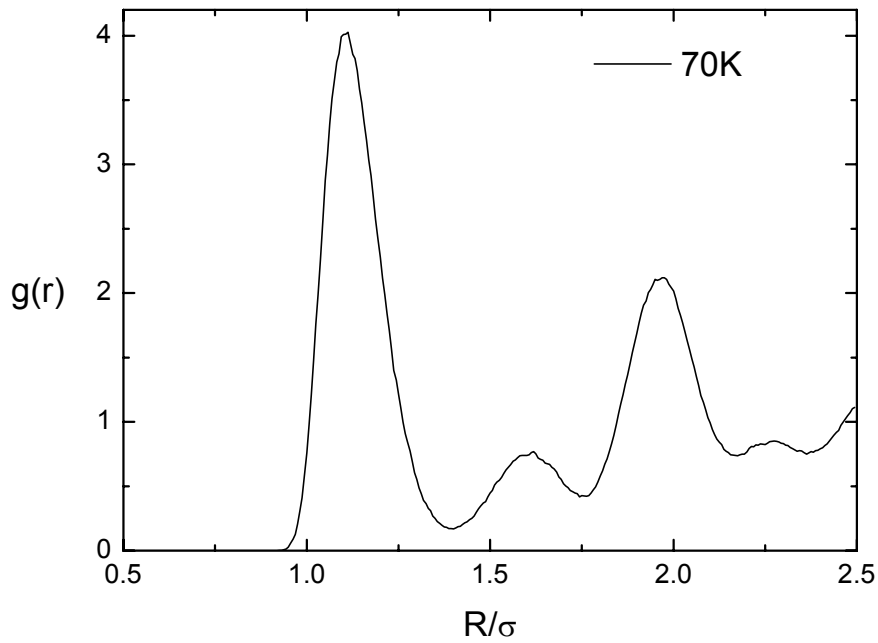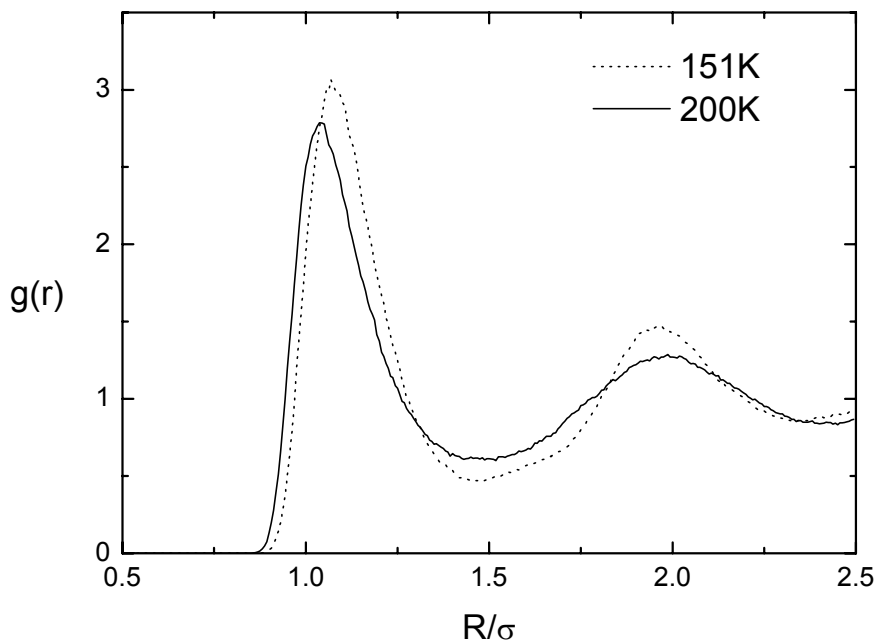

Figure 4. Pressure of a LJ system as a function of temperature.

(a)

(b)

Figure 5. Pair distribution functions of LJ particles at temperatures of: (a) 70K, (b) 151 and 200 K.

The pair distribution function for the system at 151 K has a shape similar to both the solid and liquid phases. The peaks are sharper than that in liquid but not as sharp as that of solid. This shows that the system at melting temperature may be in a solid-liquid phase equilibrium. Both phases exist in the system and the particles are changing their arrangement continuously in that state.

The structure of the particles can be observed through the visualization program and it is easy to tell from the image of the structure the difference in solid and liquid phases. In a solid phase, the particles are packed in a regular structure as shown in Figure 6a. We can see clearly defined planes of particles arranged in a regular pattern in the box. On the other hand, there is a random distribution of particles in the box with high temperature (Fig. 6b) and there is no regular pattern in the arrangement of particles in the box. As a result, the system is in liquid state at that temperature.

The process of melting of a solid can be observed using MDVision program by changing the temperature during the simulation. When we increase the temperature during the simulation by changing the position of the temperature bar, the particles in the box move more vigorously and the structure melts down. This resembles a real situation of melting of a solid. The reverse of the process from liquid to solid, however, is more difficult to observe since the entropy of the system decreases during the freezing process. It may take a longer simulation time and a decrease of temperature in small intervals at a time in order to observe the formation of solid in crystalline structure.
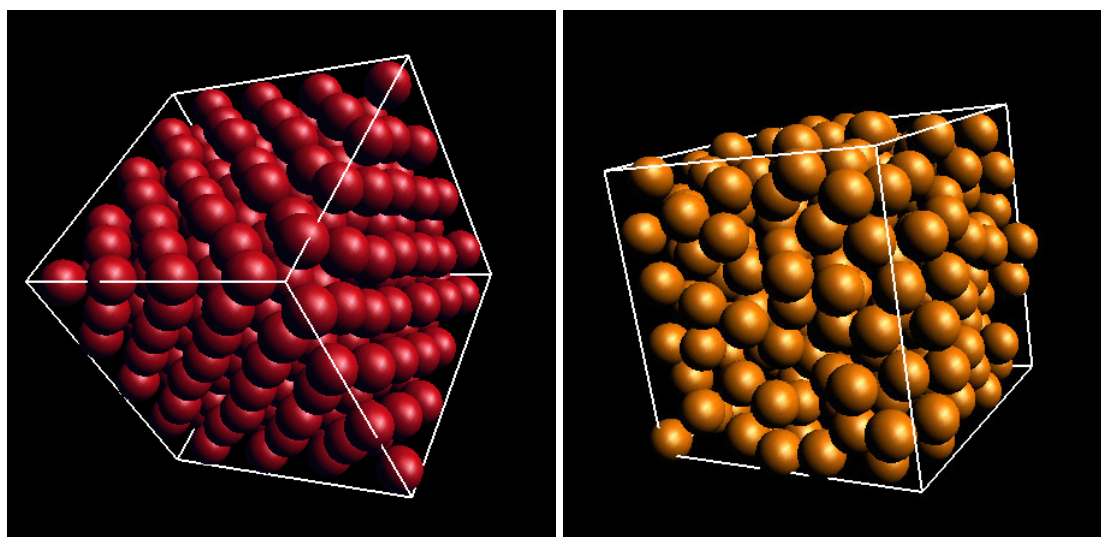

Figure 6. LJ particles in: (a) solid state (70 K) and (b) liquid state (200 K).

Conclusions

The Molecular Dynamics Vision program was used to perform a study on the phase behaviour of Lennard-Jones fluids and a system with a constant reduced density was simulated. Thermodynamic data of the system were recorded for different temperature and phase transition temperature was found to be 151 K at a reduced density of 0.95. From the visualization feature of the program, distinguishable structures are observed for liquid and solid phases of the particles. In solid state, the particles are packed in a regular crystalline structure inside the box.