Molecular Dynamics Vision

Liquid-Vapour Phase Equilibria

Introduction

The phase behaviour of an element or a compound is usually studied by a pressure versus volume graph at different isotherms. For a system that obeys ideal gas behaviour, the isotherm of pressure is inversely proportional its volume. When the temperature decreases, the system reaches a critical point at certain volume. The system can be condensed to liquid from vapour phase below the critical isotherm. The isotherms can be described by the Van der Waal's equation, which presents the behaviour of real gases. Exact description of the equations of states require numerical solutions and they are usually obtained from the experimental investigations of systems in different conditions or results from computer simulations.

Molecular dynamics simulation method provides an efficient way to investigate the behaviour of fluid at different temperature and volume. In addition to that, it can be used to simulate critical conditions that are difficult to conduct in real experiments such as investigations in a very high pressure and temperature. In this module, results of simulations of Lennard-Jones (LJ) fluids carried out at 3 different temperatures will be reported with densities vary between a very low and high value.

Setup of Simulations

Molecular Dynamics Vision program is used to perform the simulations of liquid-vapour phase of LJ particles. The principles of the particles' interaction have been written down in the manual. In this simulation, 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 simulations are carried out at temperatures of 135K, 162 K and 300K respectively. The particles are put in the simulation box with a density varies from 0.03 to 0.8 in reduced unit. The points simulated are plotted in the phase diagram in Figure 1. The line joining the points at a temperature of 135K crosses the liquid-gas dual phase while the point at a temperature of 162K and a reduced density of 0.35 touches the critical point of the fluid derived theoretically. In order to observe the behaviour of LJ fluid during phase change from gas to liquid-vapour dual phase, a set of simulations were carried out at a constant reduced density of 0.3 and a temperature range from 125 to 170K.

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 cutoffs are 2.5σ for reduced densities larger than 0.5 and 4.0σ for reduced densities smaller than 0.5. In each data set, the system is run from a regular lattice structure to equilibrium. After that, 2000 steps of simulations are carried out and thermodynamic data are recorded during the simulation.

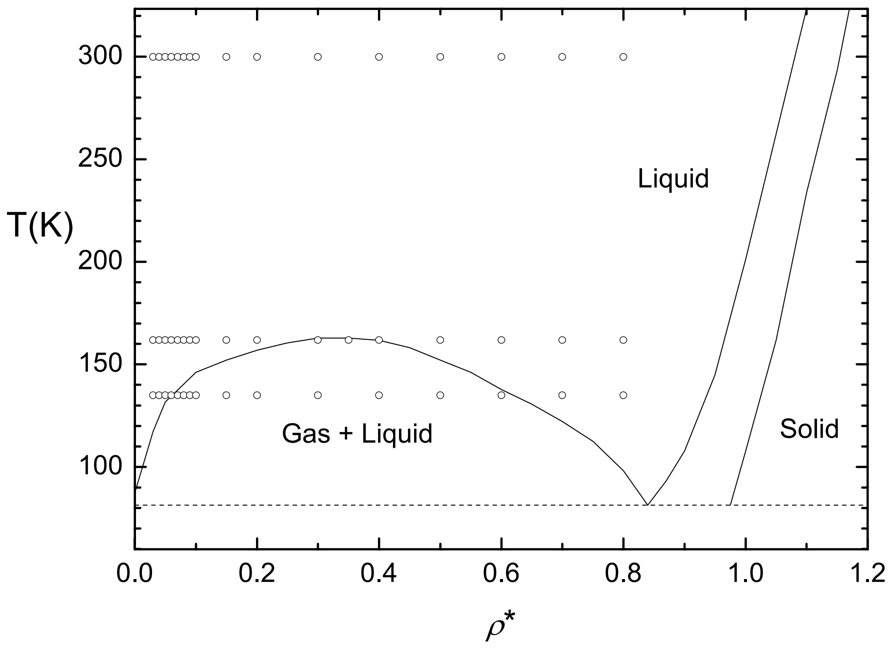

Figure 1. Phase diagram of Lennard-Jones (argon) particles. The circles are points of simulation setup conditions in this study.

Results and Discussions

The values of potential energies with different density of fluid carried out at constant temperatures of 135, 162 and 300K are shown in Table 2. Their trends with respect to molar volume of the box are plotted as isotherms in Figure 2. Potential energy of the system increases monotonically with molar volume because the higher the volume, the lower the density of the fluid and the interaction energies among molecules are smaller.

Pressure of the LJ system is shown in Table 3 for the 3 different temperatures and isotherms of the volume dependent pressure are plotted in Figure 3. For the system in 300K, pressure decreases monotonically with volume and the function curve is similar to an ideal case PV curve. It shows that at the corresponding temperature, the system exists in gas phase no matter what the density is. Pressure increases exponentially at small volume of box because the high temperature causes the molecules to hit each other vigorously. The high collision force and pressure explain the difficulty in forming liquid at high temperature.

Pressure curve for 162K shows a point of insection at $V_m = 0.017$ ($\rho^* = 0.4$) at which both the first and second derivatives of the function are zero. According to the phase behaviour of fluid, the system is close to the critical point at that situation. However, it is practically very difficult to determine the exact location of the critical point by simulation. One may do so by examining the isotherms of very small intervals of temperature, but that approach requires tedious simulations of large array of variables.

Table 2. Potential energy (in kJ) per mole of LJ particles. The values in each column correspond to the result at a temperature shown at the top.

ρ^*	135K	162K	300K
0.03	-0.230 ± 0.016	-0.205 ± 0.015	-0.193 ± 0.024
0.04	-0.357 ± 0.019	-0.292 ± 0.021	-0.262 ± 0.025
0.05	-0.425 ± 0.024	-0.358 ± 0.025	-0.305 ± 0.023
0.06	-0.494 ± 0.028	-0.473 ± 0.051	-0.370 ± 0.034
0.07	-0.597 ± 0.025	-0.533 ± 0.031	-0.445 ± 0.032
0.08	-0.655 ± 0.030	-0.645 ± 0.039	-0.494 ± 0.041
0.09	-0.761 ± 0.032	-0.670 ± 0.033	-0.552 ± 0.040
0.10	-0.840 ± 0.041	-0.748 ± 0.028	-0.629 ± 0.034
0.15	-1.27 ± 0.05	-1.13 ± 0.04	-0.917 ± 0.046
0.20	-1.61 ± 0.05	-1.46 ± 0.08	-1.23 ± 0.05
0.30	-2.26 ± 0.08	-2.14 ± 0.07	-1.80 ± 0.06
0.35	--	-2.39 ± 0.05	--
0.40	-2.96 ± 0.07	-2.70 ± 0.05	-2.41 ± 0.07
0.50	-3.46 ± 0.05	-3.35 ± 0.05	-2.98 ± 0.08
0.60	-4.10 ± 0.05	-4.00 ± 0.05	-3.53 ± 0.09
0.70	-4.79 ± 0.05	-4.64 ± 0.06	-4.02 ± 0.10
0.80	-5.40 ± 0.05	-5.23 ± 0.07	-4.41 ± 0.12

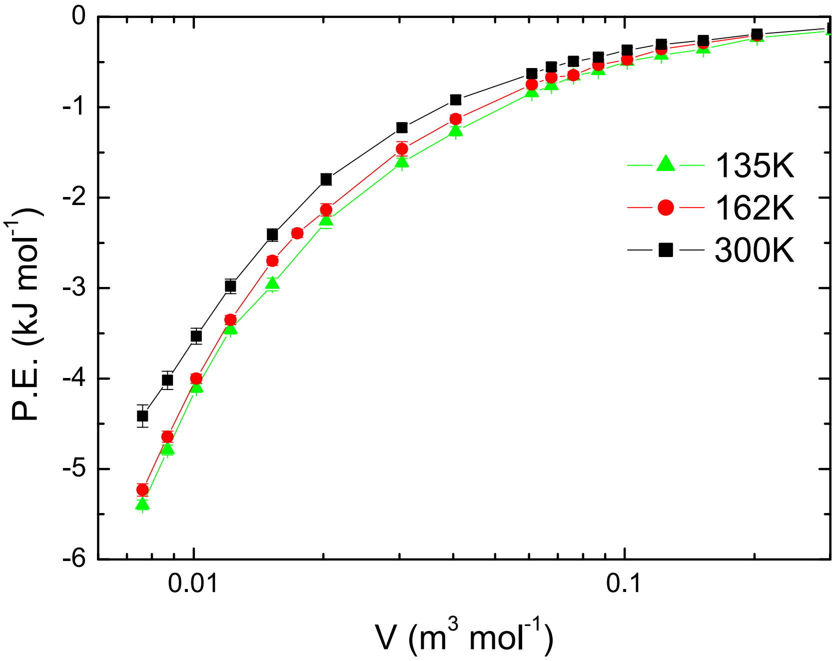

Figure 2. Potential energy of a LJ system as a function of molar volume of box.

Table 3. Pressure (in 10^6 Pa) of LJ particles.

ρ^*	135K	162K	300K
0.03	1.26 ± 0.09	1.56 ± 0.10	3.09 ± 0.14
0.04	1.54 ± 0.16	2.02 ± 0.17	4.10 ± 0.23
0.05	1.90 ± 0.20	2.45 ± 0.21	5.13 ± 0.31
0.06	2.17 ± 0.26	2.81 ± 0.30	6.00 ± 0.37
0.07	2.39 ± 0.34	3.17 ± 0.36	7.12 ± 0.50
0.08	2.61 ± 0.40	3.41 ± 0.42	8.11 ± 0.66
0.09	2.77 ± 0.53	3.88 ± 0.56	9.04 ± 0.77
0.10	2.95 ± 0.56	4.13 ± 0.68	9.99 ± 0.87
0.15	3.13 ± 1.2	5.28 ± 1.2	14.9 ± 1.6
0.20	2.92 ± 1.7	5.83 ± 1.7	19.9 ± 2.1
0.30	1.43 ± 2.9	6.67 ± 3.1	31.8 ± 4.6
0.35	--	6.22 ± 3.9	--
0.40	-0.240 ± 4.9	5.83 ± 4.8	47.2 ± 7.2
0.50	-4.43 ± 6.2	9.02 ± 6.7	72.9 ± 10
0.60	-0.243 ± 7.5	19.6 ± 8.8	114 ± 13
0.70	18.5 ± 10	47.5 ± 11	184 ± 17
0.80	68.7 ± 10	109 ± 13	296 ± 22

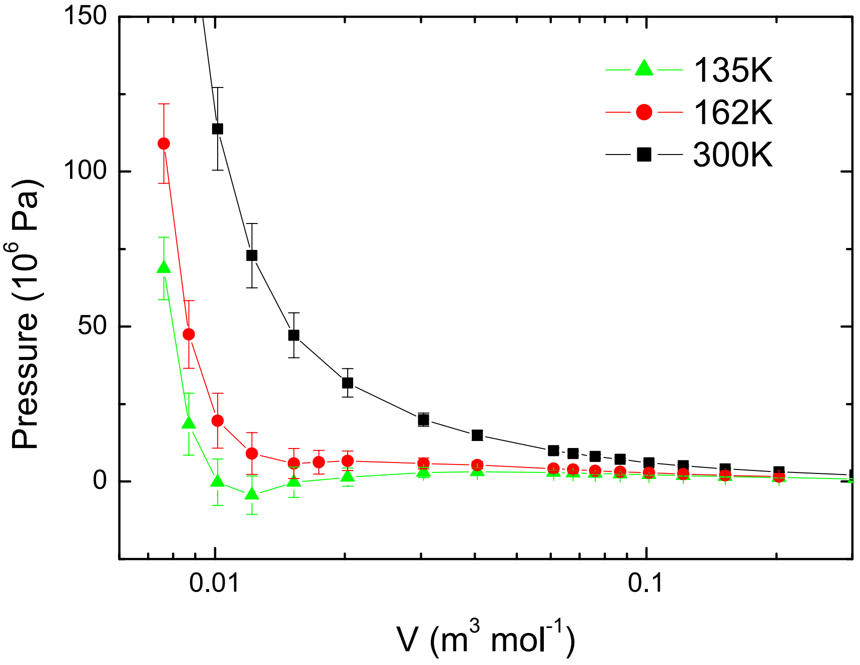

Figure 3. Pressure of a LJ system as a function of molar volume of box.

At a temperature of 135K and reduced density of the particles falls between 0.3 and 0.6, the system enters the 2-phase region. Pressure of the system reaches a local minimum at that region and the negative values of pressure suggest that attractive forces dominate the interaction among the particles in the system. In a 2-phase system, interactions among particles are stronger and the density is high enough to force the particles to stick together. As a result, the attractive forces among molecules are higher than their collision forces and the system in that situation have a negative pressure.

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 and density are shown in Table 4 and the trend is plotted in Figure 4. From the figure, the isotherms approach 1 when molar volume approaches infinity. The molecules are separated far apart from each other when the density of gas is low and the lack of interactions among particles resembles an ideal gas case. The shape of the isotherms is similar to the corresponding pressure curves in Figure 3 and at temperatures of 135 and 162K, a local minimum is observed which symbolised a non-gas phase in that region.

Table 4. Compression factor of LJ particles.

ρ*	135K	162K	300K
0.03	0.890	0.920	0.982
0.04	0.815	0.892	0.976
0.05	0.803	0.865	0.978
0.06	0.765	0.827	0.953
0.07	0.724	0.798	0.969
0.08	0.690	0.751	0.966
0.09	0.651	0.761	0.957
0.10	0.624	0.730	0.952
0.15	0.441	0.620	0.947
0.20	0.309	0.514	0.949
0.30	0.101	0.392	1.01
0.35	--	0.314	--
0.40	-0.0127	0.257	1.12
0.50	-0.187	0.319	1.39
0.60	-0.00857	0.577	1.81
0.70	0.559	1.20	2.50
0.80	1.82	2.41	3.52

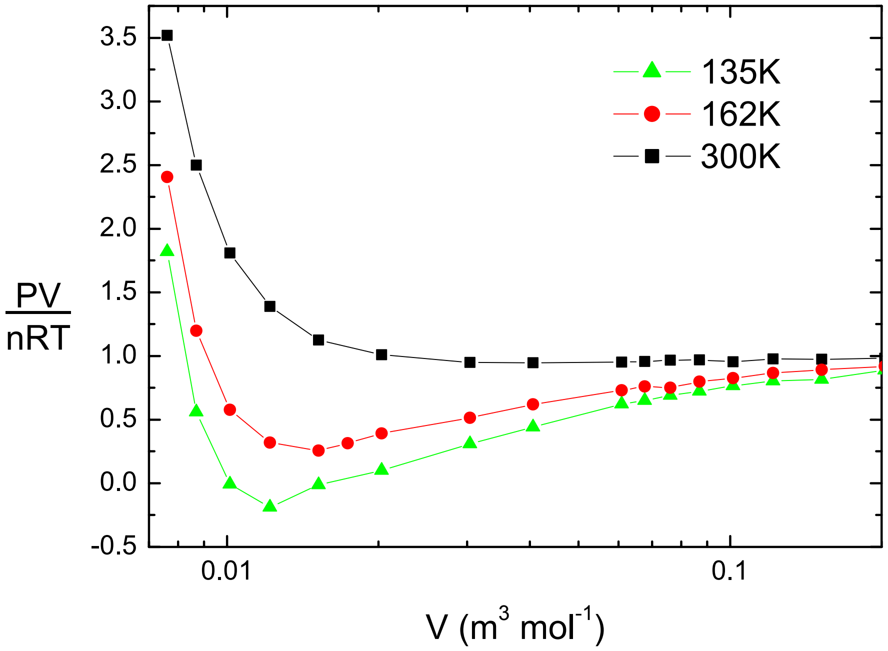

Figure 4. Compression factor of LJ particles as a function of molar volume of box.

The structure of the particles in different state can be studied by the help of a pair distribution function. Figure 5 shows the pair distribution functions of the LJ system at a reduced density of 0.04 and temperature of 135, 162 and 300 K respectively. The pair distribution function approaches the unity value quickly when the distance from the molecule centre is larger than 2 times its size. It suggests that the system is in a gas phase. The peak of the curve at the temperature of 135K is higher than the rest because at low temperature, the interaction forces among particles are stronger.

Figure 6 shows the pair distribution functions at a reduced density of 0.4. The curve for the lowest temperature shows an easily located second peak at the point $r = 2.2d$ as the molecules in the box give a liquid phase behaviour. The second peak is not apparent for the distributions of other 2 temperatures because at those temperatures, the systems do not enter the 2-phase region.

Pair distribution functions at a high density of 0.8 in reduced unit are plotted in Figure 7. The shape of the curves for the temperatures 135K and 162K are typical liquid ones. The curve for the temperature 300K is different from the rest. As explained before, the system above critical temperature cannot form liquid no matter how high the temperature is. Thus the system at 300K is a high-density gas state rather than a liquid state.

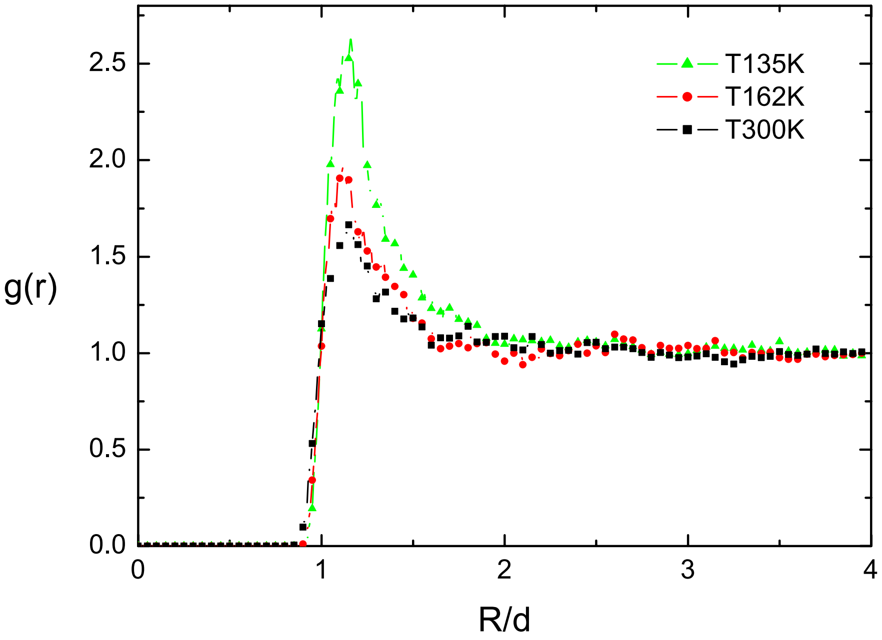

Figure 5. Pair distribution functions of LJ particles at reduced density of 0.04 and temperatures of 135K, 162K and 300 K.

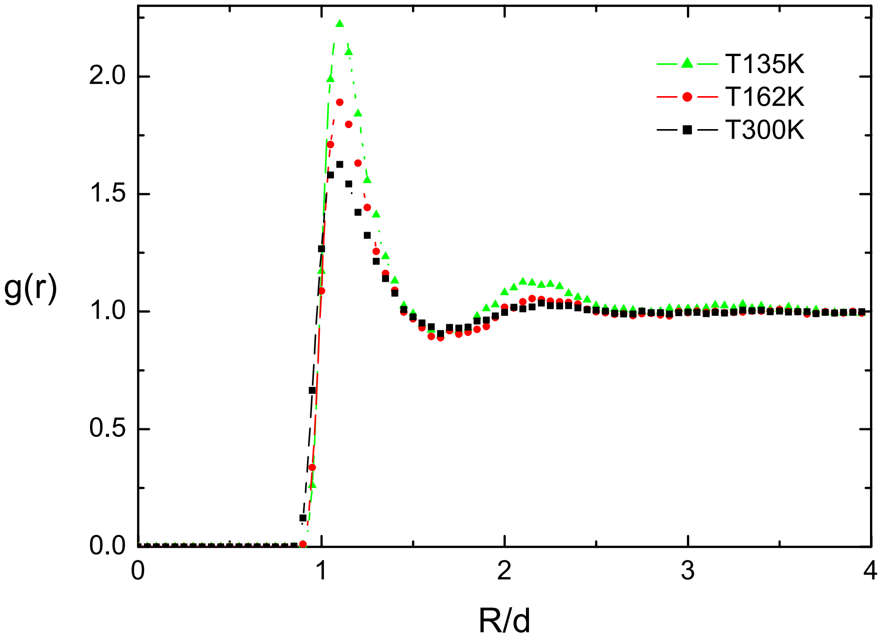

Figure 6. Pair distribution functions of LJ particles at reduced density of 0.4 and temperatures of 135K, 162K and 300 K.

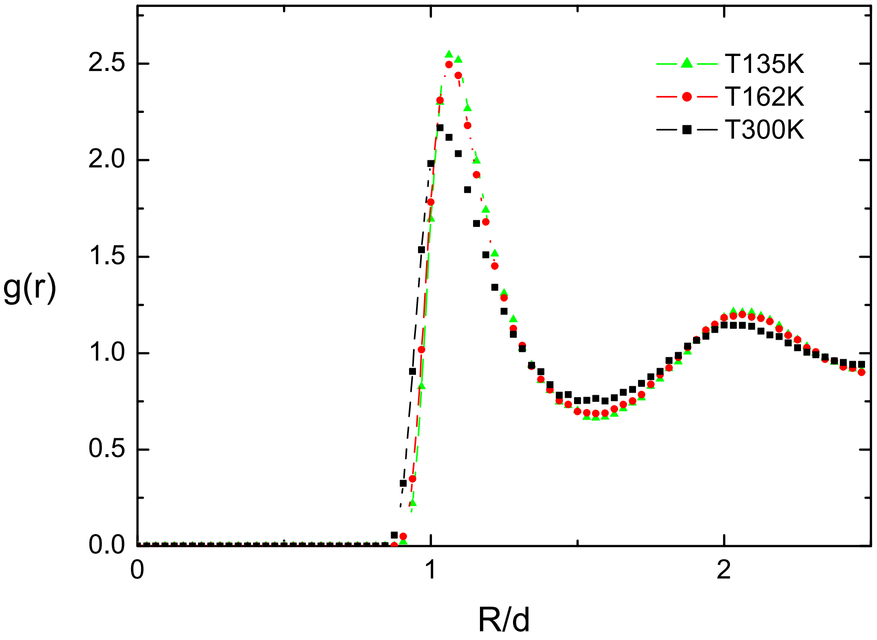

Figure 7. Pair distribution functions of LJ particles at reduced density of 0.8 and temperatures of 135K, 162K and 300 K.

Liquid-Vapour Phase

When a system is brought to a temperature below the critical point, the system enters a two phase region where there is a coexistence of a liquid phase and a vapour phase that gives a vapour pressure. By the help of the visualization program, it is possible to view the structure of molecules inside box and explain the thermodynamic properties of the system.

A set of simulations of the LJ system at a constant reduced density of 0.3 and temperature varies between 125K and 170K were carried out in order to observe the phase change of the system. The system in a mixture of liquid and vapour phases shows a large fluctuation in potential. Therefore 10,000 time steps after the system is equilibrated were simulated to get the data.

The variation of potential energy with temperature is shown in Figure 8. The slope of the function for a temperature $T < 140$K is larger than for $T > 140$K. So there is a phase boundary at a temperature of 140K. At a temperature lower than 140K, the particles are in a 2 phase equilibrium. Snap shots of the system at a temperature of 125K show that there is a large fluctuation of local density of the particles in the box (Fig. 9). At one snapshot of the system with a minimum potential energy, the particles are packed in a small region, leaving a large empty space in the box. The high density region resembles a liquid phase while the low density region represents the vapour phase. One the other hand, the snap shot of the system with a relatively high potential energy shows that the molecules are more evenly distributed inside the box. There is a rapid change of local density inside the box and that results in a continuous change of phase. The argument is support by the fluctuation of potential energy of molecules during the simulation period (Fig. 10). From the figure, the curve shows a large fluctuation of potential energy and sharp local minima are observed which indicates a condensation of particles inside the box. Such a configuration has a short life time because the collision force among particles are strong enough to break the meta-stable high local-density structure.

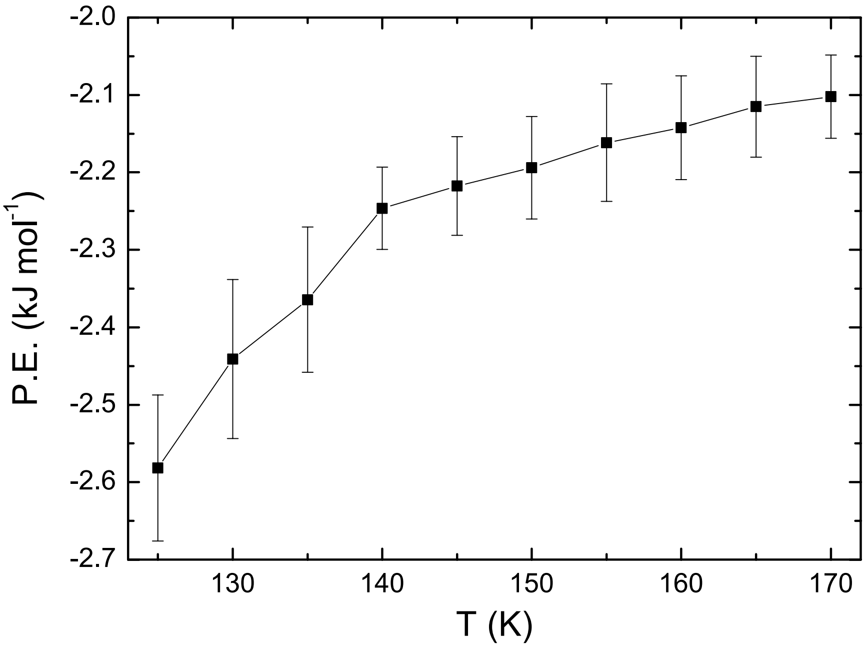

Figure 8. Potential energy of a LJ system as a function of temperature.

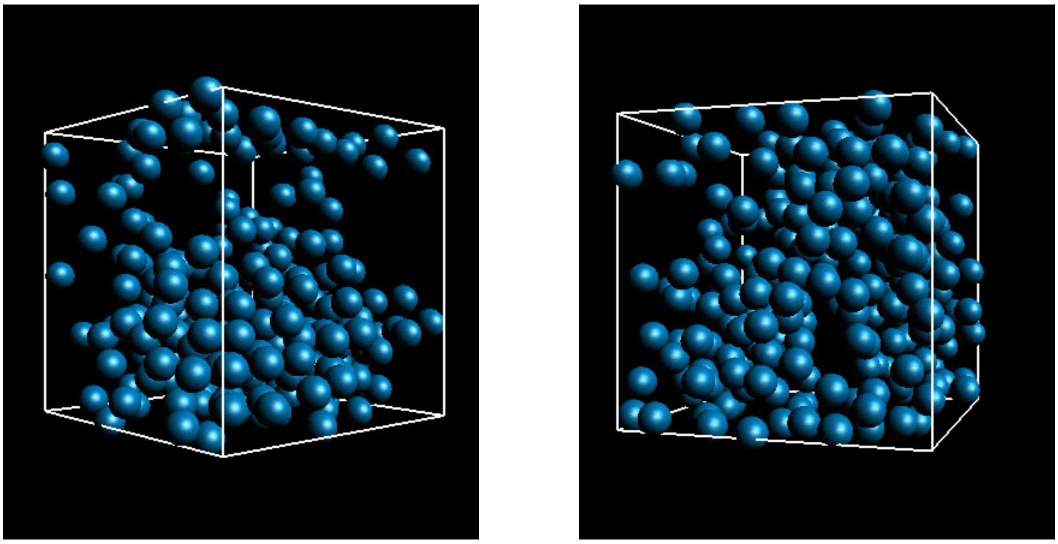

Figure 9. LJ particles in two phases. The snap shot were taken at a simulation of the box with $\rho^* = 0.3$, $T = 125$K and at the instance with the lowest potential energy (left) and highest potential energy (right).

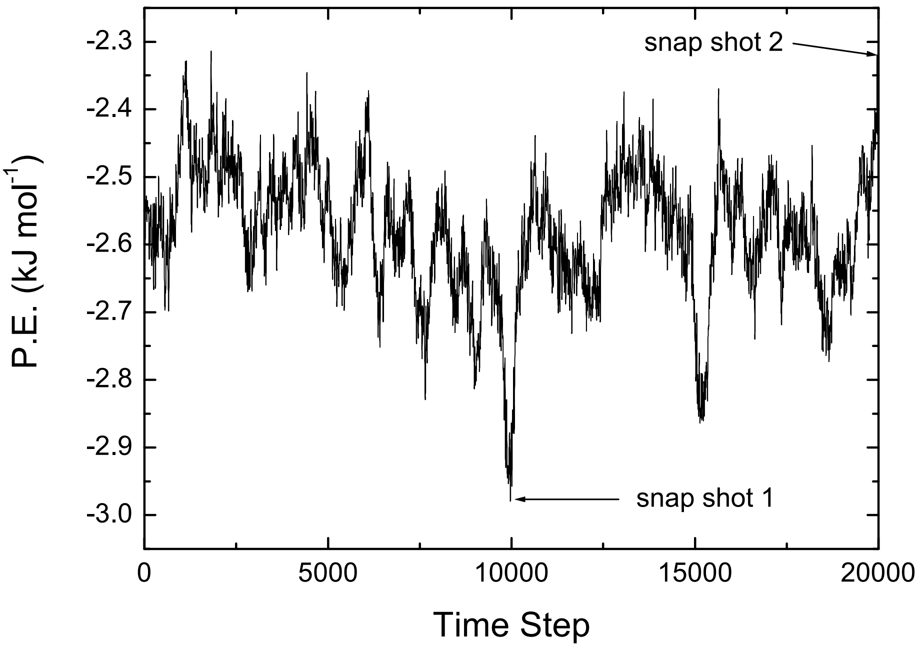

Figure 10. Large fluctuation of potential energy of the system against time step for a system in the liquid-gas two-phase region ($\rho^* = 0.3$, $T = 125$K).

Conclusions

Molecular Dynamics Vision program was used to perform a study on the phase behaviour of Lennard-Jones fluids and a system with temperatures of 135, 162 and 300K and reduced densities vary from 0.03 to 0.8. The system is in gas phase at high temperature and low density while it is in liquid phase at low temperature at high density. Below the critical point, the system is in both liquid and vapour phases. A set of simulation carried out at a fixed reduced density and temperature range from 125 to 170K shows that when a system is in a 2 phase equilibrium, the fluctuation of potential energy in the system is large and the system continuously transfers between a state with uniform local density and another with largely deviated local density.