Real Gases

The equations that we have derived
cannot describe liquids and solids.

So far, we have only consider ideal gases.

Let us consider deviations from the ideality of gases:
in real gases interatomic forces are present

10.1 Interatomic Forces

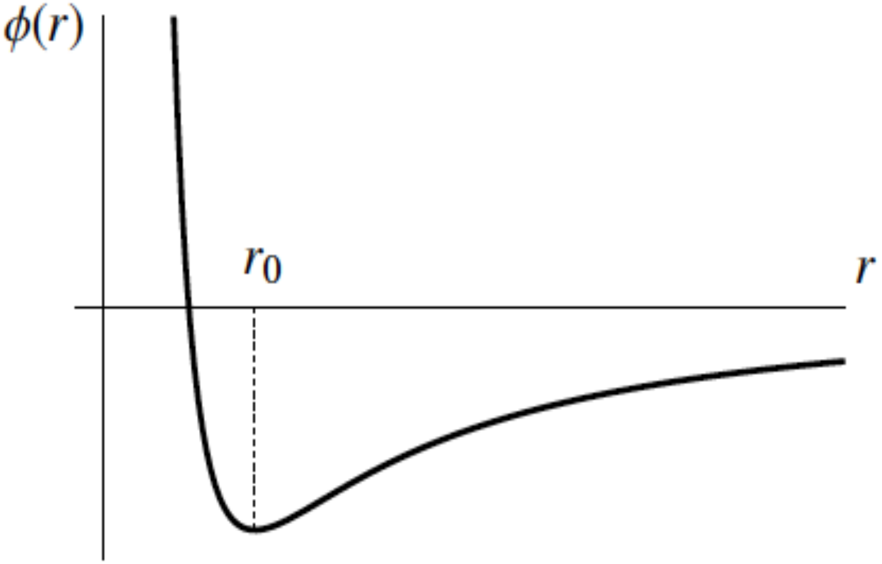
Interatomic forces are the forces that real atoms exert on each other

When very close they repel,
whereas at large distances the forces become weakly attractive.

A classical picture for the long-range attraction is that fluctuations in the electron distribution give a dipole moment to an atom which induces a similar dipole moment in another atom and the two are attracted.

The repulsion can be viewed in terms of the electrostatic repulsion of the nuclei in combination with the Pauli exclusion principle.

The interaction between atoms can be represented by the potential energy $\Phi(r)$ between atoms separated by distance r.
The force f between atoms is related to the potential energy
by $f = -d\Phi/dr$
And $f > 0$ is a repulsive force,
so the negative gradient at short distance corresponds to repulsion.



A schematic figure of the potential energy between two atoms as a function of distance between them.
r_0 denotes the equilibrium separation.

potential energy $\Phi(r)$ between atoms separated by distance r

force f between atoms is $f = -d\Phi/dr$

10.2 The van der Waals equation

The van der Waals equation is a modification of the ideal gas equation of state
to approximate the effects of interatomic forces:

- the short-range repulsive force reduces the available volume
- the attractive force reduces the pressure

Consider N molecules in a volume V.

Each occupies a volume that we call b, therefore the available volume becomes (V - Nb).
We can estimate b, considering the zone around a molecule in which no other centres of molecules can lie.
For spherical molecules of radius r this is a sphere of radius 2r, and volume $4\pi(2r)^3/3$.
To avoid double counting (we are counting pairs of molecules and want to consider each pair only once), we divide this volume by 2 and obtain: $b = 4v_m$ where v_m is the volume of one molecule. With the correction to the volume, the ideal gas equation becomes:

$$P(V - Nb) = NkT$$

The reduced volume accounts for the short-range repulsion and increases the pressure for a given V

The attractive forces act to reduce the pressure.

Imagine a molecule hitting the wall of its container: it feels a general attractive force towards the rest of the molecules which will reduce its speed as it approaches the wall.

Any forces exerted by atoms in the wall are irrelevant because if they attract for example, then while approaching atoms are accelerated towards the wall, an equal but opposite force is felt by the wall which is cancelled on average by the collision of the speeded-up atoms.

The correction to P is proportional to the collision rate per unit area which is proportional to (N/V).

The force decelerating each molecule will also depend upon the density of molecules, N/V, and thus we end with a correction factor of the form $(N/V)^2 a$ where a is a constant.

This then leads to an equation of the form:

van der Waals equation

$$\boxed{\left(P + N^2\frac{a}{V^2}\right)(V - Nb) = NkT}$$

The constants *a* and *b* are the van der Waal's coefficients:

a depends upon the long-range attractive forces,
b depends upon the short-range repulsive forces which define the "size" of an atom.

If we consider the number of moles n_m,
instead of the number of molecules N and rescale *a* and *b* accordingly:

$$\left(P + n_m^2 \frac{a}{V^2}\right)(V - n_m b) = n_m RT$$

Let us now consider the expression for the Helmoltz Free Energy:

$$F = U - TS$$

The potential of a molecule due to other molecules in a small volume dV at distance r is:

$$\mathrm{d}u = \phi(r)n(r)\,\mathrm{d}V$$

and assuming that the number density n is constant, except for r < D, where D is the diameter of the molecules when n = 0, then:

$$u = n\int_D^\infty \phi(r)\,\mathrm{d}V = -2an$$

↓

we set the integral to be -2*a*

The total change in U can thus be written as:

$$\Delta U = \frac{N}{2}(-2an) = -\frac{N^2 a}{V}$$

We are dividing by 2 to avoid double counting the effect of each molecule

⬇

The total energy is:

$$U = \frac{3}{2}NkT - \frac{N^2 a}{V}$$

The entropy is:

$$\begin{aligned} S &= S_0 + n_m C_V \ln T + n_m R \ln(V - Nb), \\ &= S_0 + \frac{3}{2}Nk \ln T + Nk \ln(V - Nb), \end{aligned}$$

Assuming a monoatomic $C_v = 3R/2$, the Helmoltz Free Energy becomes:

$$\begin{aligned} F &= U - TS, \\ &= \frac{3}{2}NkT - \frac{N^2 a}{V} - \frac{3}{2}NkT\ln T + NkT\ln(V - Nb) - TS_0 \end{aligned}$$

We can thus extract the pressure considering:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\frac{N^2 a}{V^2} + \frac{NkT}{V - Nb}$$

⬇

$$\left(P + \left(\frac{N}{V}\right)^2 a\right)(V - Nb) = NkT$$

van der Waals equation obtained via mean-field theory

10.2.1 P-V diagrams of a van der Waals gas

let's see how the van der Waals equation differs from the ideal gas case

For one mole, the van der Waals equation becomes:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT.$$

Note that as V → ∞, this tends towards the ideal gas equation as expected.

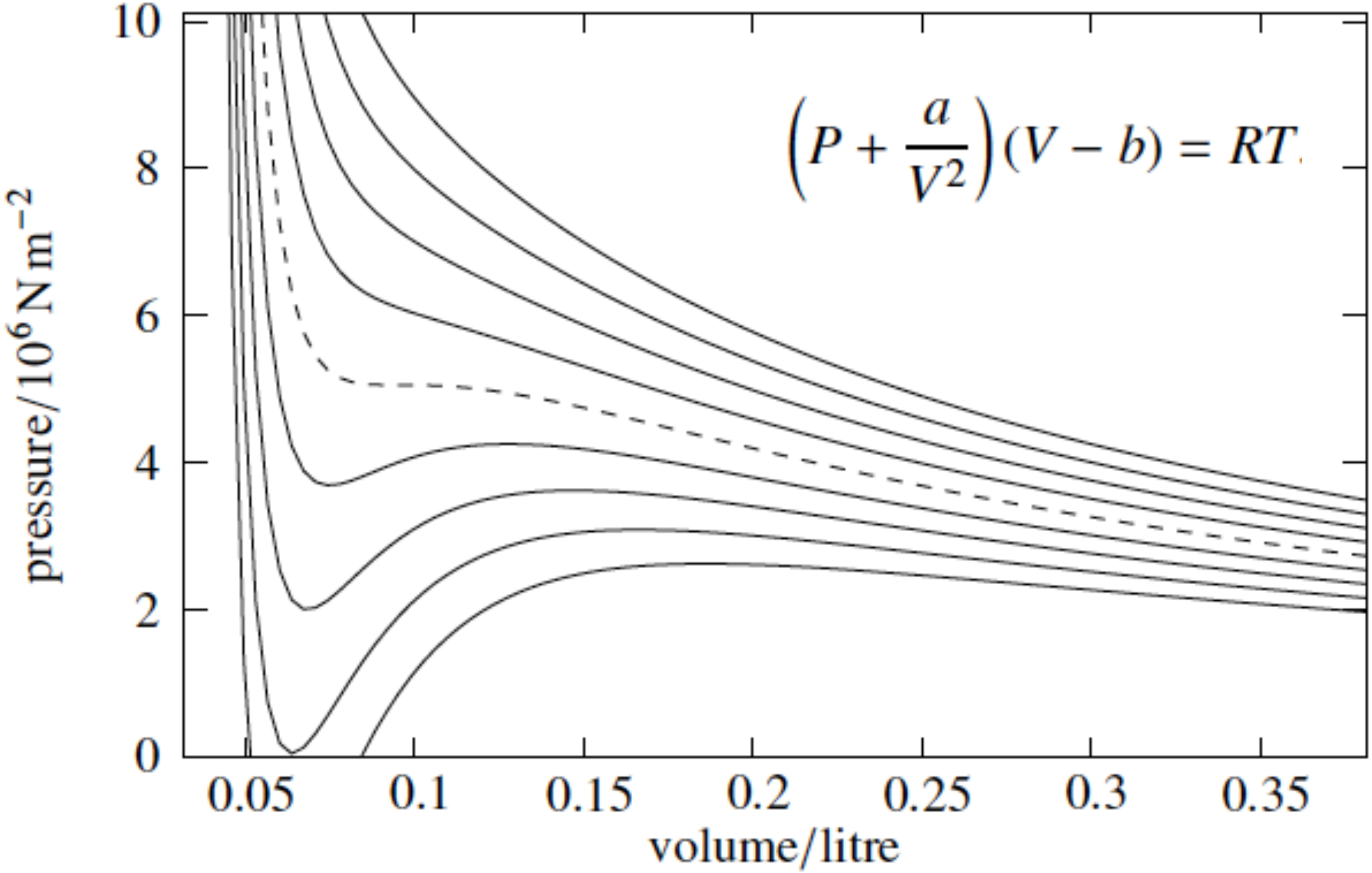
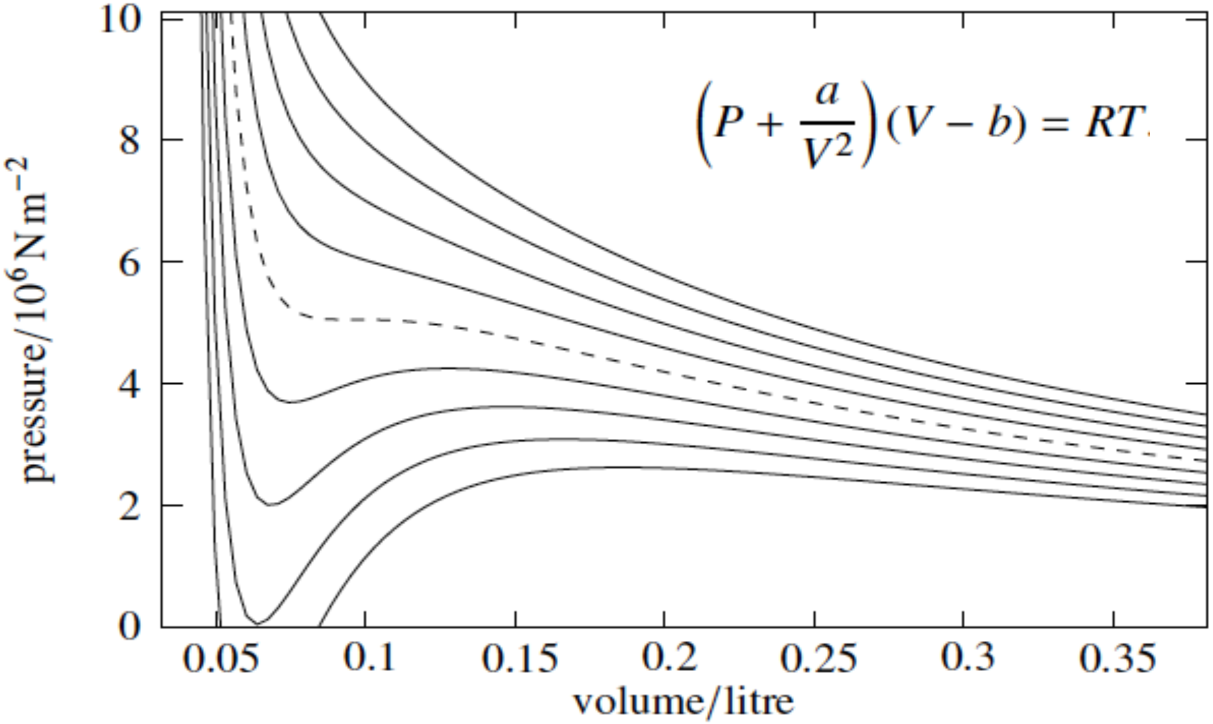


Figure 10.2 Isotherms of a van der Waals gas. The plot uses values $a = 0.138\,\mathrm{N\,m^4}$ and $b = 3.18 \times 10^{-5}\,\mathrm{m^3}$, appropriate for one mole of oxygen gas (O_2). The critical isotherm is drawn dashed, corresponding to a temperature of 155 K. The other isotherms are drawn in steps of 8 K for the temperature.



At small volumes the curves are very steep because of the *b* term, while at large volumes they tend to the ideal gas case.

In between, a kink develops and there are negative values of pressure. Liquids are in fact able to support a certain level of negative pressure, they can be in tension rather than compression.

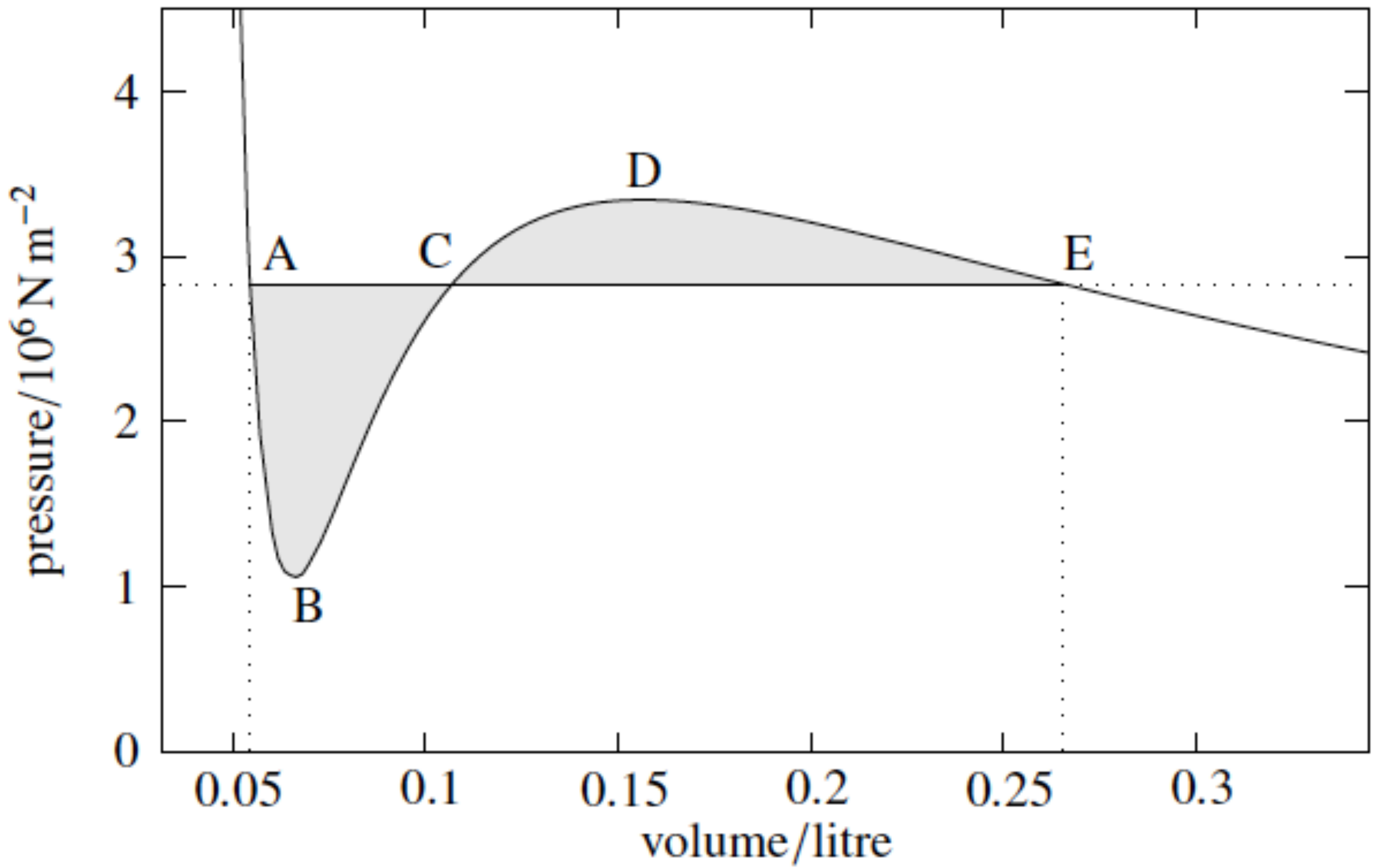
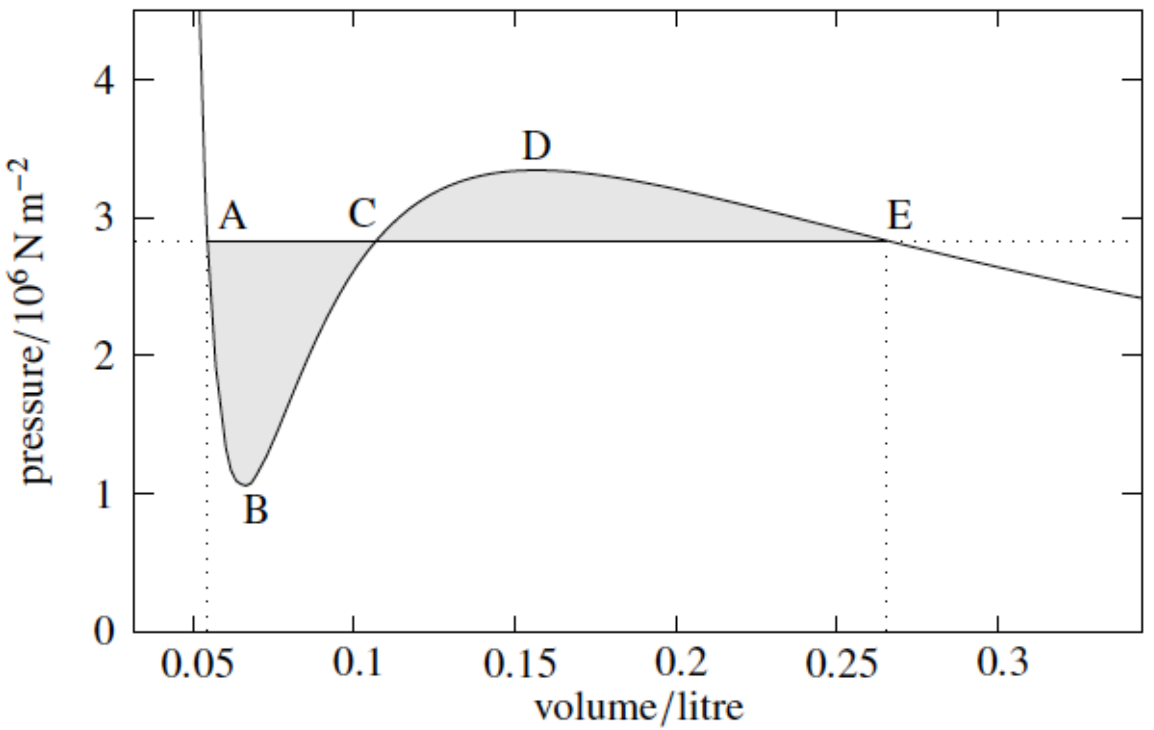
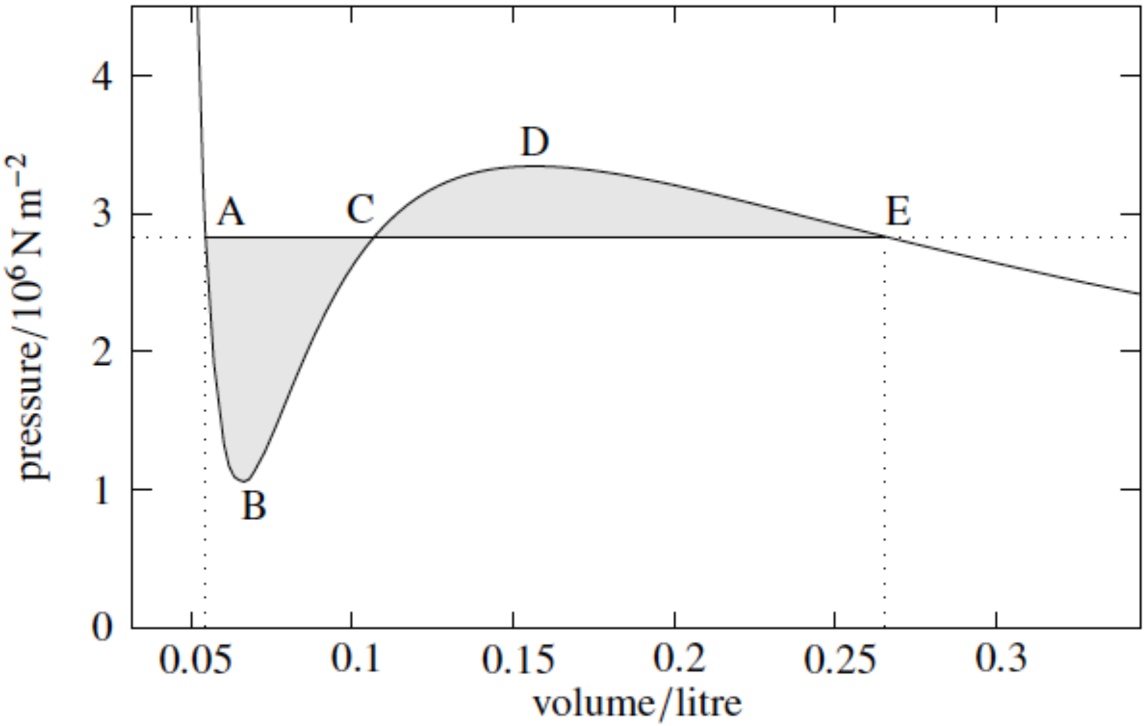


Figure 10.3 Isotherm of a van der Waals gas. The plot shows the $T = 135$ K isotherm for one mole of oxygen (O_2) with $a = 0.138\,\mathrm{N\,m^4}$ and $b = 3.18 \times 10^{-5}\,\mathrm{m^3}$. The equal-areas construction gives $P_A = P_E = 2.83 \times 10^6$ Pa, with $V_A = 0.055$ litre and $V_E = 0.265$ litre.



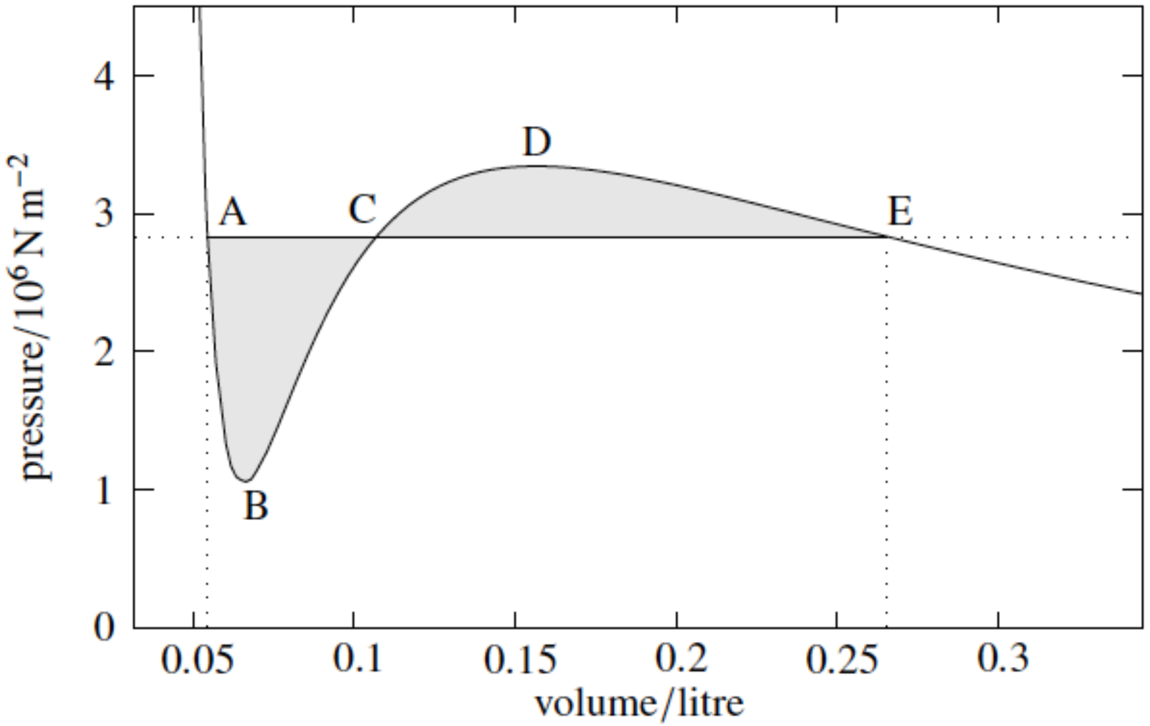
Eventually once points B and D have been passed,
the normal P-V behaviour would return

We would expect equilibrium to be reached with two fluids, one dense and one light, that is a liquid and a gas!
(at A and E)



In the region BCD the pressure increases with increasing volume.
This is unstable:

consider the two halves of a box filled by such a fluid,
the slightest perturbation, which say caused the left-half to compress while the right-half expanded, would run away because as the left-half compressed its pressure would drop while the pressure in the right-half increased, so driving the process further still.

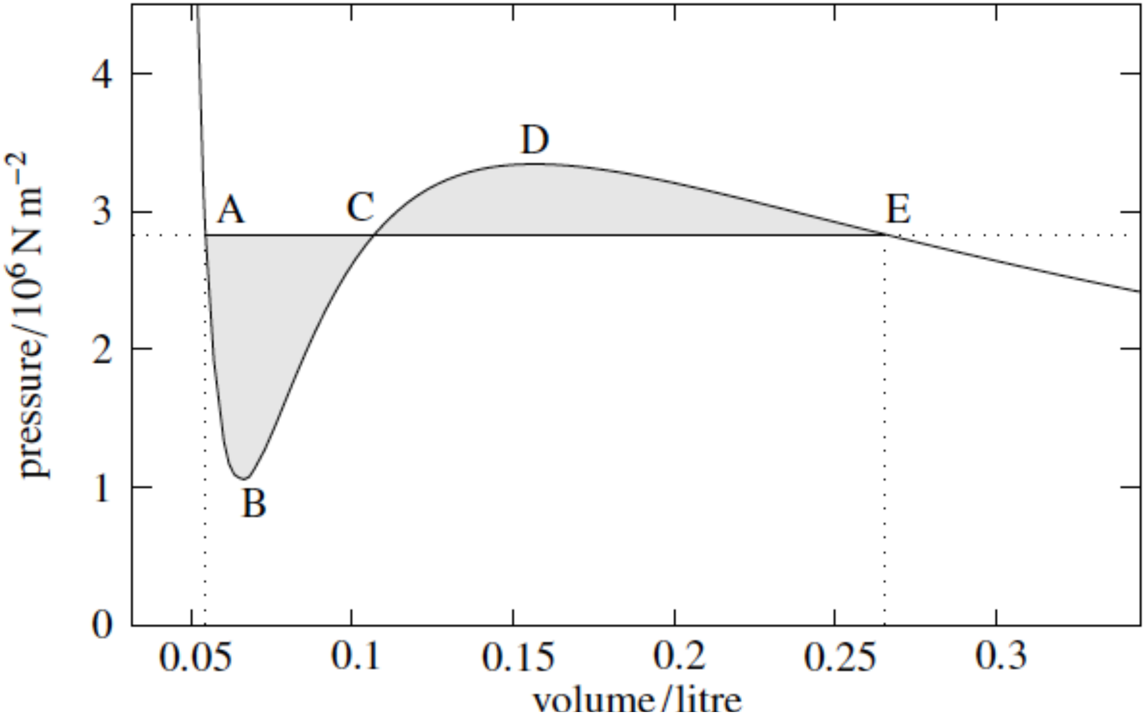


Points A and E must have the same temperature and pressure, we also have $g_A = g_E$, the condition for phase equilibrium

We know that: $$dg = -s\,dT + v\,dP$$

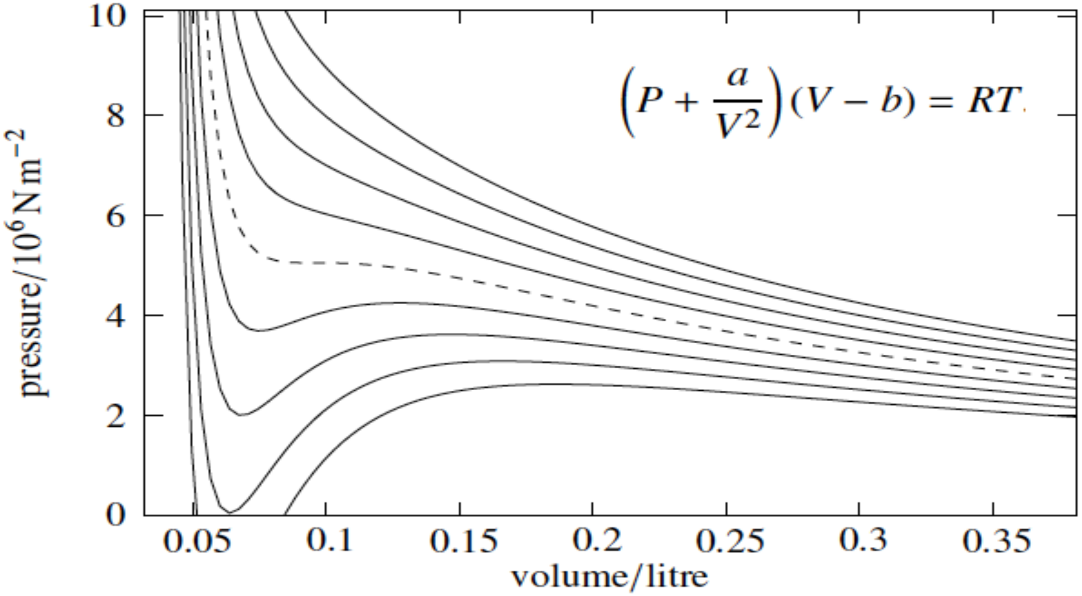
Given the isotherm conditions, dT = 0, so:

$$g_E = g_A + \int_A^E v\,dP \quad \Rightarrow \quad \int_A^E v\,dP = 0$$



$$\int_{A}^{E} v\,dP = 0$$

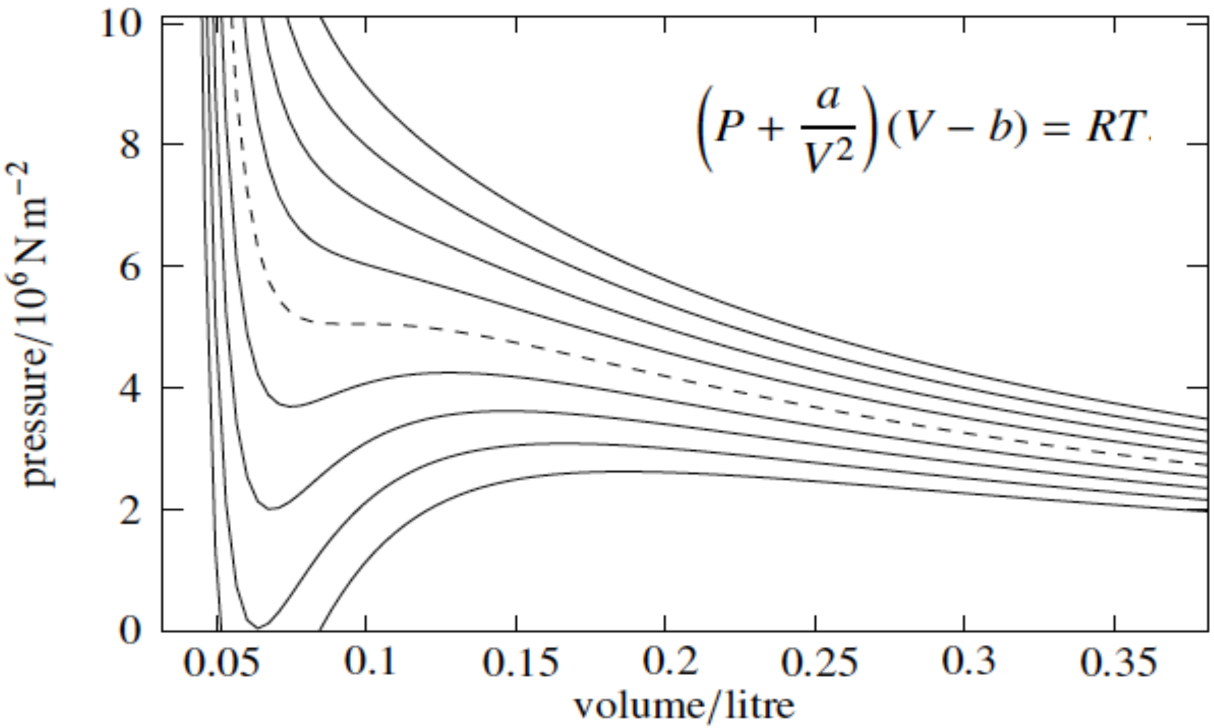
For this reason, the shaded areas ABC and CDE are equal.
This construction (usually known as the Maxwell construction)
can be used to define the region where the liquid gas/separation is
expected to occur.



there comes a point when there is no longer any kink (dashed line and lines above):
at this point there will only be a single phase, and there will be no distinction between a liquid and a gas.

This is known as the critical point: there is a certain temperature above which no matter the pressure, you will not see the formation of a separate liquid phase, the gradient of pressure with respect to volume at constant temperature tends to zero.

$$\left(\frac{\partial P}{\partial V}\right)_T \to 0$$

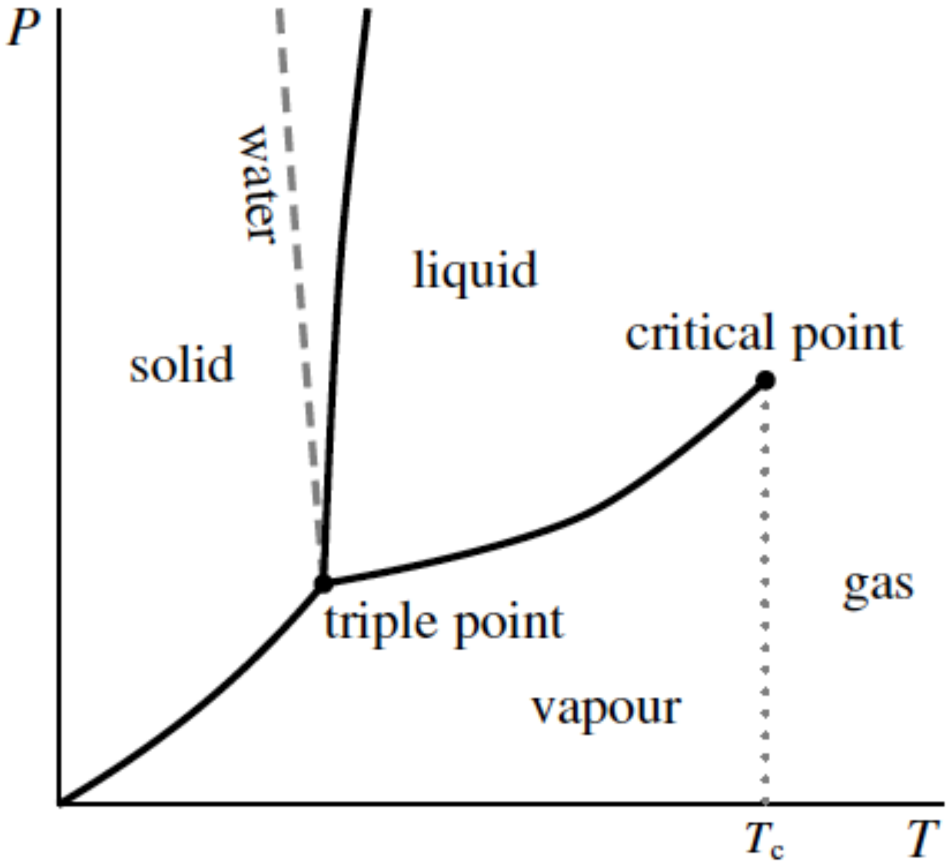


This means that huge density fluctuations occur and that one can see significant density gradients develop due to gravity even in a small container.

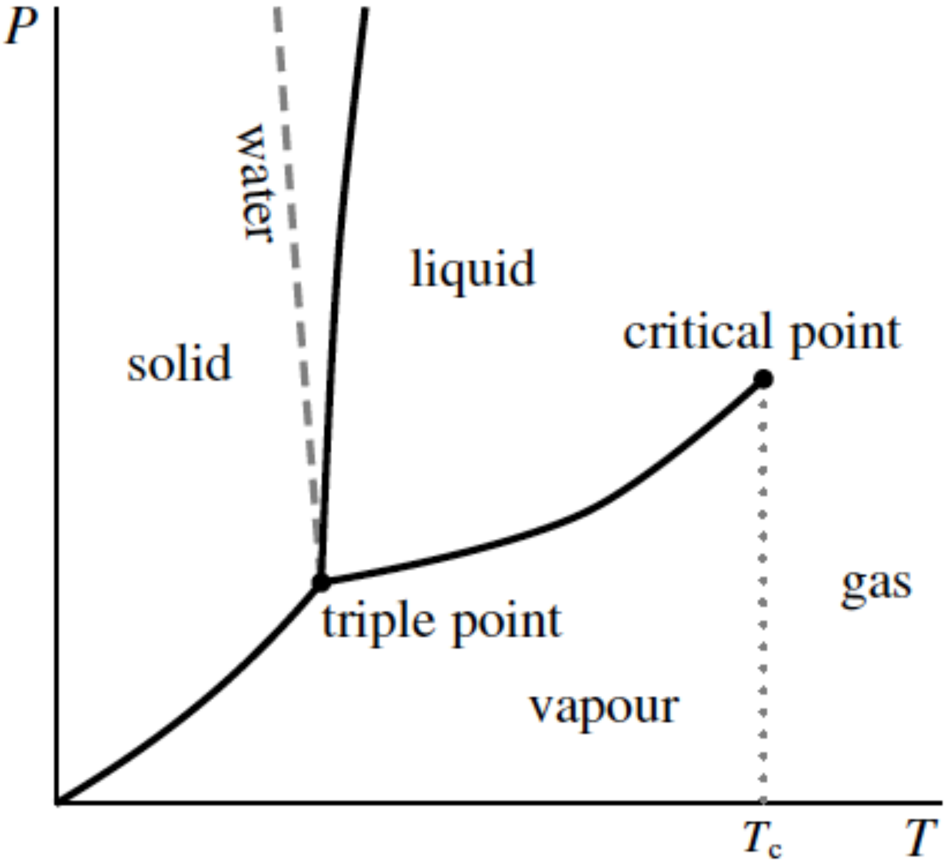
The density fluctuations scatter light and the gas becomes milky white, a phenomenon known as critical opalescence.

10.3 Phase diagrams

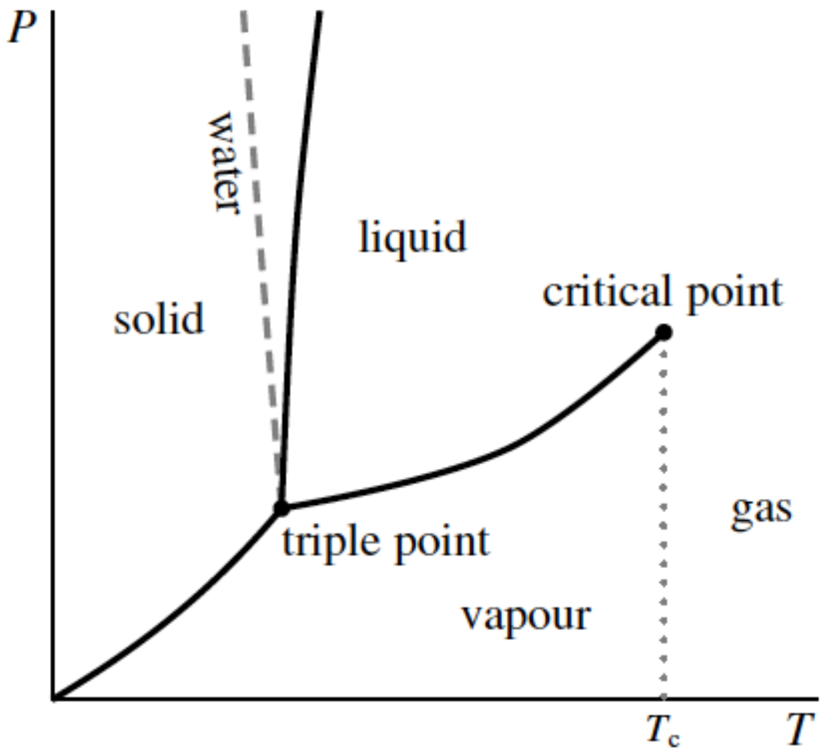
Given that P and T are the variables in G, it is useful to plot P-T diagrams:



The lines indicate the values of pressure and temperature for which the various phases are in equilibrium.



- Solid-liquid equilibrium is reached along the so-called "melting line", where $g_s = g_l$
- Liquid-vapour equilibrium along the "vaporisation line"
- Solid-vapour equilibrium along the "sublimation line"



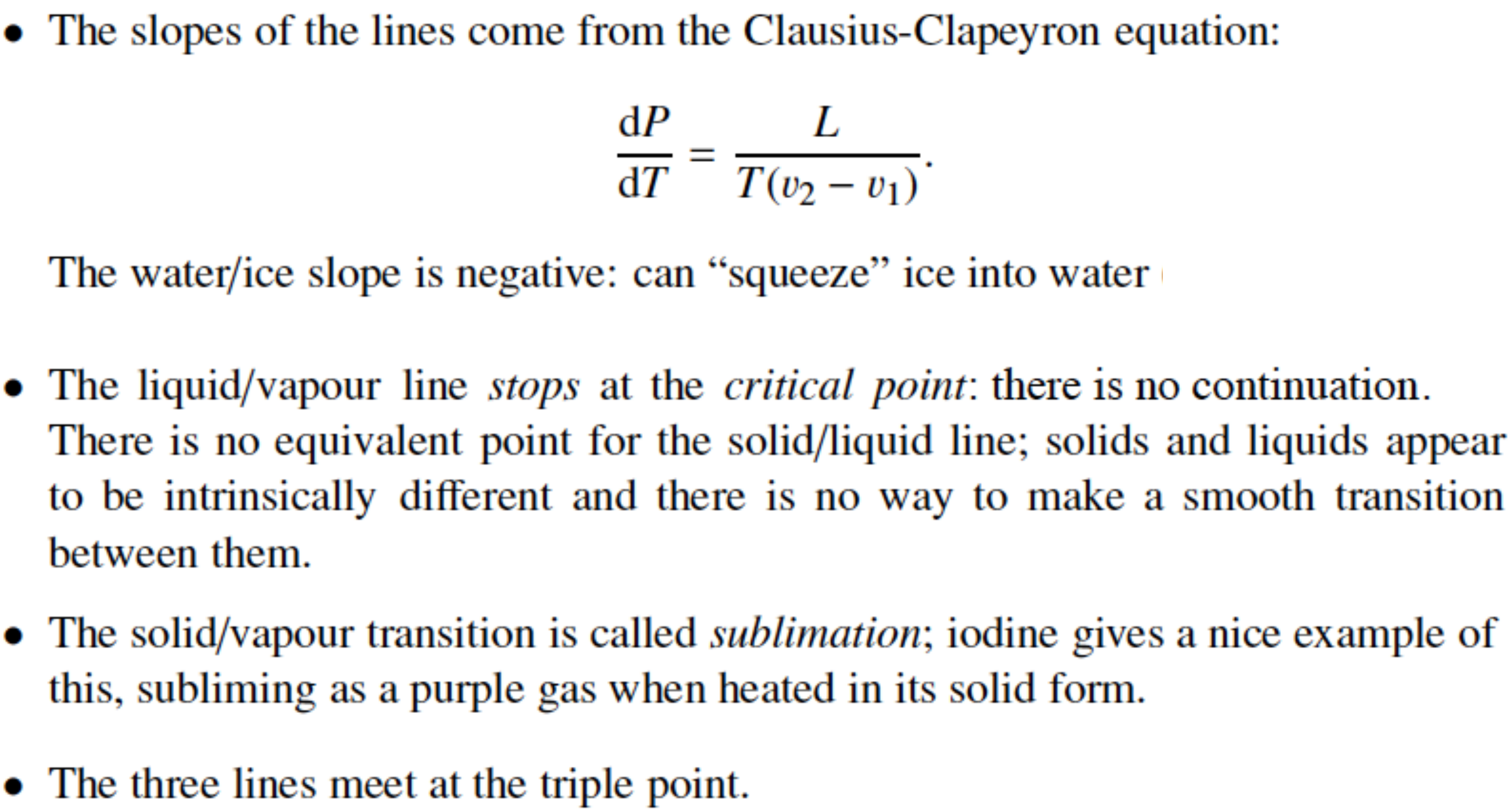
When all three phases are in equilibrium then $g_s = g_l = g_v$

there are no degrees of freedom

at the triple point

the triple point occurs at a unique temperature and pressure, which is why it makes a good temperature reference.

The key features of phase diagrams:



- The slopes of the lines come from the Clausius-Clapeyron equation:

$$\frac{dP}{dT} = \frac{L}{T(v_2 - v_1)}.$$

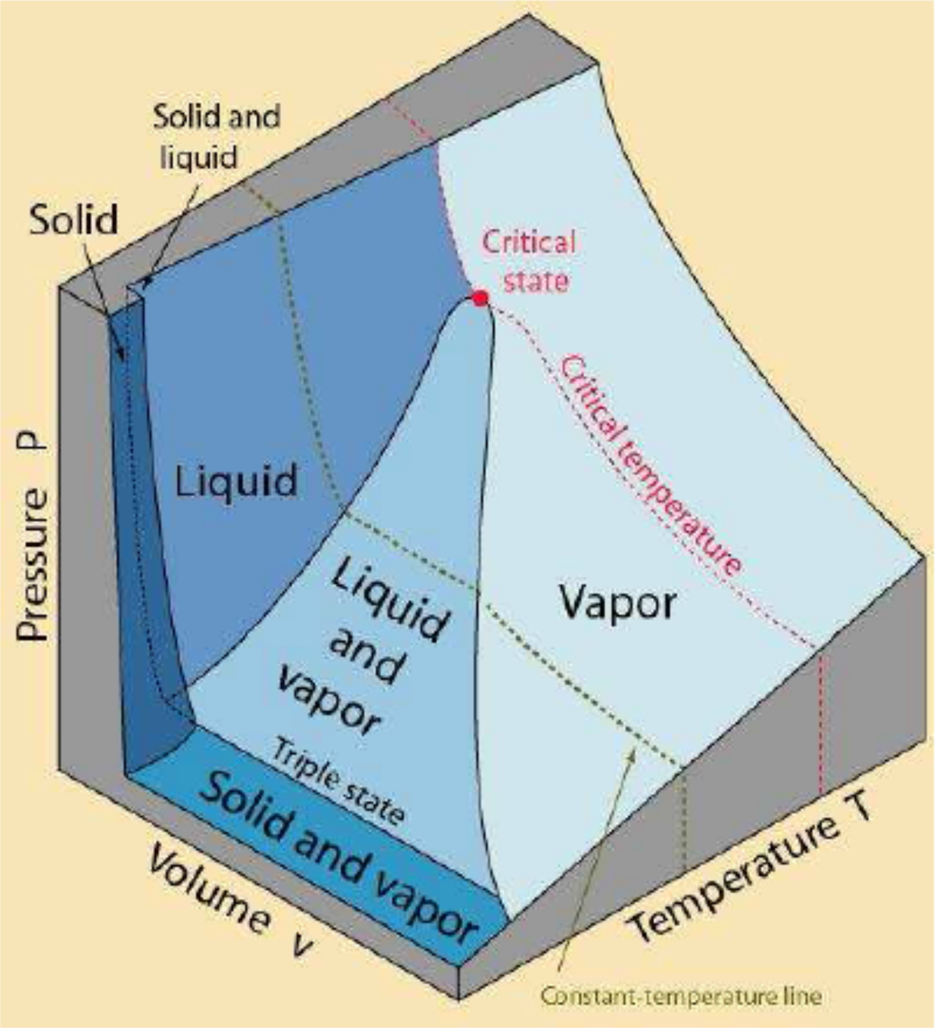
  The water/ice slope is negative: can "squeeze" ice into water

- The liquid/vapour line *stops* at the *critical point*: there is no continuation. There is no equivalent point for the solid/liquid line; solids and liquids appear to be intrinsically different and there is no way to make a smooth transition between them.

- The solid/vapour transition is called *sublimation*; iodine gives a nice example of this, subliming as a purple gas when heated in its solid form.

- The three lines meet at the triple point.

10.3.1 P-V-T surfaces



obtained combining the phase diagram with a P-V indicator diagram

P-V-T surface for water

10.4 Summary

Classical thermodynamics can explain some of the features of phase diagrams, however, to understand the existence of phases we need to delve down to the microscopic level with the inclusion of interactions amongst atoms and molecules.

The van der Waals equations shows how even the simplest inclusion of the effects of interactions introduces features that can be identified with phase changes.

To explain the properties of liquids and solids, more sophisticated models are needed.