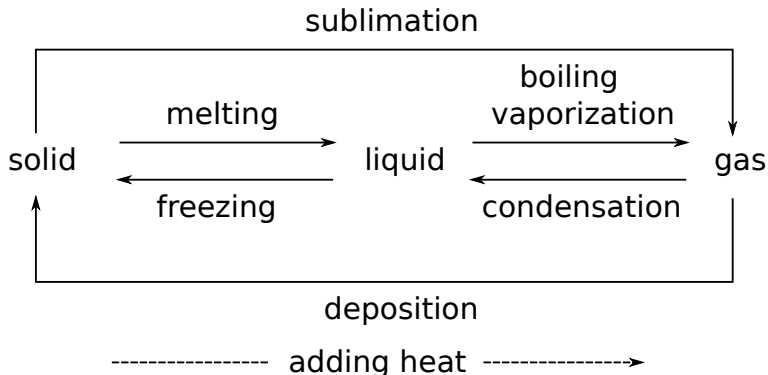


OVERVIEW

- Real (non-ideal) gases. Van der Waals equation.
- Phases of matter and phase transitions.

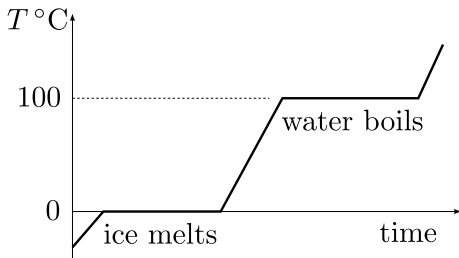
(FOUR WEEKS AGO) PHASE TRANSITIONS



melting \longrightarrow the latent heat of fusion, L_f .
boiling \longrightarrow the latent heat of vaporization, L_v
sublimation \longrightarrow the latent heat of sublimation, L_s

(FOUR WEEKS AGO) PHASE TRANSITIONS

Imagine taking a block of ice at $T < 0^\circ\text{C}$ at atmospheric pressure and slowly adding heat at a constant rate.



To completely melt m kg of ice, we need to add $Q = mL_f$

PHASE TRANSITIONS

Q: What is the entropy change during the phase transition?

A: Heat is added at constant temperature T_{PT} , thus

$$\Delta S = \frac{mL_f}{T_{PT}}$$

Define the *specific entropy* of a substance (entropy per unit mass)

$$\mathcal{S} = S/m.$$

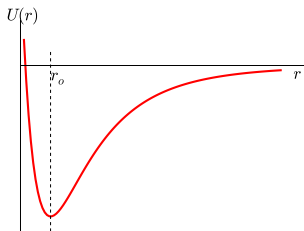
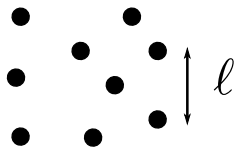
$$L_f = T_{PT} [\mathcal{S}_{\text{liquid}} - \mathcal{S}_{\text{solid}}]$$

where the entropies are evaluated at $T = T_{PT}$.

Likewise, the latent heat of vaporization

$$L_v = T_{\text{boiling}} [\mathcal{S}_{\text{gas}} - \mathcal{S}_{\text{liquid}}]$$

(TWO WEEKS AGO) MOLECULAR THEORY OF GASES



For, e.g. noble gases, $r_o = 2\text{--}5 \text{ \AA}$
($1 \text{ \AA} = 10^{-10} \text{ m}$)

For N molecules of gas confined to a volume V , *concentration* $n = N/V$. The typical distance between molecules $\ell \sim n^{-1/3}$
For air at standard conditions $n \sim 3 \times 10^{25} \text{ m}^{-3}$, hence $\ell \sim 30 \text{ \AA}$

For gases at around room temperature and around atmospheric pressure

$$\ell \gg r_o$$

And neglecting the interactions is a good first approximation.

IDEAL GAS APPROXIMATION

Assumptions of the ideal gas model:

- molecules are pointlike
- no interactions between molecules

This leads to the ideal gas law

$$pV = \nu RT$$

Which works very well as long as the gas is dilute.

NB: An ideal gas does not liquefy—ever.
While real gases certainly do.

VAN DER WAALS EQUATION

An empirical way of relaxing the ideal gas assumptions.

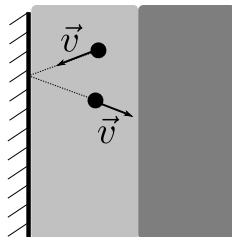
Excluded volume correction:

$$V \longrightarrow V - \nu b$$

Here b is the *excluded volume* occupied by a mole of molecules.
Units of b are m^3/mol :

(Attractive) interaction between molecules:

$$p \longrightarrow p + a \frac{\nu^2}{V^2}$$



VAN DER WAALS EQUATION

VAN DER WAALS EQUATION

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

which reduces to the ideal gas equation for dilute gases (small ν/V).

INTERNAL ENERGY OF A VAN DER WAALS GAS

$$U = \underbrace{\frac{f}{2} \nu RT}_{\text{ideal gas term}} - \frac{a\nu^2}{V}$$

where f is the number of degrees of freedom of molecules.

VAN DER WAALS EQUATION

van der Waals equation:

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

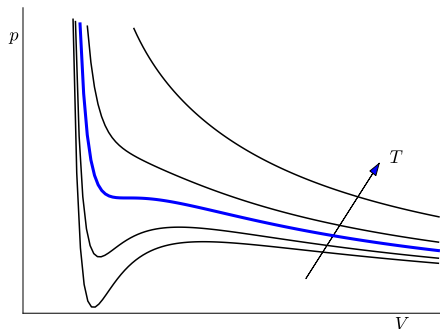
which reduces to the ideal gas equation for dilute gases (small ν/V).

For CO_2 : $a = 0.36 \text{ m}^3/\text{mol}^2$ and $b = 4.3 \times 10^{-5} \text{ m}^3/\text{mol}$.

At standard conditions ($T = 0^\circ\text{C}$ and $p = 1.01 \times 10^5 \text{ Pa}$) the molar volume of an ideal gas is $22.4 \text{ L/mol} = 0.0224 \text{ m}^3/\text{mol}$

If a mole of CO_2 at standard conditions occupies this volume, van der Waals equation predicts the pressure being smaller than the ideal gas pressure by $\sim 500 \text{ Pa}$

ISOTHERMS OF VAN DER WAALS EQUATION



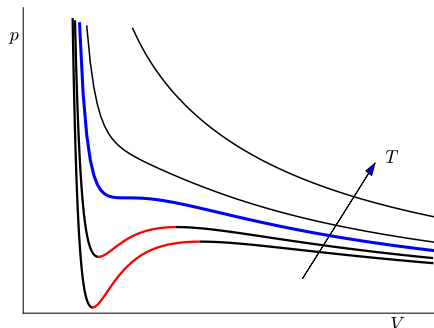
$$\left(p + a \frac{\nu^2}{V^2}\right) (V - \nu b) = \nu RT$$

The relation between p and V is a cubic parabola.

- for T larger than some T_c , isotherms resemble the ideal gas isotherms
- for T smaller than $T < T_c$, isotherms are non-monotonic

T_c is called the *critical temperature* (and the blue line is the *critical isotherm*)

ISOTHERMS OF VAN DER WAALS EQUATION



Isothermal compressibility:

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

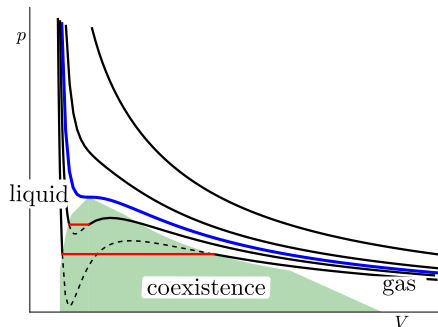
For stability need $\kappa > 0$

Q: So, the red-colored parts of the isotherms have $\kappa < 0$ \Rightarrow are unstable?

A: In fact, these are *metastable* states (an overcooled gas).

ISOTHERMS OF VAN DER WAALS EQUATION

Van der Waals equation describes a liquid-gas phase transition

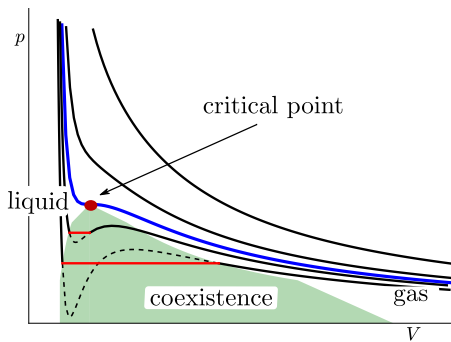


Shaded region: liquid-gas equilibrium

Flat parts of the isotherms (the so-called Maxwell construction): when compressed at $T = \text{const}$, the gas condenses into liquid, and $p = \text{const}$

NB: Condensation \Rightarrow the corresponding latent heat needs to be removed in order to maintain $T = \text{const}$

CRITICAL POINT



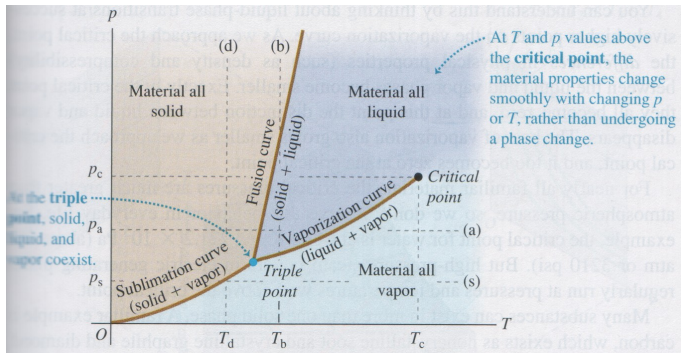
For $T > T_c$, there is no sign of phase coexistence. Isotherms look just like the ideal gas isotherms.

Indeed, for $T > T_c$ there is *no difference between a gas and a liquid*.

At $T \rightarrow T_c - 0$ the latent heat of vaporization $L_v \rightarrow 0$

	Argon	CO ₂	Mercury	Water
$T_c, ^\circ\text{C}$	-122.4	31	1477	374
p_c, atm	48.1	72.8	1720	217.7

TRIPLE POINT



	Argon	CO ₂	Mercury	Water
$T_{\text{triple}}, ^\circ\text{C}$	-189.3	-56.6	-38.8	0.01
$p_{\text{triple}}, \text{atm}$	0.68	5.1	1.6×10^{-9}	0.6×10^{-2}

PHASE DIAGRAM OF WATER

