Molecular Dynamics Simulation Phase Coexistence Curve and Properties of Lennard-Jones Fluid

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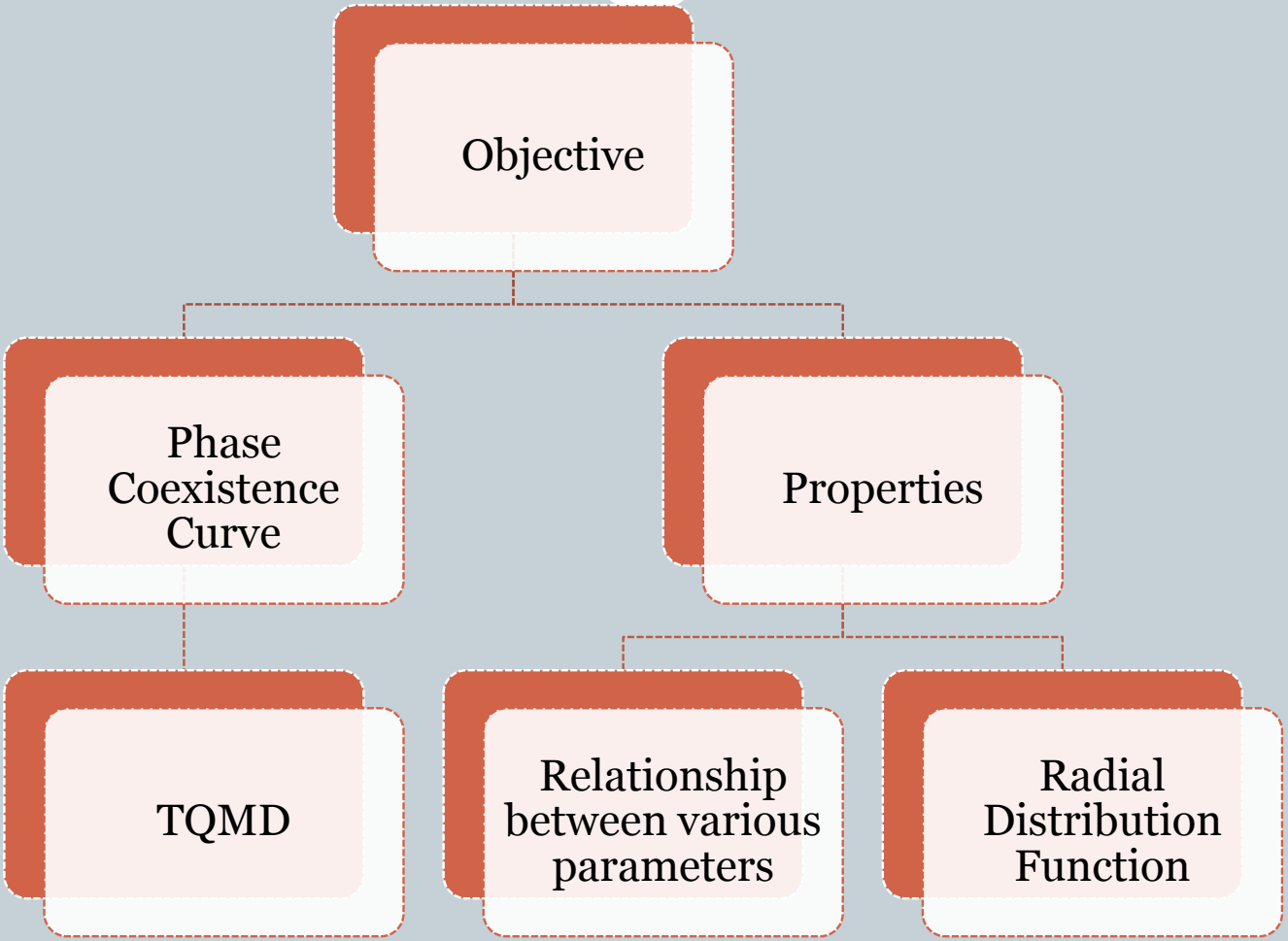
Overview

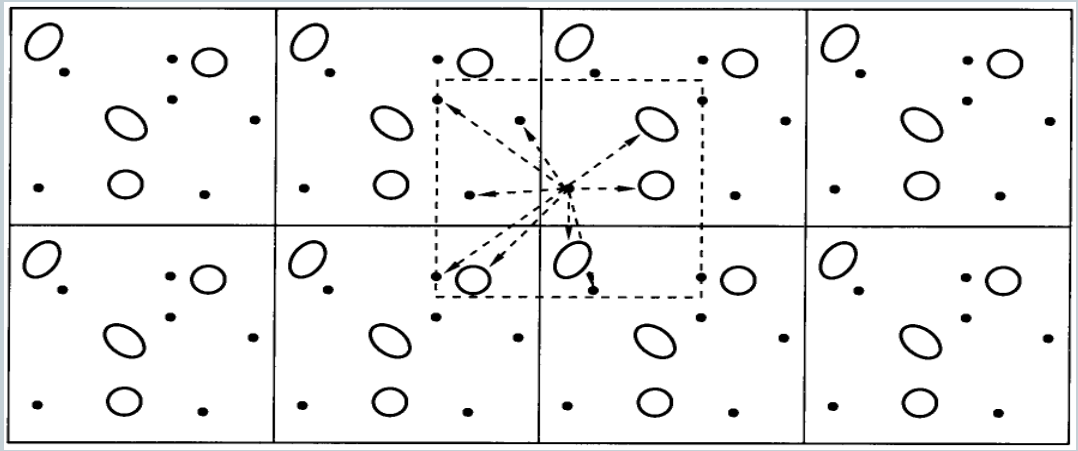

Objective
Phase Coexistence Curve
Properties
TQMD
Relationship between various parameters
Radial Distribution Function

Molecular Dynamics Simulation

- Atomic
  - Simulation of a collection of atoms
- Infinite system
  - Periodic boundary condition
- Classical approach
  - Each atom is treated as a simple structureless particle with wavelength that is much smaller than the particle separation.
- Deterministic technique
  - Initial set of positions and velocities is given.
  - Equations of motion are integrated to track the atoms.

Periodic Boundary Condition

- An atom that leaves the simulation region through a particular bounding face immediately reenters the region through the opposite face.
- Minimum separation rule
  - For the equations of motion to be consistent, particles should only be allowed to interact once.

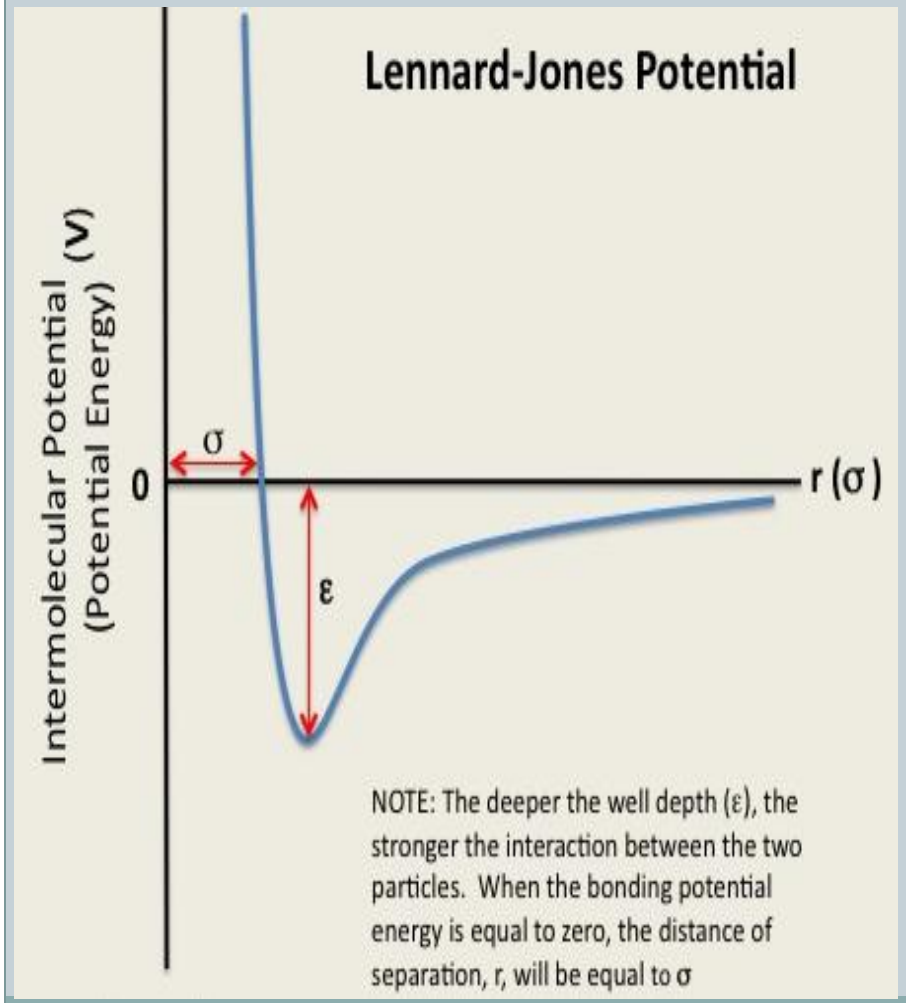


Reduced Units

- Usually denoted by superscript of *.
- Simulation results obtained in reduced units can be translated back into real units.

Quantities	Units	Reduced Units
Length, L	σ	$L^* = L\sigma^{-1}$
Energy, U	ϵ	$U^* = U\epsilon^{-1}$
Mass, m	$\mathfrak{m}$	$m^* = m\mathfrak{m}^{-1}$
Time, t	$\sigma\sqrt{\mathfrak{m}/\epsilon}$	$t^* = t\left(\sigma\sqrt{\mathfrak{m}/\epsilon}\right)^{-1}$
Temperature, T	ϵ/k_B	$T^* = T(\epsilon/k_B)^{-1}$
Pressure, P	$^3/\epsilon$	$P^* = P(\ \ ^3/\epsilon)^{-1}$
Density,ρ	^{3}	$\rho^* = \rho\sigma^{-3}$

Lennard – Jones Potential



$$U_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

where r is the separation of the particles.

Newtonian Mechanics

- From the Lennard-Jones Potential

$$\boldsymbol{f_{ij}}(r_{ij}) = -\frac{\partial U}{\partial \boldsymbol{r}_{ij}} = \frac{\boldsymbol{r_{ij}}}{{r_{ij}}^2}\left\{48\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \frac{1}{2}\left(\frac{\sigma}{r_{ij}}\right)^{6}\right]\right\}$$

- Newton's Third Law

$$\boldsymbol{f}_{ij} = -\boldsymbol{f}_{ji}$$

Velocity Verlet Algorithm

- Update positions

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}(\Delta t)^2$$

- Half-update velocities

$$v\left(t+\frac{\Delta t}{2}\right) = v(t) + \frac{f(t)}{2m}\Delta t$$

- Compute forces

$$r(t+\Delta t) \rightarrow f(t+\Delta t)$$

- Half update velocities

$$v(t+\Delta t) = v\left(t+\frac{\Delta t}{2}\right) + \frac{f(t+\Delta t)}{2m}\Delta t$$

Truncation of Interactions

- Truncation and Shift

$$U^{tr-sh}(r) = \begin{cases} U_{LJ}(r) - U_{LJ}(r_c), & r \le r_c \\ 0, & r > r_c \end{cases}$$

  - No discontinuities in the intermolecular potential.

- Correction terms
  - To reduce the systematic error in the simulation

$$U^{tail} = \frac{8}{3}\pi\rho\epsilon\sigma^3\left[\frac{1}{3}\left(\frac{\sigma}{r_c}\right)^9 - \left(\frac{\sigma}{r_c}\right)^3\right]$$

$$\Delta P^{tail} = \frac{16}{3}\pi\rho^2\epsilon\sigma^3\left[\frac{2}{3}\left(\frac{\sigma}{r_c}\right)^9 - \left(\frac{\sigma}{r_c}\right)^3\right]$$

Temperature and Pressure

- Instantaneous temperature
  - Equipartition theorem

$$\frac{3}{2}Nk_BT = \frac{1}{2}\sum_{i=1}^{N} m_i|\boldsymbol{v}_i|^2$$

- Instantaneous pressure

$$P = \rho T + \frac{vir}{V}$$

where V is the volume of system and vir is the virial:

$$vir = \frac{1}{3}\sum_{i>j} \boldsymbol{f}(r_{ij}) \cdot \boldsymbol{r}_{ij}$$

Berendsen Thermostat and Barostat

- Berendsen Thermostat

$$\lambda = \left[1 + \frac{\Delta t}{\tau_T}\left(\frac{T}{T_0} - 1\right)\right]^{1/2}$$

- Berendsen Barostat

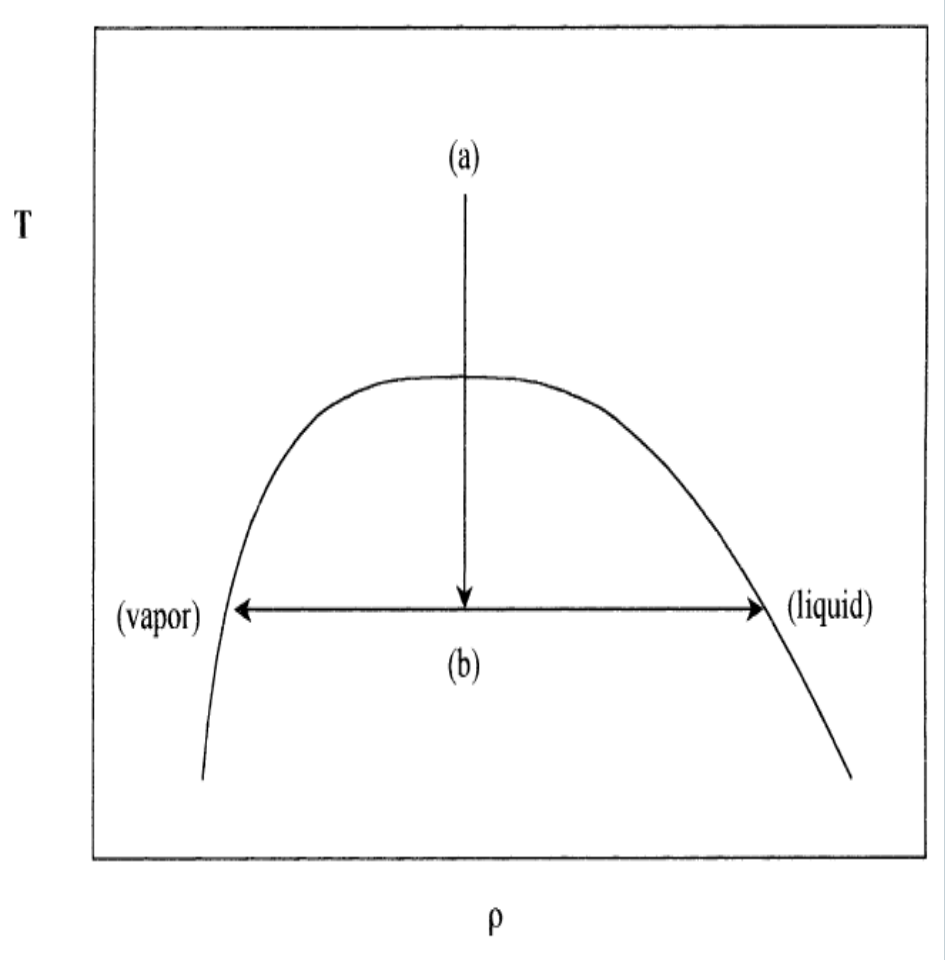
$$\mu = \left[1 - \frac{\Delta t}{\tau_P}(P - P_0)\right]^{1/3}$$

Temperature-Quench Molecular Dynamics

- Locating fluid phase coexistence through single canonical simulation in which the temperature is changed in a single time step, which is known as quenching.

- At this unstable state, the single phase is spontaneously separated into domains of coexisting phases.

Temperature-Quench Molecular Dynamics



Prepare the simulation system

Quench the system

Perform interface detection

Eliminate cells that containing interface

Determine the equilibrium properties

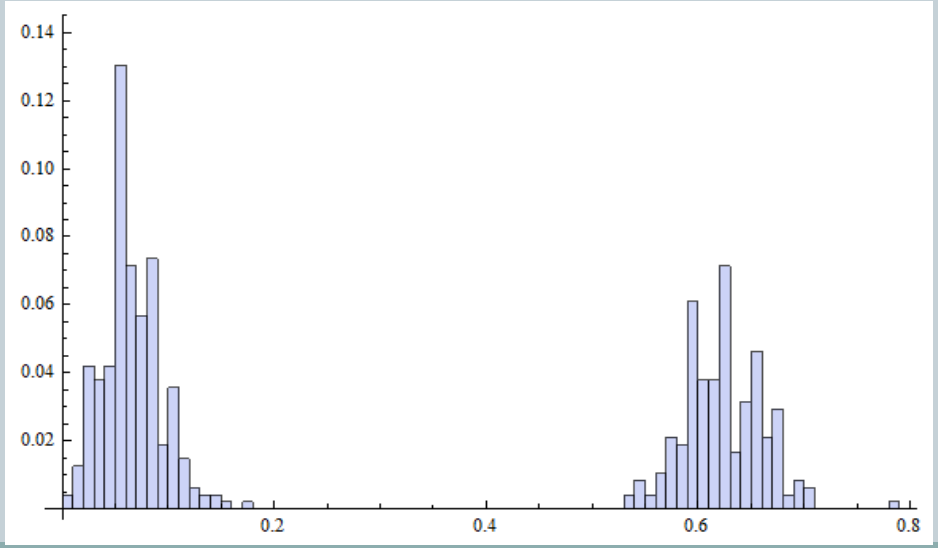
Generate phase coexistence curve

Temperature-Quench Molecular Dynamics

- Interface Detection
  - Divide the system into small sub-cells.
  - Local density for each sub-cell is determined.
- Eliminate cells that containing interface
  - Only collect histogram data in sub-cells that contain entirely one phase.
  - Define the number of neighbours a molecule will have within a fixed radius, i.e. upper (CNU) and lower (CNL) bound coordination numbers.
  - In vapour-liquid equilibria, particles in interface have neighbours lesser than particles in vapour phase, and greater than particles in the vapour phase.
  - Sub-cells that contain more than 15% “interfacial” particles are then excluded from the histogram count.

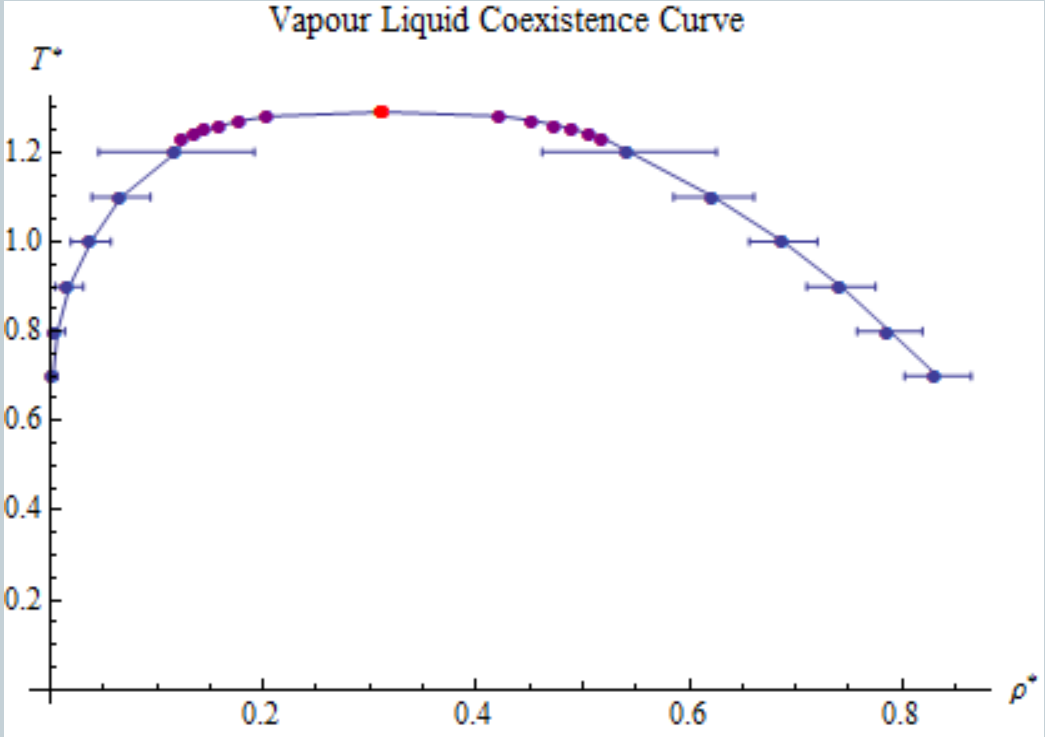
Temperature-Quench Molecular Dynamics

- Determination of Equilibrium Properties
  - Plot histogram of frequency versus density.
  - Two obvious peaks, corresponding to the vapour and liquid average densities
  - By using maximum likelihood analysis, density of each phase is determined by weighted average of the histogram method.



Results & Discussion : TQMD

- Phase Coexistence Curve
  - Vapour liquid coexistence curve for LJ system with 32,000 particles in 120,000-step-simulation with $r_c^* = 5$.



Results & Discussion : TQMD

- Comparison with GEMC

	TQMD			GEMC	
T*	ρ_v^*	ρ_l^*		ρ_v^*	ρ_l^*
0.7	0.00259387(4)	0.833345 (31)			
0.8	0.00662778(7)	0.788268(31)		0.0071(5)	0.79(1)
0.9	0.0178247(13)	0.742599(32)		0.016(2)	0.74(2)
1.0	0.0380098(19)	0.688202(32)		0.034(2)	0.69(1)
1.1	0.0664918(28)	0.622972(38)		0.063(6)	0.625(10)
1.2	0.118373(73)	0.543659(81)		0.117(7)	0.54(1)
1.2896(7)	0.313224(1)*	0.313224(1)*			

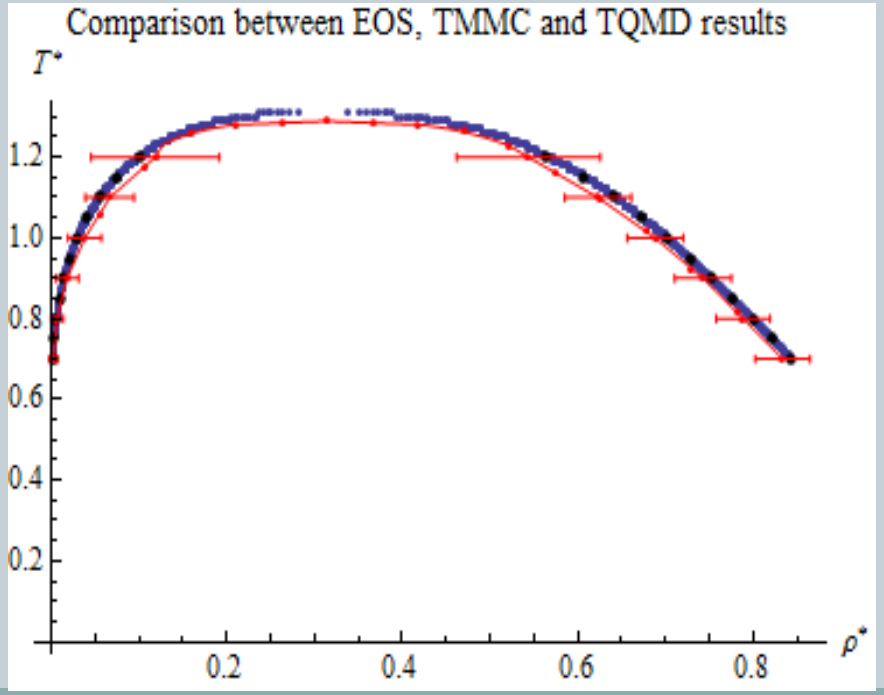
Results & Discussion : TQMD

- Comparison by Using Different Total Simulation Steps

	TQMD (120,000 steps)		TQMD (330,000 steps)	
T*	ρ_v^*	ρ_l^*	ρ_v^*	ρ_l^*
0.7	0.00259387(4)	0.00433121(30)	0.00261529(4)	0.836016(25)
0.8	0.00662778(7)	0.788268(31)	0.00691875(7)	0.786721(35)
0.9	0.0178247(13)	0.742599(32)	0.0171754(12)	0.743123(31)
1.0	0.0380098(19)	0.688202(32)	0.0349213(19)	0.686836(34)
1.1	0.0664918(28)	0.622972(38)	0.0644553(27)	0.626188(36)
1.2	0.118373(73)	0.543659(81)	0.115772(70)	0.549937(80)
	$T_c^* = 1.2896(7)$	$\rho_c^* = 0.313224(1)$	$T_c^* = 1.28969(12)$	$\rho_c^* = 0.313735(2)$

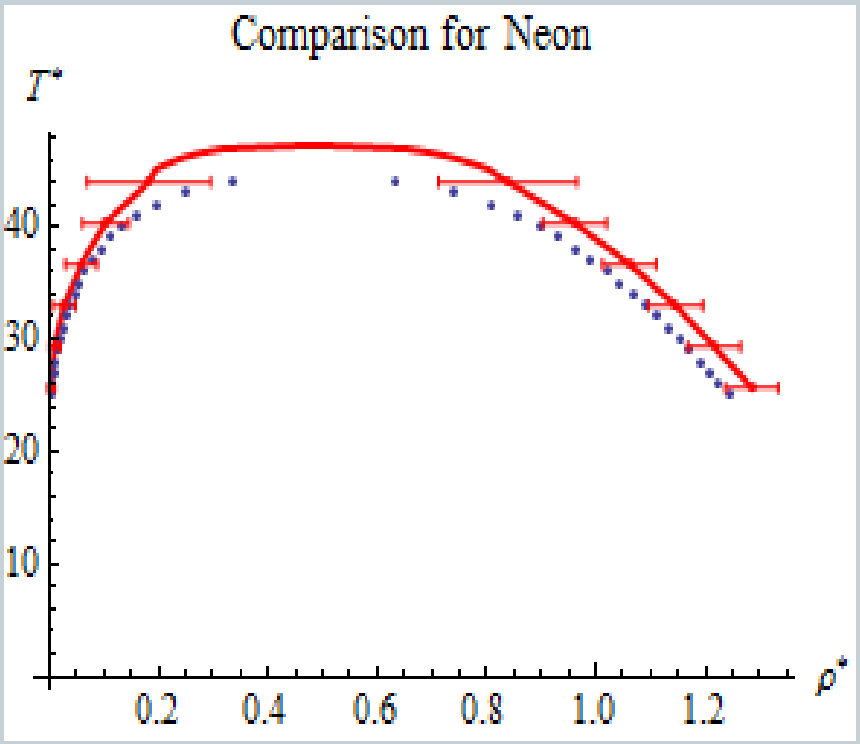
Results & Discussion : TQMD

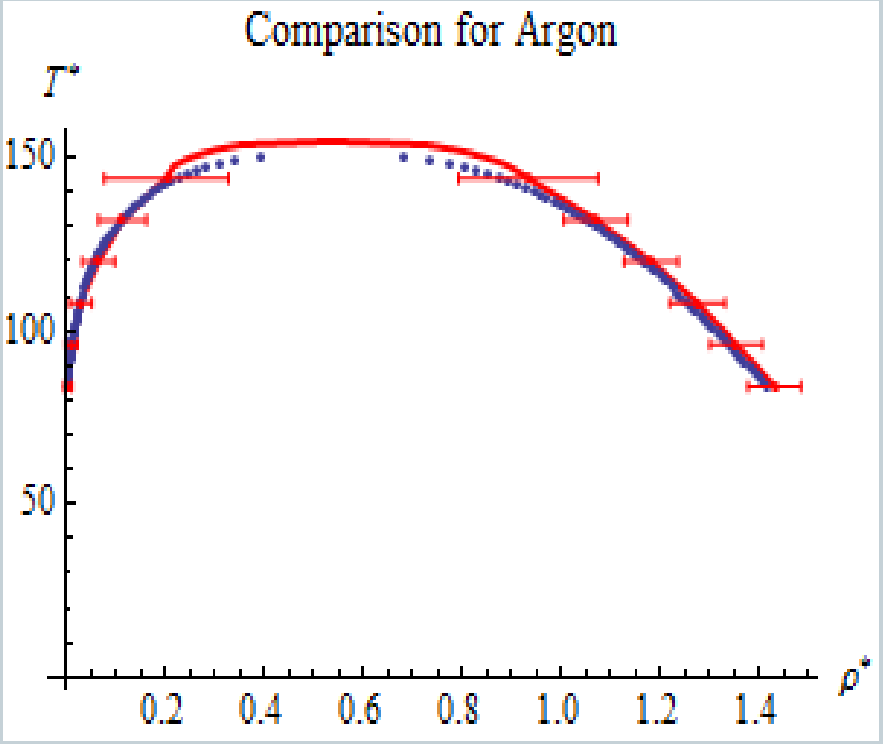
- Comparison by Using Different Methods
  - Johnson's equation of state (blue), grand-canonical transition-matrix Monte Carlo and histogram re-weighting (black) and TQMD (red).



Results & Discussion : TQMD

- Comparison with Standard Values for Noble Gases
  - Comparison between the vapour-liquid coexistence curve from simulation (red) and that from literature (blue).





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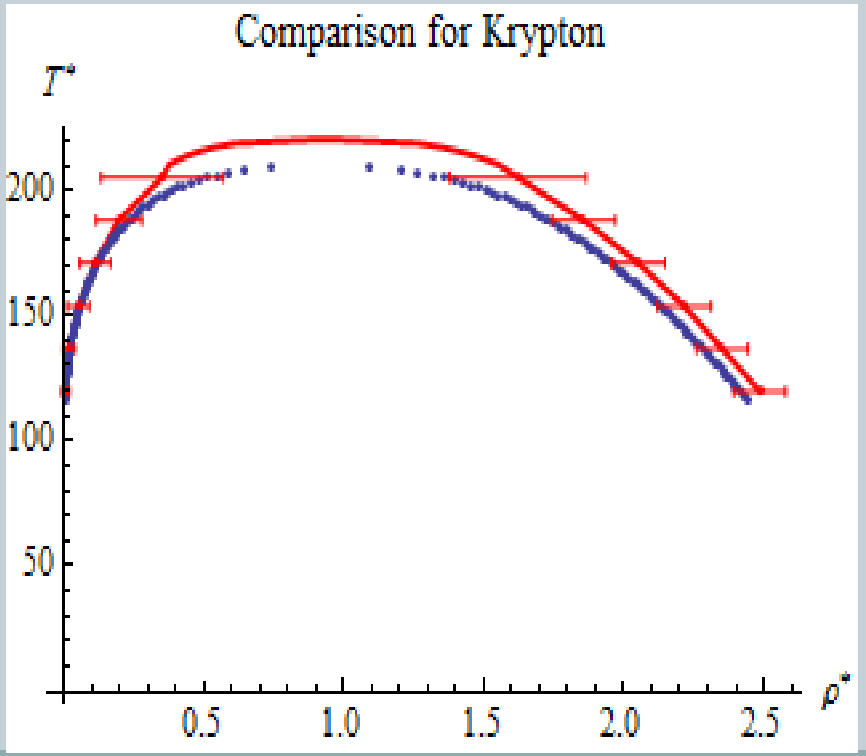
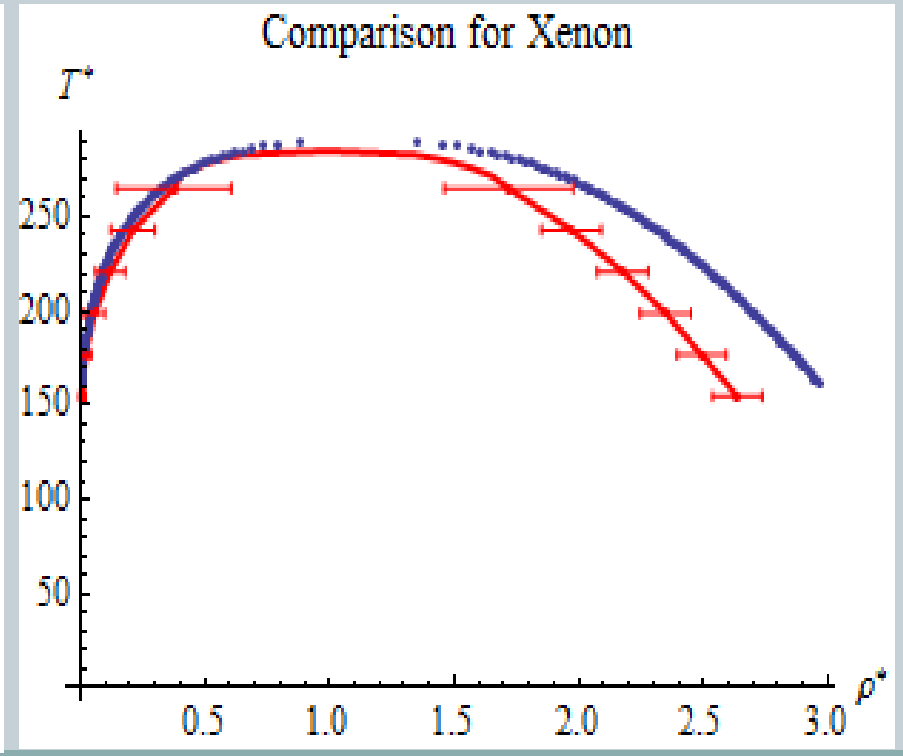
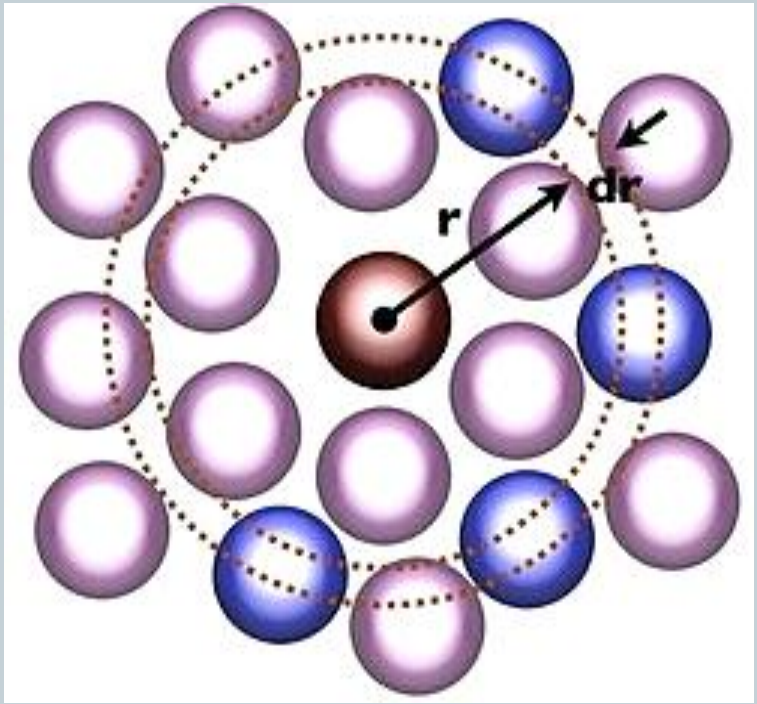




Radial Distribution Function



- Gives the probability of finding a particle in the distance *r* from another particle.
- The neighbours around each atom or molecule are sorted into distance bins.
- The number of neighbours in each bin is averaged over the entire simulation.
- The radial distribution function is usually plotted as a function of the interatomic separation *r*.
  - A peak indicates a particularly favored separation distance for the neighbors to a given particle.

Radial Distribution Function

- At small *r*, the radial distribution function is zero.
  - Effective width of the atoms, since they cannot approach any more closely.
- A number of obvious peaks appear.
  - The atoms pack around each other in 'shells' of neighbors.
- At high temperature the peaks are broad, at low temperature they are sharp.
  - Thermal motion,

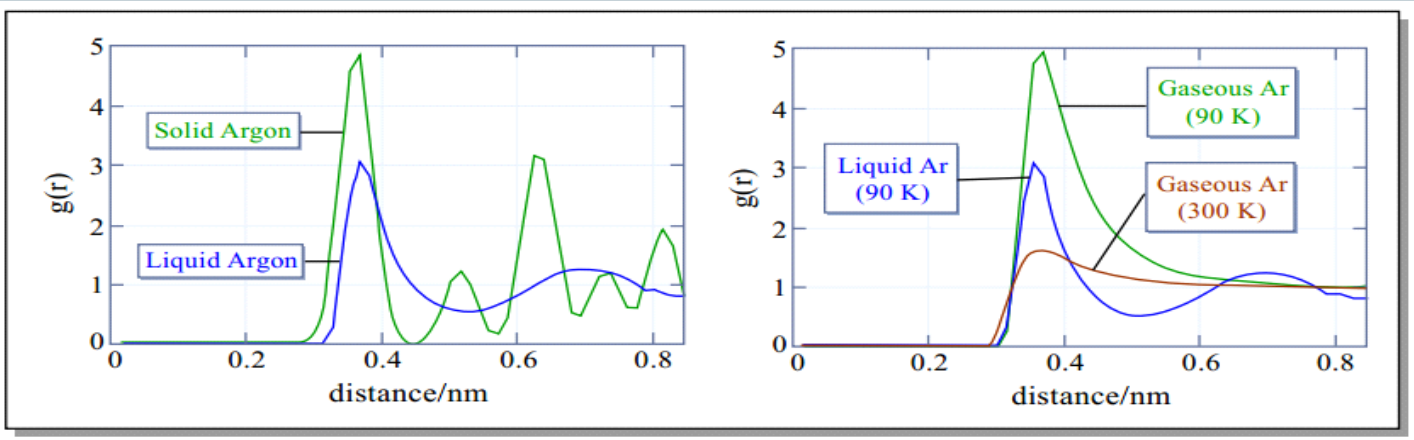
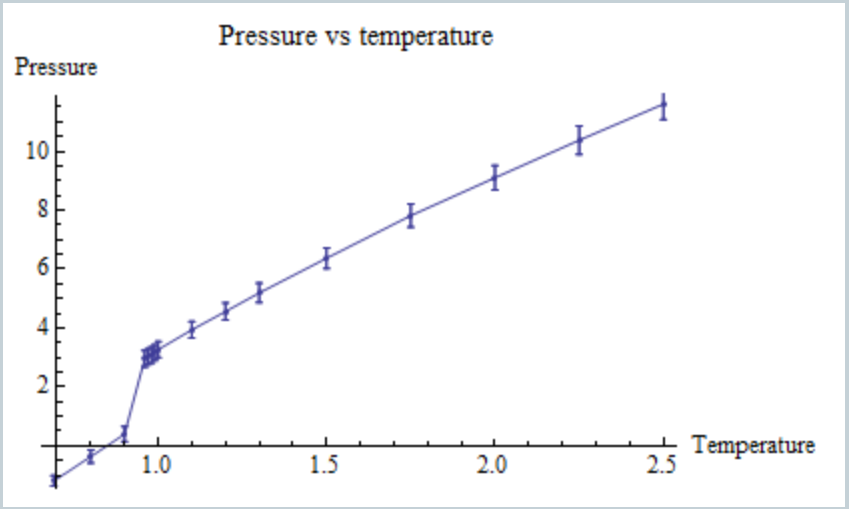
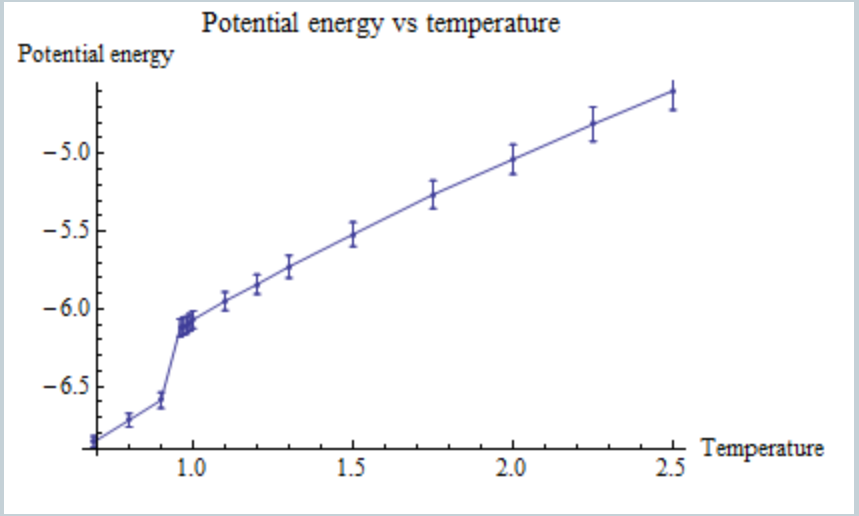


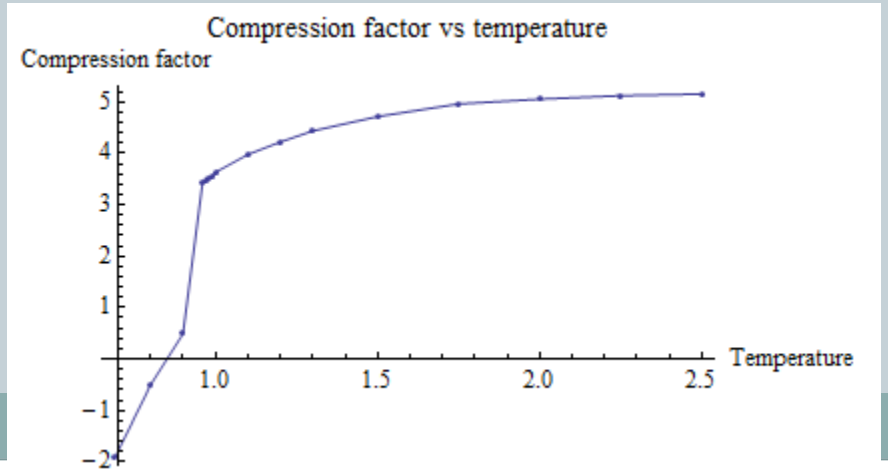
Image by MIT OpenCourseWare.

Properties of LJ Fluid

- Abrupt changes in gradient of graphs

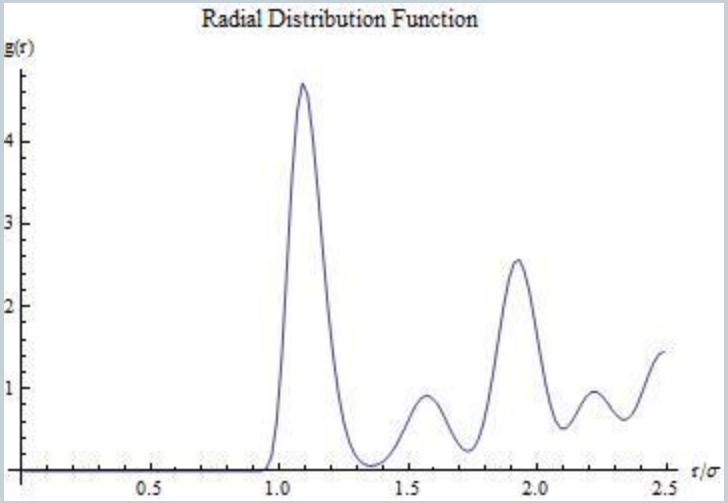


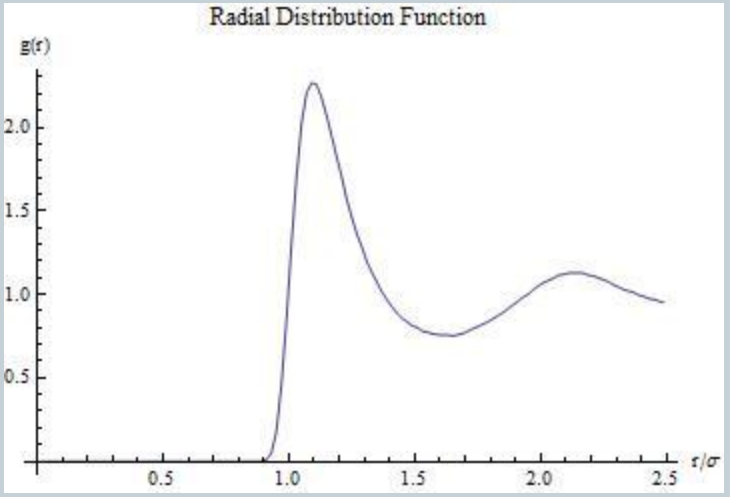


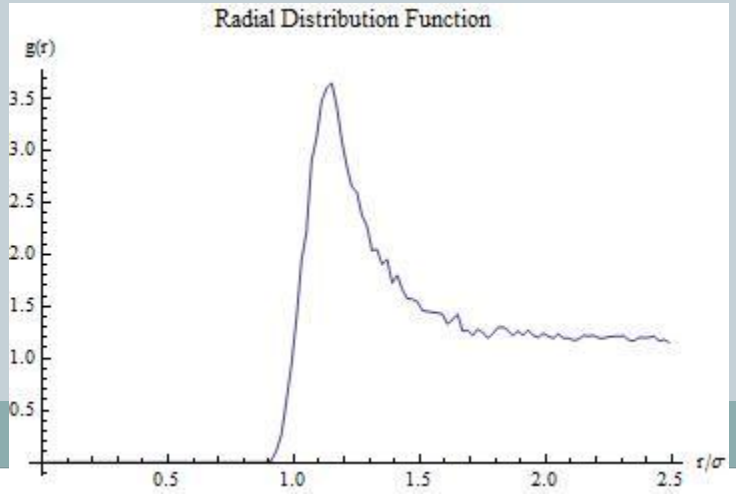


Properties of LJ Fluid

- Radial Distribution Function

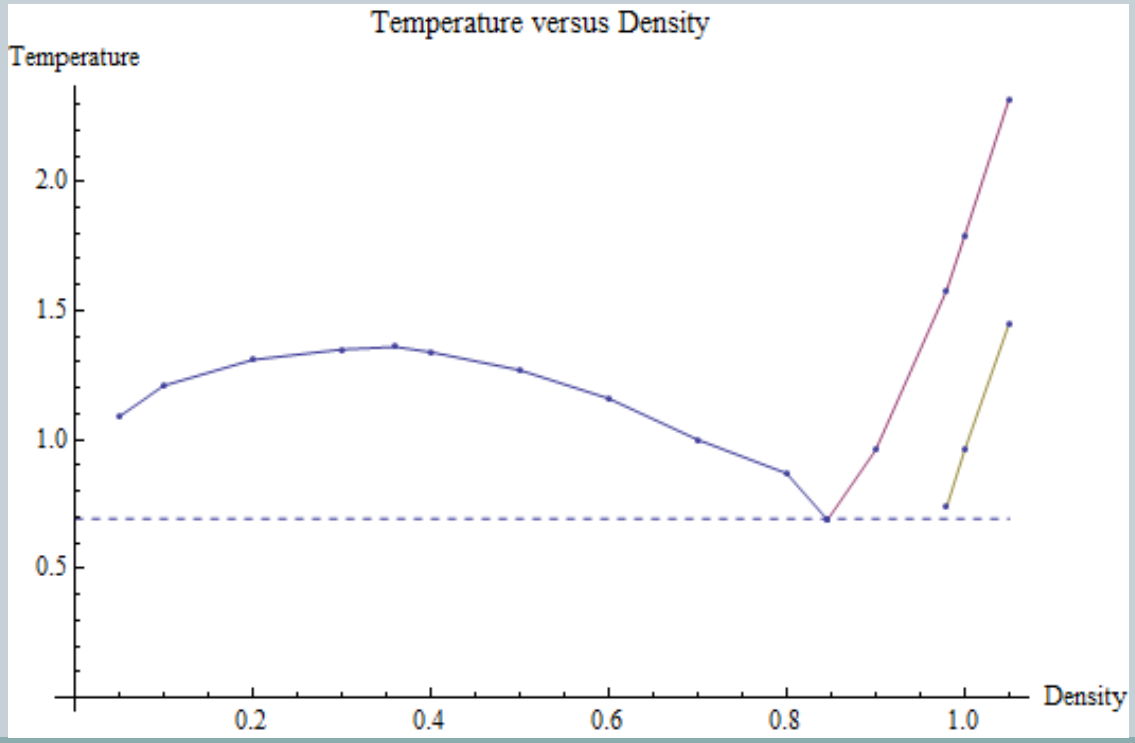






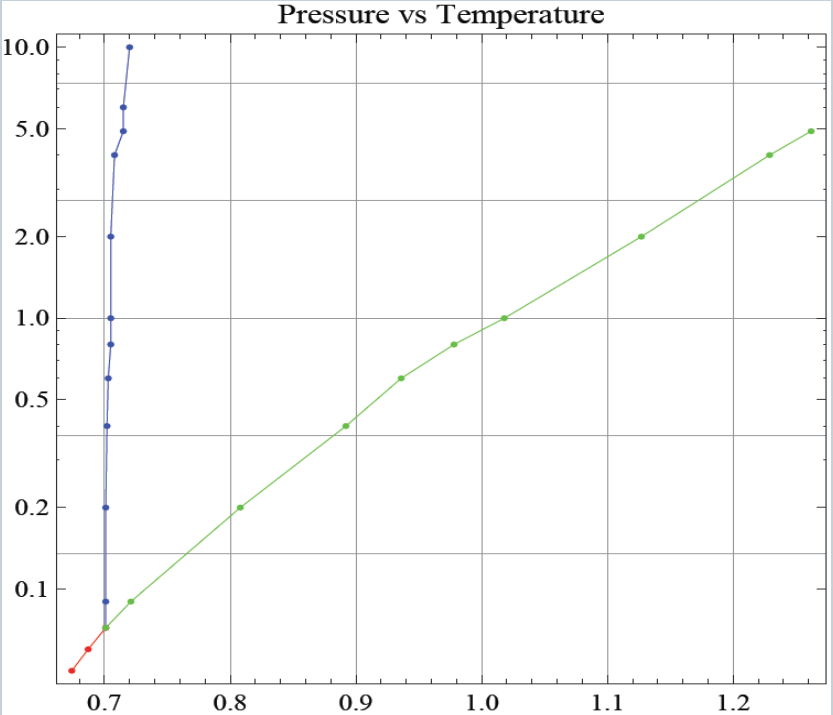
Relation between Temperature and Density

- NVT ensemble
  - Simulation is repeated for various values of density.
- Phase diagram of temperature against density



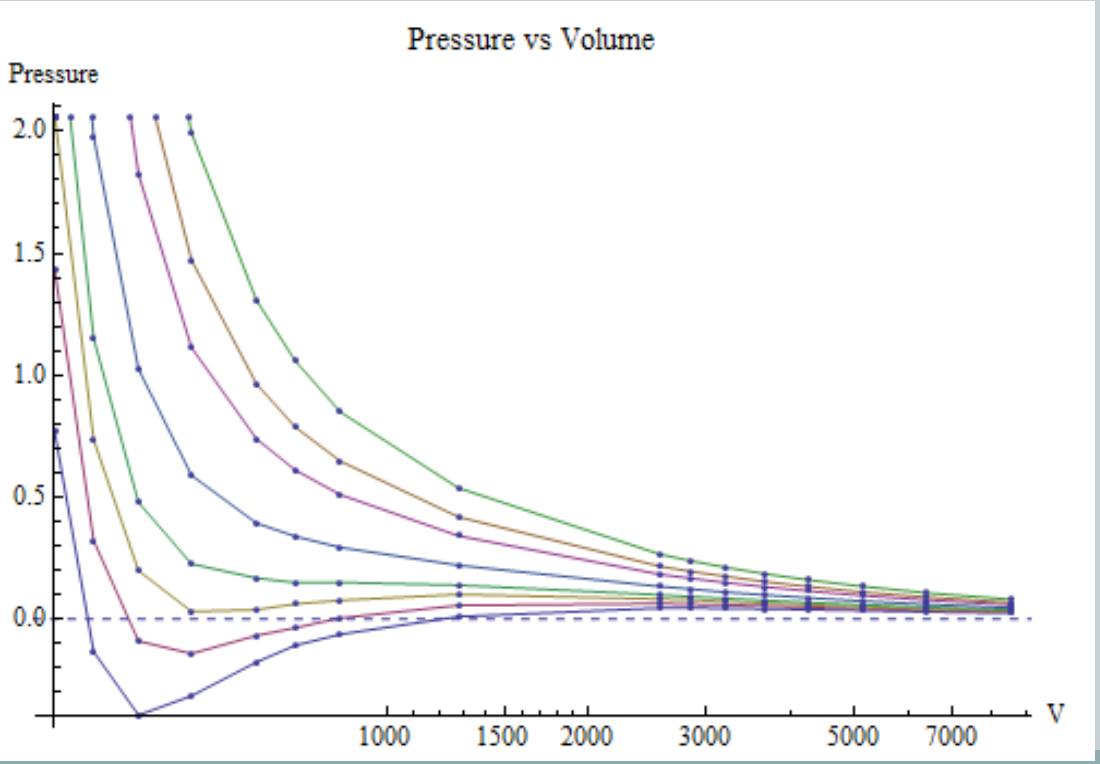
Relation between Pressure and Temperature

- NPT ensemble
  - Simulation is repeated for various values of pressure.
- Phase diagram of pressure against temperature

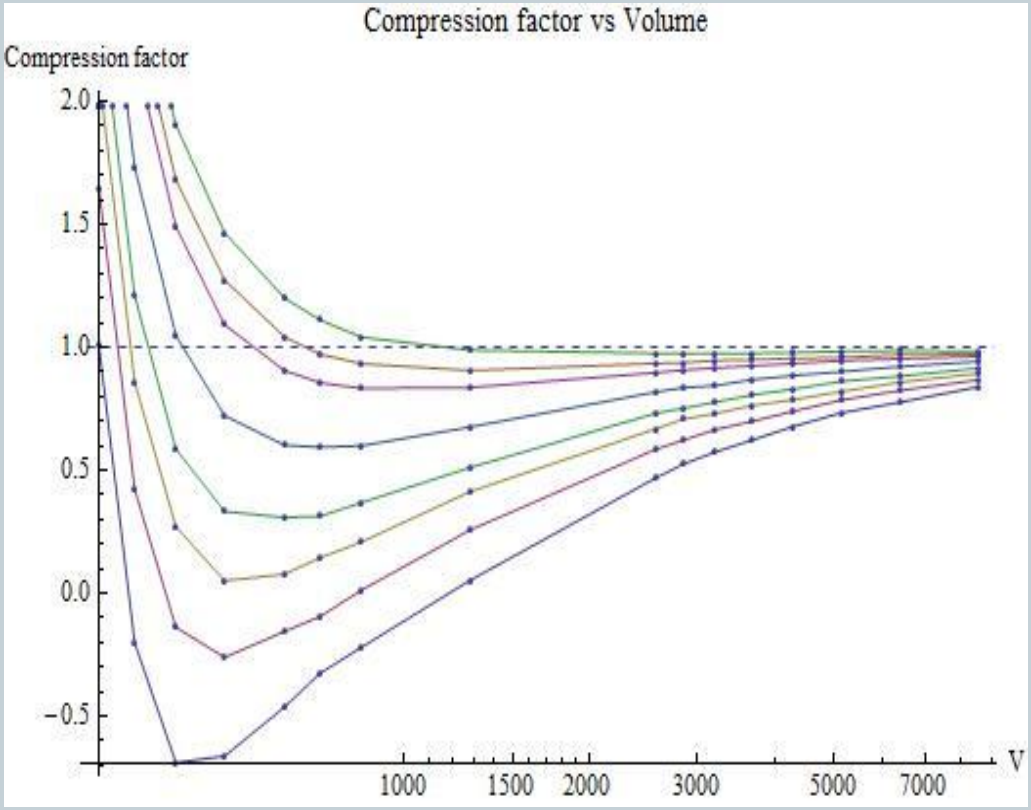


Relation between Pressure and Volume

- Simulation is repeated for various values of temperature by scaling the density for each temperature.



Compression Factor



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

- Describe the deviations of gases from ideality.
- When a gas obeys ideal gas law, $Z = 1$.

Conclusion

- Phase coexistence curve is successfully generated by using TQMD.
  - Results obtained made good agreement with the results obtained from the literatures.
  - TQMD can be a suitable method to study the phase equilibria of an unfamiliar system.
- Properties of LJ fluid is studied and phase diagrams are successfully generated.
  - The system behaves like an ideal gas when the system has a large volume at high temperature.
  - The system built fulfils the requirement to build a model of the real system.

The End

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