Imperfect Gases

(Non-ideal or Real Gases)

The Compression Factor

One way to represent the relationship between ideal and real gases is to plot the deviation from ideality as the gas is compressed (i.e. as the pressure is increased).
The compression factor is defined as:

$$Compression\ Factor\ = \frac{Molar\ volume\ of\ gas}{Molar\ volume\ of\ perfect\ gas}$$

Written in symbols this becomes:

$$Z = \frac{V_m}{V_m^{perfect}} = \frac{PV_m}{RT}$$

Note that perfect gases are also called ideal gases.
Imperfect gases are sometimes called real gases.

The Compression Factor

A plot of the compression factor reveals that many gases exhibit Z < 1 for low pressure. This indicates that attractive forces dominate under these conditions.

As the pressure increases Z crosses 1 and eventually becomes positive for all gases. This indicates that the finite molecular volume leads to repulsions between closely packed gas molecules. These repulsions are not including the ideal gas model.

Attractive
Region

Repulsive
Region
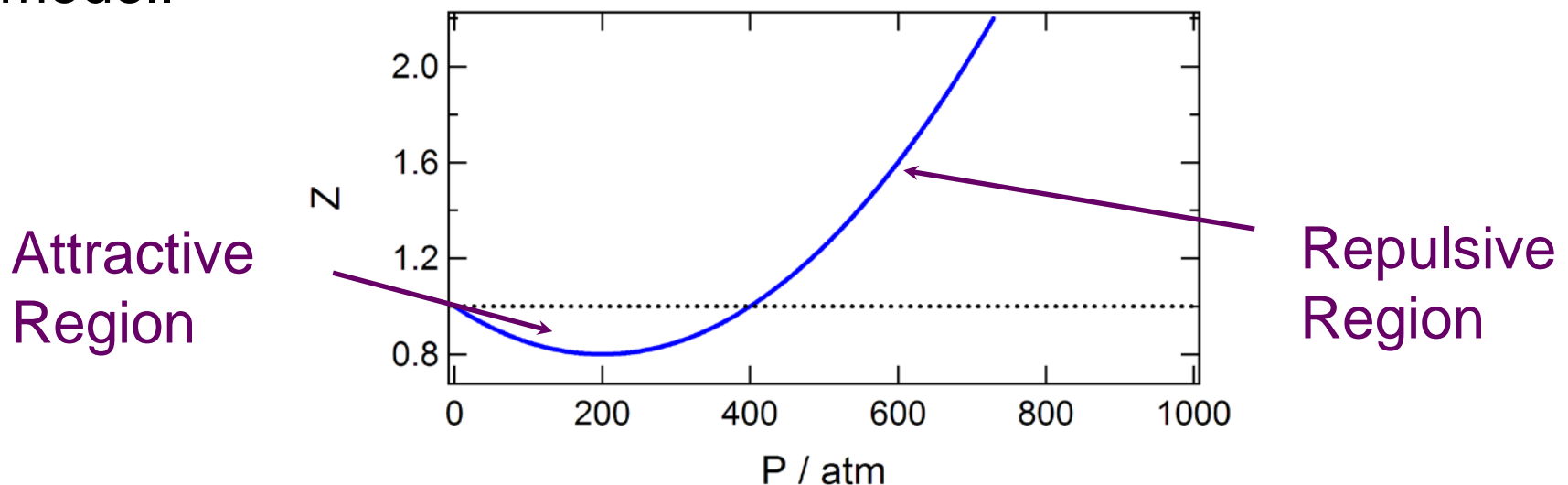
The Virial Expansion

One way to represent the deviation of a gas from ideal (or perfect) behavior is to expand the compression factor in powers of the inverse molar volume. Such an expansion is known as a virial expansion.

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \ldots$$

The coefficients B, C etc. are known as virial coefficients.
For example, B is the second virial coefficient.
Virial coefficients depend on temperature. From the preceding considerations we see the B < 0 for ammonia, ethene, methane and B > 0 for hydrogen.

The Virial Equation of State

We write Z in complete form as:

$$\frac{PV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots$$

An then solve for the pressure:

$$P = \frac{RT}{V_m}\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots\right)$$

This expression is known as the virial equation of state. Note that if B, C etc. are all equal to zero this is just the ideal gas law. However, if these are not zero then this equation contains corrections to ideal behavior.

Relating the microscopic to the macroscopic

Real gases differ from ideal gases in two ways.
First they have a real size (extent). The excluded volume results in a repulsion between particles and larger pressure than the corresponding ideal gas (positive contribution to compressibility).
Secondly, they have attractive forces between molecules. These are dispersive forces that arise from a potential energy due to induced-dipole induced-dipole interactions.
We can relate the potential energy of a particle to the terms in the virial expansion or other equation of state. While we will not do this using math in this course we will consider the graphical form of the potential energy functions.

Hard Sphere Potential

A hard sphere potential is the easiest potential to parameterize. The hard sphere diameter corresponds to the interatomic spacing in a closest packed geometry such as that shown for the noble gas argon.

The diameter can be estimated from the density of argon in the solid state. The hard sphere potential is widely used because of its simplicity.

$u(r) = \infty$ $r < \sigma$
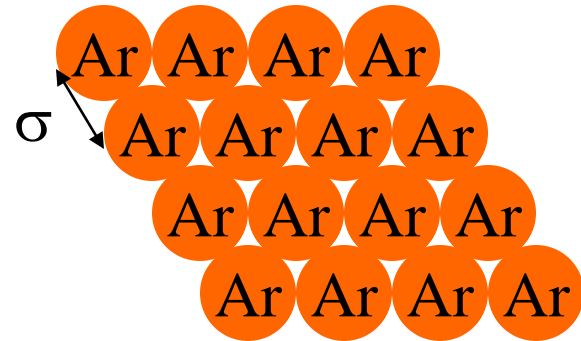
$u(r) = 0$ $r > \sigma$
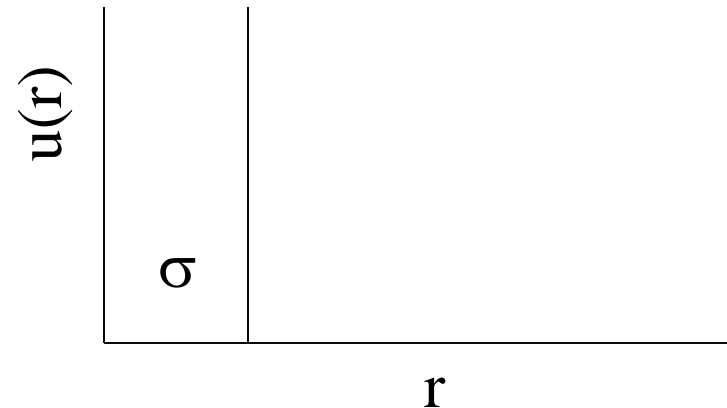
The Hard Sphere Equation of State

As a first correction to the ideal gas law we can consider the fact that a gas has finite extent. Thus, as we begin to decrease the volume available to the gas the pressure increases more than we would expect due to the repulsions between the spheres of finite molar volume, b, of the spheres.
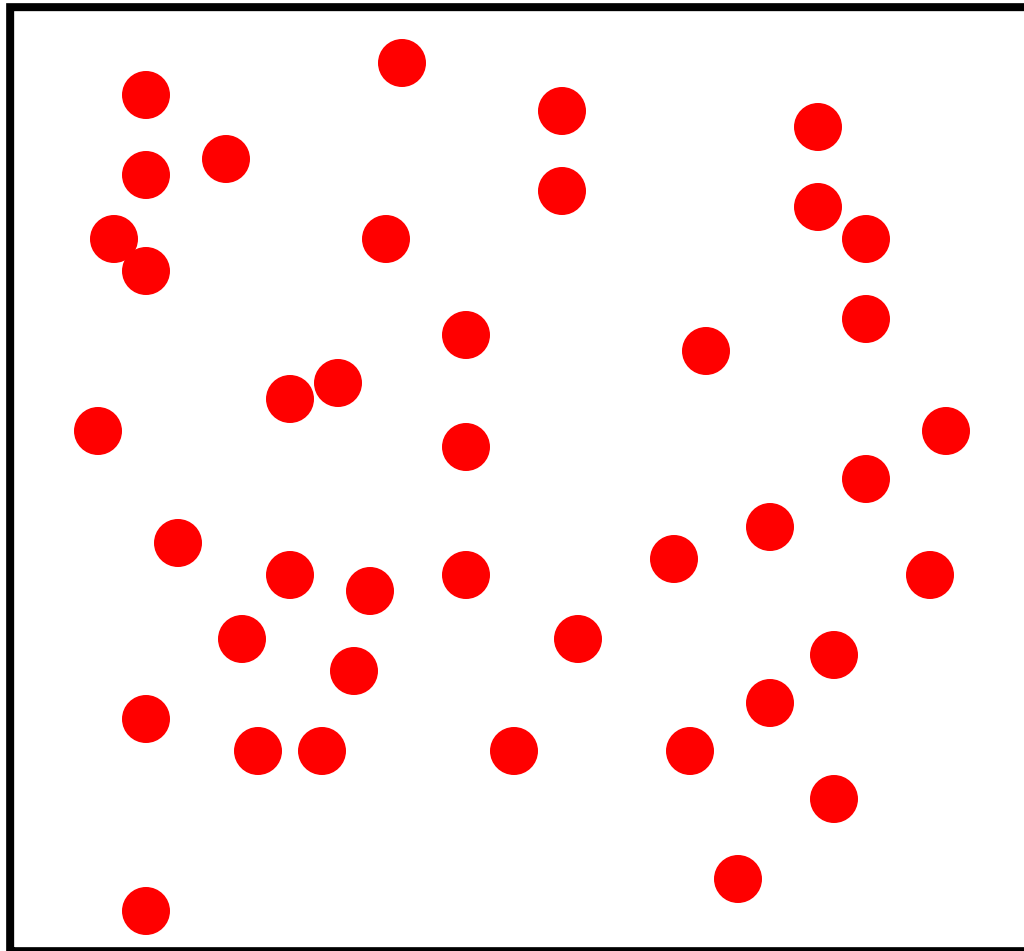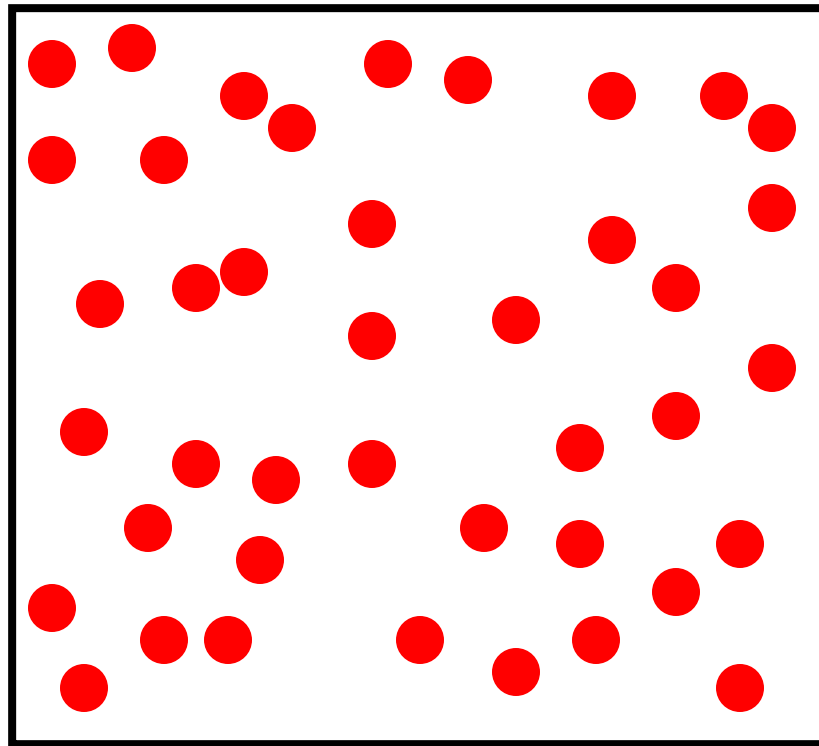
$$P = \frac{nRT}{V - nb}$$

Gas molecule of volume B

The Hard Sphere Model

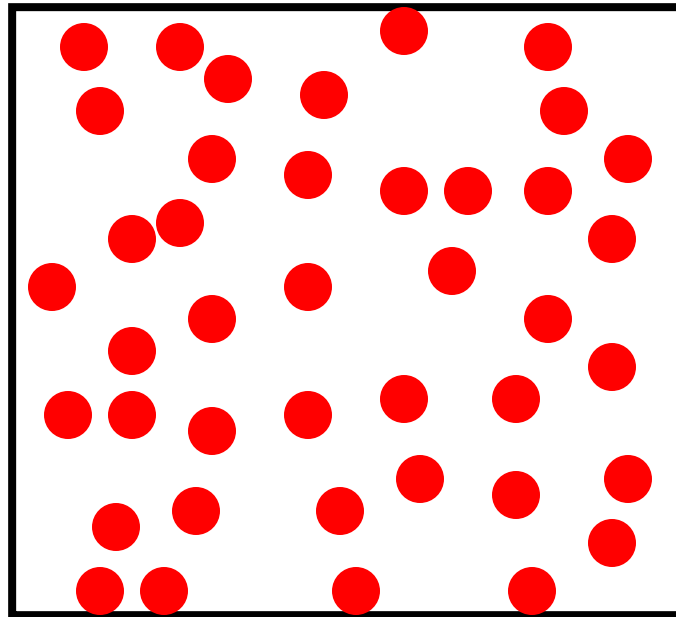Low density: These are ideal gas conditions

The Hard Sphere Model

Increasing density: the volume is V
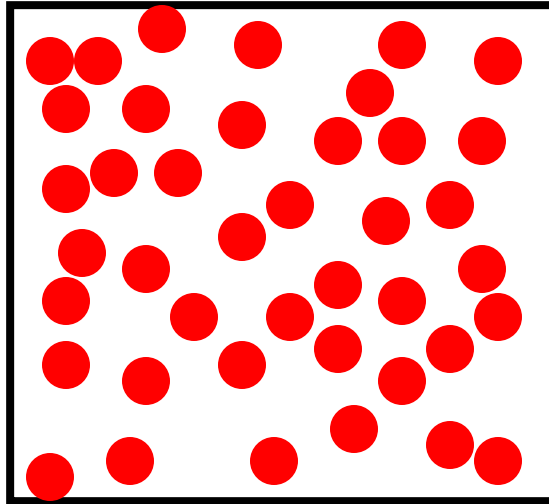b is the molar volume of the ● spheres.

The Hard Sphere Model
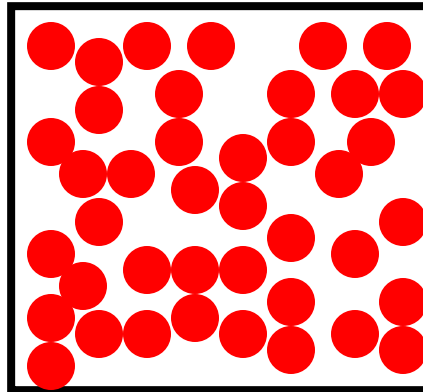
Increasing density

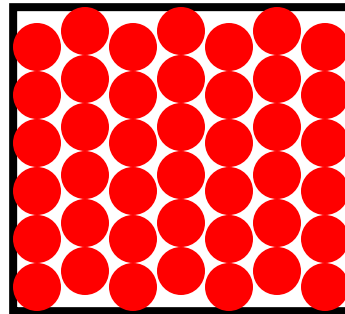# The Hard Sphere Model

Increasing density

The Hard Sphere Model

High density: At sufficiently high density the gas becomes a high density fluid or a liquid.

The Hard Sphere Model

Limiting density: at this density the hard spheres have condensed into an ordered lattice. They are a solid. The "gas" cannot be compressed further.

The volume is nb
When the gas is completely compressed.

If we think about the density in each of these cases we can see that it increases to a maximum value.

Lennard-Jones Potential Function

The Lennard-Jones potential is a most commonly used potential function for non-bonding interactions in atomistic computer simulations.

$$V^{LJ}(R) = 4\varepsilon\left(\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right)$$

The potential has a long-range attractive tail $-1/r^6$, and negative well depth ε, and a steeply rising repulsive wall at R = σ. Typically the parameter σ is related to the hard sphere diameter of the molecule. For a monoatomic condensed phase σ is determined either from the solid state or from an estimate of the packing in dense liquids. The well depth e is related to the heat of vaporization of a monatomic fluid. For example, liquid argon boils at ~120K at 1 atm. Thus, ε ~ kT or 1.38×10^{-23} J/K(120 K) = 1.65×10^{-21} J. This also corresponds to 1.03 kJ/mol.

Graphical Representation L-J Potential

The L-J potential function has a steep rise when r < σ. This is the repulsive term in the potential that arises from close contacts between molecules. The minimum is found for Rmin = $2^{1/6}$ σ. The well depth is ε in units of energy.

Reduced Lennard-Jones Potential
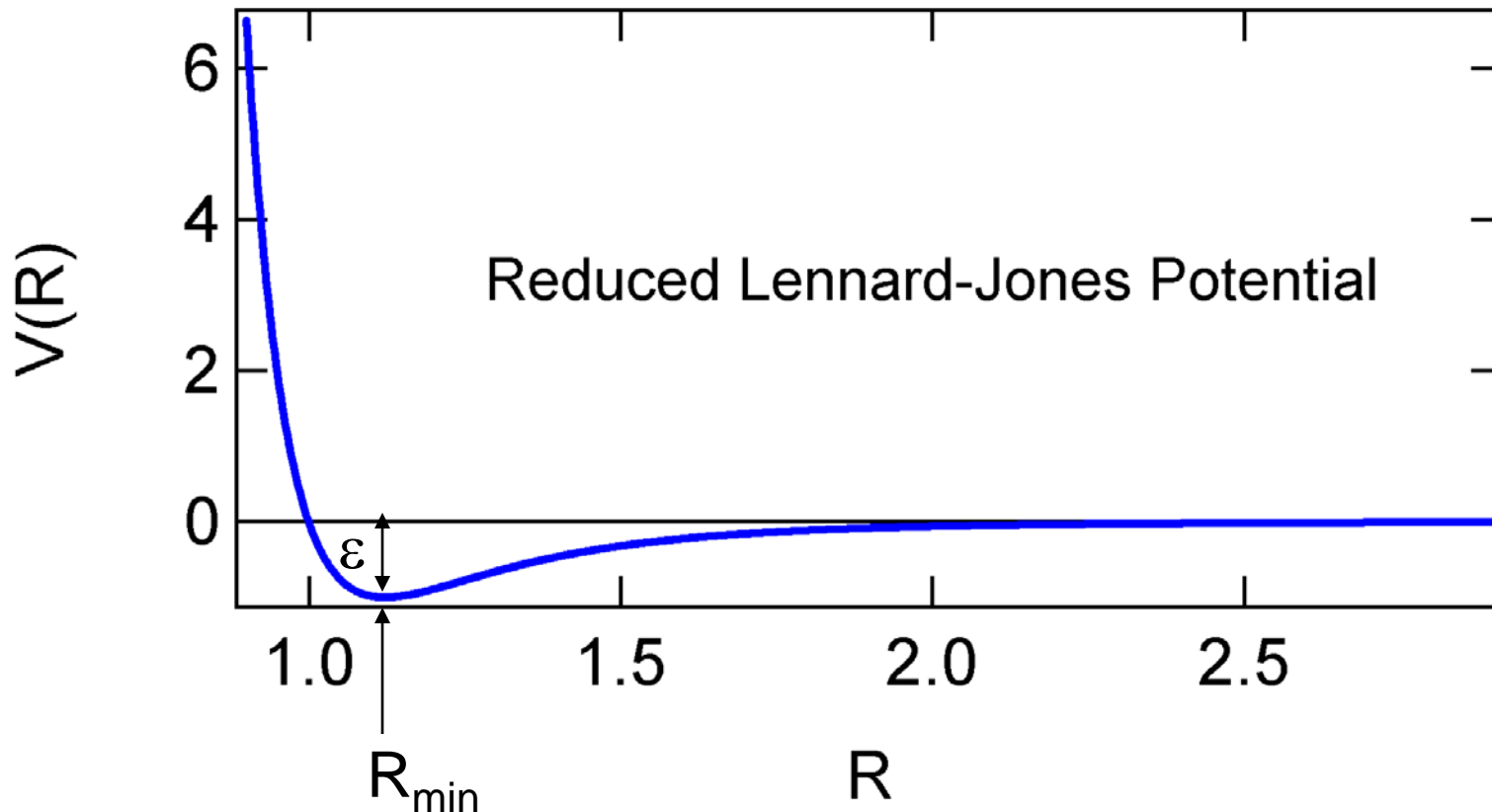
The van der Waal's Equation of State

The microscopic terms ε and σ in the L-J potential can be related to the a and b parameters in the van der Waal's equation of state below.

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

The significance of b is the same as for the hard sphere potential. The parameter a is related to the attractive force between molecules. It tends to reduce the pressure compared to an ideal gas.

The van der Waal's Equation of State in terms of molar volume

Recall that $V_m = V/n$ so that the vdW equation of state becomes:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

We can plot this function for a variety of different temperatures. As we saw for the ideal gas these are isotherms. At sufficiently high temperature the isotherms of the vdW equation of state resemble those of the ideal gas.

The argon phase diagram

For argon
$T_c = 150.8$ K
$P_c = 4934.5$ Pa
$V_c = 74.9$ cm^3/mol
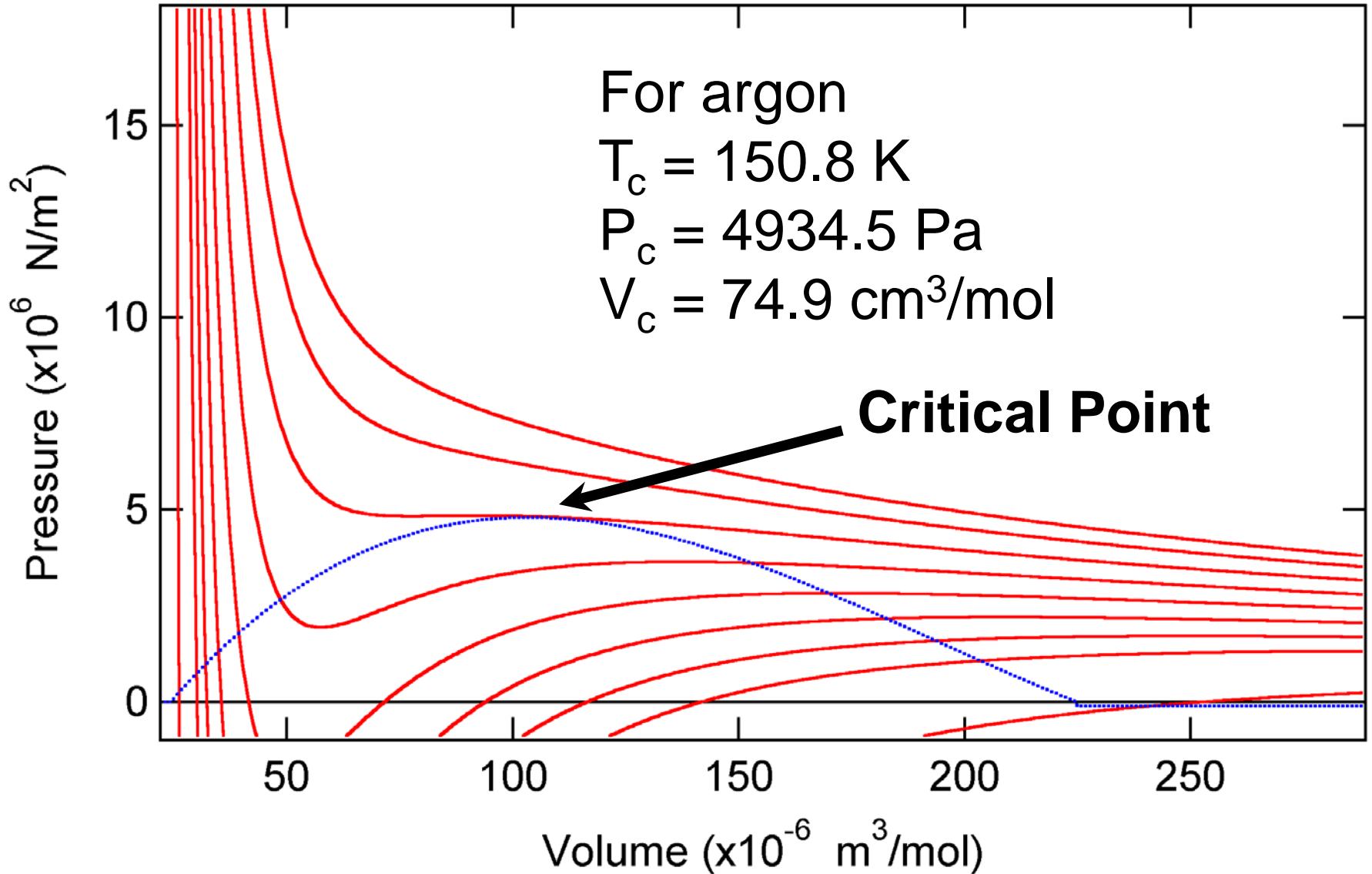
Critical Point

Significance of the critical point

Note that the vdW isotherms look very different from those of the ideal gas below the critical point. Below the critical point there are two possible phases, liquid and gas. The liquid phase is found at small molar volumes. The gas phase is observed at larger molar volumes. The shape of the isotherms is not physically reasonable in the transition region between the phases. Note that the implication is that there is a sudden change in volume for the phase transition from liquid to gas.

View of the liquid region
of the argon phase diagram
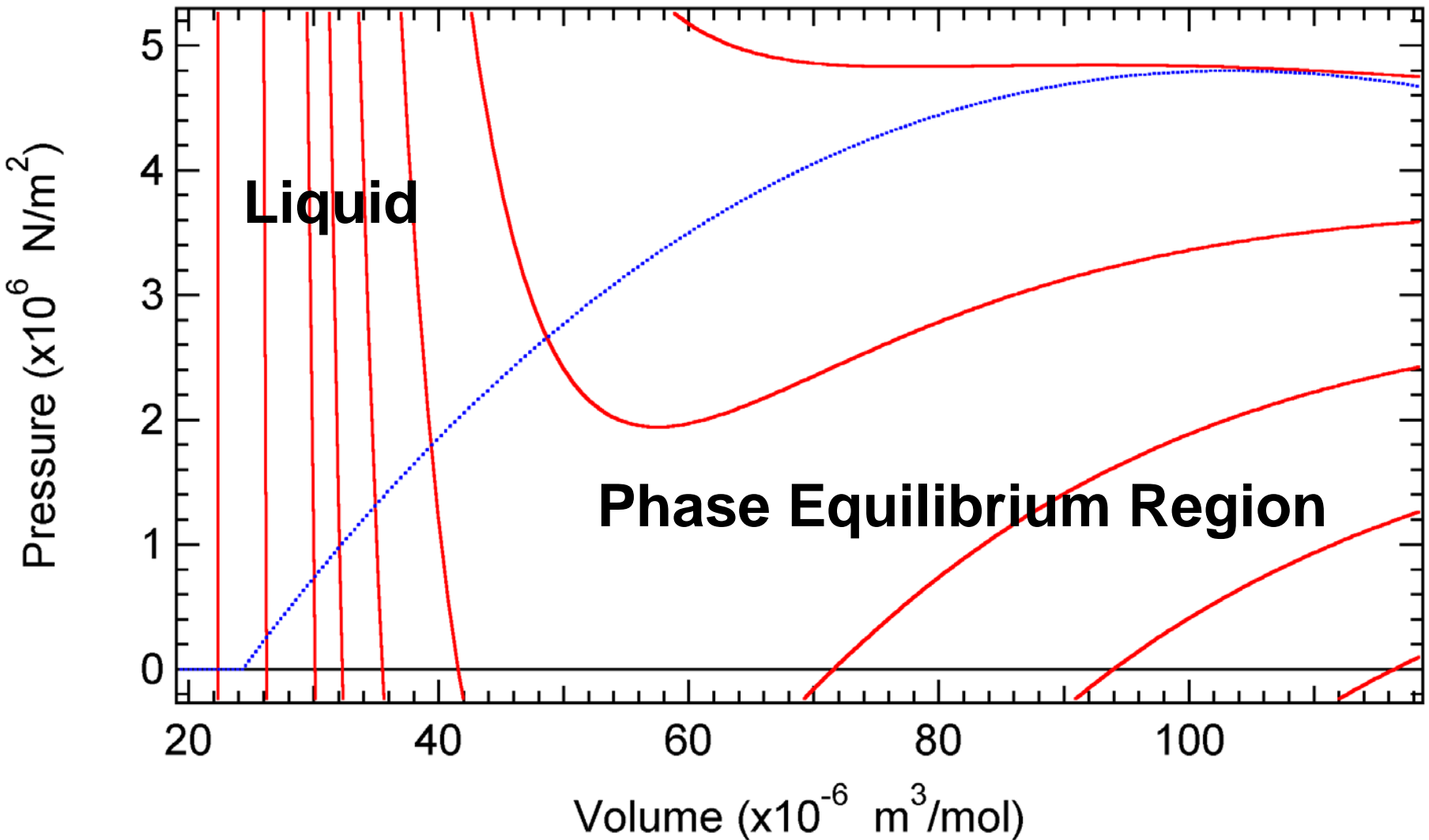
Critical Parameters

The critical parameters can be derived in terms of the vdW a and b parameters as well as the gas constant R.

The derivation can use calculus since the derivative of the vdW equation of state is zero at the critical point.

Given that this is also an inflection point the second derivative is also zero.

$$P_c = \frac{a}{27b^2}$$

$$T_c = \frac{8a}{27Rb}$$

$$V_c = 3b$$