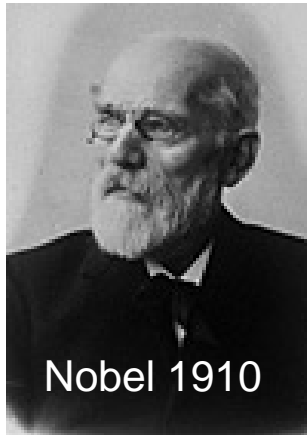


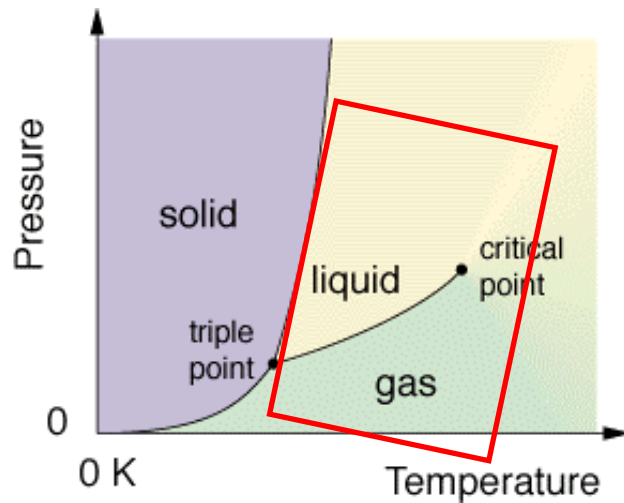
Lecture 15. The van der Waals Gas (Ch. 5)

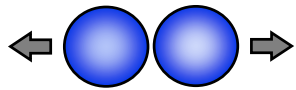


The simplest model of a liquid-gas phase transition - the van der Waals model of “real” gases – grasps some essential features of this phase transformation. (Note that there is no such transformation in the ideal gas model). This will be our attempt to take intermolecular interactions into account.

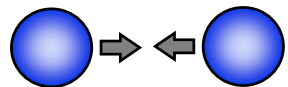
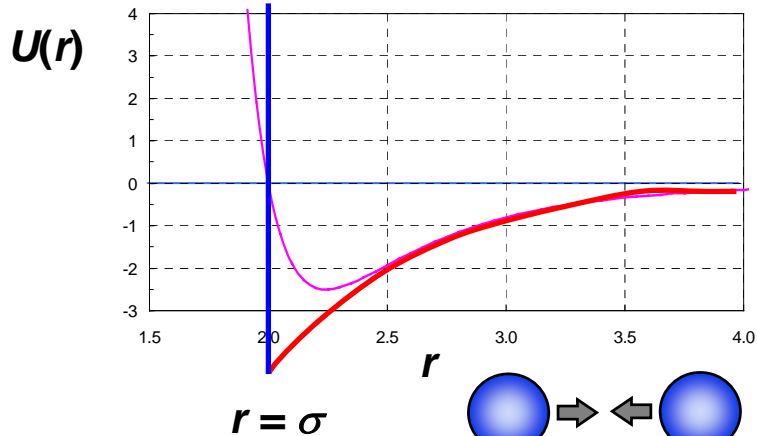
In particular, van der Waals was able to explain the existence of a critical point for the vapor-liquid transition and to derive a Law of Corresponding States (1880).

In his Nobel prize acceptance speech, van der Waals saw the qualitative agreement of his theory with experiment as a major victory for the atomistic theory of matter – stressing that this view had still remained controversial at the turn of the 20th century!





short-distance
repulsion



long-distance
attraction

$$U(r) \propto \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6$$

● **the strong short-range repulsion:** the molecules are rigid: $P \rightarrow \infty$ as soon as the molecules “touch” each other.

$V_{\text{eff}} = V - Nb$ - the constant b ($\sim 4\pi\sigma^3/3$) is a measure of the short-range repulsion, the “excluded volume” per particle

The van der Waals Model

The main reason for the transformation of gas into liquid at decreasing T and (or) increasing P - **interaction between the molecules.**

Two ingredients of the model:

● **the weak long-range attraction:** the long-range attractive forces between the molecules tend to keep them closer together; these forces have the same effect as an additional compression of the gas.

$$P_{\text{eff}} = P + \frac{N^2 a}{V^2}$$

- the constant a is a measure of the long-range attraction

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

$$P = \frac{Nk_B T}{(V - Nb)} - \frac{N^2 a}{V^2}$$

The vdW equation
of state

The van der Waals Parameters

b – roughly the volume of a molecule, $(3.5 \cdot 10^{-29} - 1.7 \cdot 10^{-28}) \text{ m}^3 \sim (\text{few } \text{Å})^3$

a – varies a lot [$\sim (8 \cdot 10^{-51} - 3 \cdot 10^{-48}) \text{ J} \cdot \text{m}^3$] depending on the intermolecular interactions (strongest – between polar molecules, weakest – for inert gases).

Substance	a' ($\text{J} \cdot \text{m}^3/\text{mol}^2$)	b' ($\times 10^{-5} \text{ m}^3/\text{mol}$)
Air	.1358	3.64
Carbon Dioxide (CO ₂)	.3643	4.27
Nitrogen (N ₂)	.1361	3.85
Hydrogen (H ₂)	.0247	2.65
Water (H ₂ O)	.5507	3.04
Ammonia (NH ₃)	.4233	3.73
Helium (He)	.00341	2.34
Freon (CCl ₂ F ₂)	1.078	9.98

$$N_A^2 a \Leftrightarrow a' \quad N_A b \Leftrightarrow b'$$

$$a \left[\frac{\text{J} \cdot \text{m}^6}{\text{molecule}^2} \right] = \frac{a' \left[\frac{\text{J} \cdot \text{m}^6}{\text{mol}^2} \right]}{\left(N_A \frac{\text{molecules}}{\text{mole}} \right)^2}$$


When can $\left(P + \frac{N^2 a}{V^2} \right) (V - Nb) = N k_B T$ **be reduced to** $PV = N k_B T$?

● $Nb \ll V$ - low densities

● $PV \approx N \left(k_B T - \frac{Na}{V} \right)$ $k_B T \gg \frac{Na}{V}$ - high temperatures
(kinetic energy \gg interaction energy)

Problem

The vdW constants for N_2 : $N_A^2 a = 0.136 \text{ Pa}\cdot\text{m}^6 \cdot\text{mol}^{-2}$, $N_A b = 3.85 \cdot 10^{-5} \text{ m}^3 \cdot\text{mol}^{-1}$. How accurate is the assumption that Nitrogen can be considered as an ideal gas at normal P and T ?

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


1 mole of N_2 at $T = 300\text{K}$ occupies $V_{1 \text{ mol}} \approx RT/P \approx 2.5 \cdot 10^{-2} \text{ m}^3 \cdot\text{mol}^{-1}$

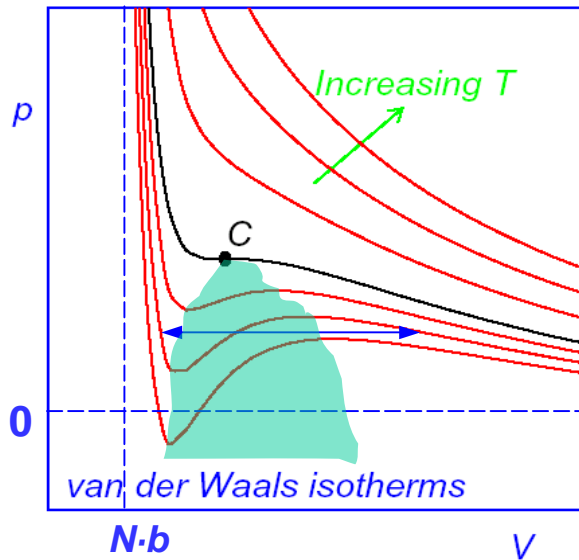
$$N_A b = 3.9 \cdot 10^{-5} \text{ m}^3 \cdot\text{mol}^{-1} \quad N_A b / V_{1 \text{ mol}} \sim 1.6\%$$

$$N_A^2 a / V^2 = 0.135 \text{ Pa}\cdot\text{m}^6 \cdot\text{mol}^{-2} / (2.5 \cdot 10^{-2} \text{ m}^3 \cdot\text{mol}^{-1})^2 = 216 \text{ Pa} \quad N_A^2 a / V^2 P = 0.2\%$$

The vdW Isotherms

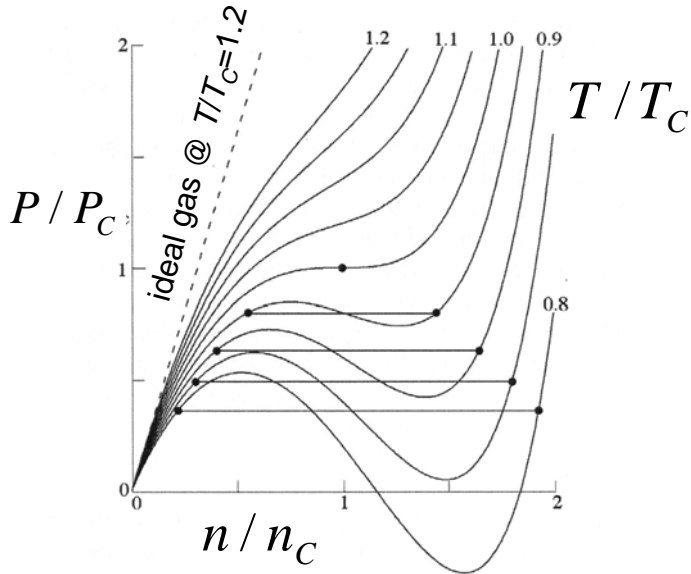
$$P = \frac{Nk_B T}{(V - Nb)} - \frac{aN^2}{V^2}$$

$$V^3 - \left(Nb + \frac{Nk_B T}{P} \right) V^2 + \frac{aN^2}{P} V - \frac{abN^3}{P} = 0$$



The vdW isotherms in terms of the gas density n :

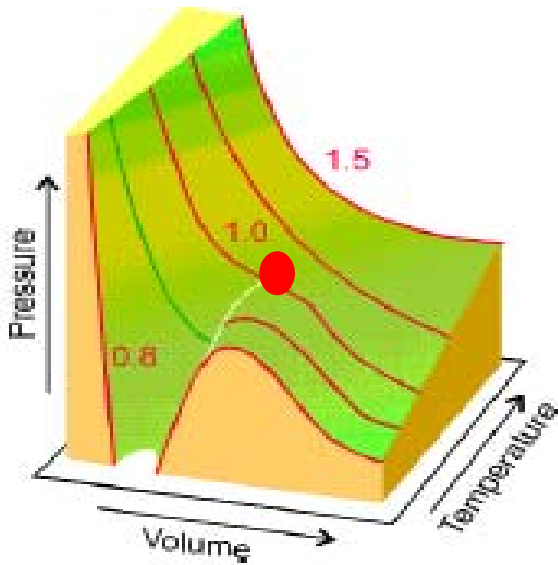
$$\frac{P}{P_C} = \frac{8}{3 \left(\frac{n}{n_C} \right) - 1} \frac{T}{T_C} - 3 \left(\frac{n}{n_C} \right)^2$$



A real isotherm cannot have a negative slope dP/dn (or a positive slope dP/dV), since this corresponds to a negative compressibility. The black isotherm at $T=T_C$ (the top panel) corresponds to the critical behavior. Below T_C , the system becomes unstable against the **phase separation** (gas \leftrightarrow liquid) within a certain range $V(P, T)$. The horizontal straight lines show the true isotherms in the liquid-gas coexistence region, the filled circles indicating the limits of this region.

The critical isotherm represents a boundary between those isotherms along which no such phase transition occurs and those that exhibit phase transitions. The point at which the isotherm is flat and has zero curvature ($\partial P / \partial V = \partial^2 P / \partial V^2 = 0$) is called a **critical point**.

The Critical Point



The critical point is the unique point where both $(dP/dV)_T = 0$ and $(d^2P/dV^2)_T = 0$ (see *Pr. 5.48*)

$$V^3 - \left(Nb + \frac{Nk_B T}{P} \right) V^2 + \frac{aN^2}{P} V - \frac{abN^3}{P} = 0$$

Three solutions of the equation should merge into one at $T = T_C$:

$$(V - V_C)^3 = V^3 - 3V_C V^2 + 3V_C^2 V - V_C^3 = 0$$

Critical parameters:

$$V_C = 3Nb \quad P_C = \frac{1}{27} \frac{a}{b^2} \quad k_B T_C = \frac{8}{27} \frac{a}{b}$$

$$\left(\hat{P} + \frac{3}{\hat{V}^2} \right) \left(\hat{V} - \frac{1}{3} \right) = \frac{8k_B T}{3}$$

- in terms of $\mathbf{P}, \mathbf{T}, \mathbf{V}$ normalized by the critical parameters:

- the materials parameters vanish if we introduce the proper scales.

$$K_C \equiv \frac{RT_C}{P_C V_C} = \frac{8}{3} = 2.67$$

- **the critical coefficient**

substance	H ₂	He	N ₂	CO ₂	H ₂ O
$RT_C/P_C V_C$	3.0	3.1	3.4	3.5	4.5
T_C (K)	33.2	5.2	126	304	647
P_C (MPa)	1.3	0.23	3.4	7.4	22.1

Problems

For Argon, the critical point occurs at a pressure $P_C = 4.83$ MPa and temperature $T_C = 151$ K. Determine values for the vdW constants a and b for Ar and estimate the diameter of an Ar atom.

$$P_C = \frac{1}{27} \frac{a}{b^2} \quad k_B T_C = \frac{8}{27} \frac{a}{b} \quad b = \frac{k_B T_C}{8 P_C} \quad a = \frac{27}{64} \frac{(k_B T_C)^2}{P_C}$$

$$a = \frac{27}{64} \frac{(k_B T_C)^2}{P_C} = \frac{27}{64} \frac{(1.38 \cdot 10^{-23} \text{ J/K} \times 151 \text{ K})^2}{4.83 \cdot 10^6 \text{ Pa}} = 3.8 \cdot 10^{-49} \text{ J}^2/\text{Pa}$$

$$b = \frac{k_B T_C}{8 P_C} = \frac{1.38 \cdot 10^{-23} \text{ J/K} \times 151 \text{ K}}{8 \times 4.83 \cdot 10^6 \text{ Pa}} = 5.4 \cdot 10^{-29} \text{ m}^3 \quad b^{1/3} = 3.86 \cdot 10^{-10} \text{ m} = 3.86 \text{ \AA}$$

Per mole: $a=0.138 \text{ Pa m}^6 \text{ mol}^{-2}$; $b=3.25 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$

Energy of the vdW Gas (low n , high T)

Let's start with an ideal gas (the dilute limit, interactions can be neglected) and compress the gas to the final volume @ $T, N = \text{const}$:

$$U_{vdW} = U_{ideal} + \int_{T=\text{const}} \left(\frac{\partial U}{\partial V} \right)_T dV$$

$$\left(\frac{\partial U}{\partial V} \right)_T = [dU = TdS - PdV] = T \left(\frac{\partial S}{\partial V} \right)_T - P = \left[\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \right] = T \left(\frac{\partial P}{\partial T} \right)_V - P$$

(see **Pr. 5.12**)

From the vdW equation:

$$P = \frac{Nk_B T}{(V - Nb)} - \frac{aN^2}{V^2} \quad \left(\frac{\partial P}{\partial T} \right)_V = \frac{Nk_B}{V - Nb} = \frac{1}{T} \left(P + \frac{N^2 a}{V^2} \right) \quad \left(\frac{\partial U}{\partial V} \right)_T = \frac{N^2 a}{V^2}$$

$$U_{vdW} = U_{ideal} + \int_{T=\text{const}} \left(\frac{\partial U}{\partial V} \right)_T dV = \frac{f}{2} N k_B T - \frac{N^2 a}{V}$$

$$U_{vdW} = U_{ideal} - N \frac{Na}{V}$$

This derivation assumes that the system is **homogeneous** – it does not work for the two-phase (P, V) region (see below).

The same equation for U can be obtained in the model of colliding rigid spheres. According to the equipartition theorem, $K = (1/2) k_B T$ for each degree of freedom regardless of V . U_{pot} – due to attraction between the molecules (repulsion does not contribute to U_{pot} in the model of colliding rigid spheres). The attraction forces result in additional pressure aN^2/V^2 . The work against these forces at $T = \text{const}$ provides an increase of U in the process of an isothermal expansion of the vdW gas:

$$\left(\Delta U_{vdW} \right)_T = N^2 a \left(\frac{1}{V_i} - \frac{1}{V_f} \right)$$

Isothermal Process for the vdW gas at low n and/or high T

$$(\Delta U_{vdW})_T = N^2 a \left(\frac{1}{V_i} - \frac{1}{V_f} \right)$$

$$\delta W = - \int_{V_i}^{V_f} P dV = - \int_{V_i}^{V_f} \left(\frac{Nk_B T}{V - Nb} - \frac{N^2 a}{V^2} \right) dV = -Nk_B T \ln \left(\frac{V_f - Nb}{V_i - Nb} \right) + N^2 a \left(\frac{1}{V_i} - \frac{1}{V_f} \right)$$

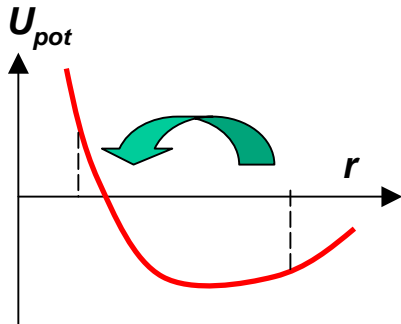
$$\Delta U = \delta Q + \delta W \quad \delta Q_{1-2} = Nk_B T_H \ln \left(\frac{V_2 - Nb}{V_1 - Nb} \right)$$

For N_2 , the vdW coefficients are $N^2 a = 0.138 \text{ kJ}\cdot\text{liter}/\text{mol}^2$ and $Nb = 0.0385 \text{ liter}/\text{mol}$. Evaluate the work of isothermal and reversible compression of N_2 (assuming it is a vdW gas) for $n=3 \text{ mol}$, $T=310 \text{ K}$, $V_1=3.4 \text{ liter}$, $V_2=0.17 \text{ liter}$. Compare this value to that calculated for an ideal gas. Comment on why it is easier (or harder, depending on your result) to compress a vdW gas relative to an ideal gas under these conditions.

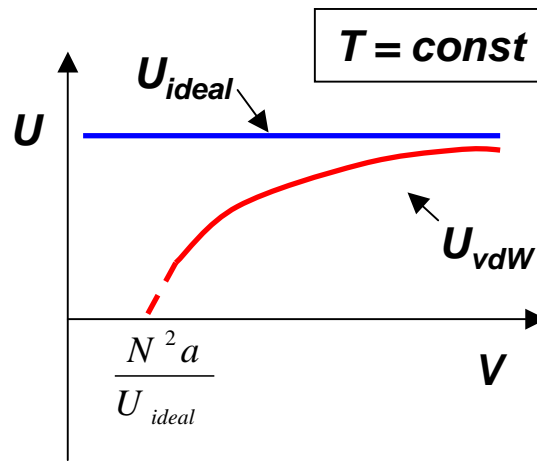
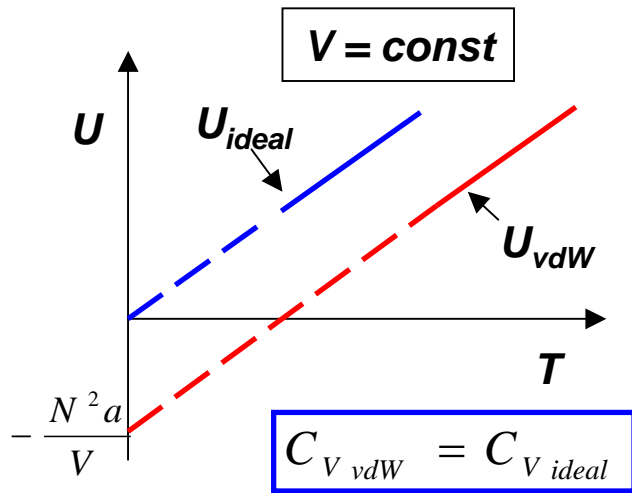
$$(\Delta W_{vdW})_T = 9 \text{ mol}^2 \cdot 0.138 \frac{\text{kJ}\cdot\text{l}}{\text{mol}^2} \left(\frac{1}{3.4\text{l}} - \frac{1}{0.17\text{l}} \right) - 3 \text{ mol} \cdot 8.3 \frac{\text{J}}{\text{K}\cdot\text{mol}} \cdot 310\text{K} \ln \left(\frac{0.17\text{l} - 3 \text{ mol} \cdot 0.0385\text{l}/\text{mol}}{3.4\text{l} - 3 \text{ mol} \cdot 0.0385\text{l}/\text{mol}} \right)$$

$$= -6.94\text{kJ} + 31.64\text{kJ} = 24.7\text{kJ}$$

$$(\Delta W_{ideal})_T = -Nk_B T \ln \left(\frac{V_2}{V_1} \right) = -3 \text{ mol} \cdot 8.3 \frac{\text{J}}{\text{mol}\cdot\text{K}} \cdot 310\text{K} \cdot \ln \left(\frac{0.17\text{l}}{3.4\text{l}} \right) = 23.12\text{kJ}$$



Depending on the interplay between the 1st and 2nd terms, it's either harder or easier to compress the vdW gas in comparison with an ideal gas. If both V_1 and $V_2 \gg Nb$, the interactions between molecules are attractive, and $\Delta W_{vdW} < \Delta W_{ideal}$. However, as in this problem, if the final volume is comparable to Nb , the work against repulsive forces at short distances overweighs that of the attractive forces at large distances. Under these conditions, it is harder to compress the vdW gas rather than an ideal gas.



$$U_{\text{vdW}} = \frac{f}{2} N k_B T - \frac{N^2 a}{V}$$

$$= C_{V \text{ ideal}} T - \frac{N^2 a}{V}$$

Problem: One mole of Nitrogen (N_2) has been compressed at $T_0=273$ K to the volume $V_0=1$ liter. The gas goes through the free expansion process ($\delta Q = 0$, $\delta W = 0$), in which the pressure drops down to the atmospheric pressure $P_{\text{atm}}=1$ bar. Assume that the gas obeys the van der Waals equation of state in the compressed state, and that it behaves as an ideal gas at the atmospheric pressure. Find the change in the gas temperature.

For 1 mole of the “vdW” Nitrogen (diatomic gas)

$$U_{\text{vdW}}(T_0, V_0) = U_{\text{ideal}} - \frac{N^2 a}{V_0} = \frac{5}{2} RT_0 - \frac{N^2 a}{V_0}$$

For 1 mole of the “ideal” Nitrogen (after expansion):

$$U_{\text{ideal}} = \frac{5}{2} RT_f \quad T_f \text{ is the temperature after expansion}$$

The internal energy of the gas is conserved in this process ($\delta Q = 0$, $\delta W = 0$), and, thus, $\Delta U = 0$:

$$\frac{5}{2} RT_0 - \frac{N^2 a}{V_0} = \frac{5}{2} RT_f \quad T_f = T_0 - \frac{2 N^2 a}{5 R V_0}$$

The final temperature is lower than the initial temperature: the gas molecules work against the attraction forces, and this work comes at the expense of their kinetic energy.

S, F, and G for the monatomic van der Waals gas

S
$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV = \frac{f}{2} Nk_B \frac{dT}{T} + \frac{Nk_B}{V - Nb} dV$$

(see **Pr. 5.12**)
$$S_{vdW} = \frac{f}{2} Nk_B \ln T + Nk_B \ln(V - Nb) + const$$

$$S_{vdW} = S_{ideal} + Nk_B \ln\left(1 - \frac{Nb}{V}\right) = Nk_B \left\{ \ln\left[\frac{(V - Nb)}{N} \left(\frac{2\pi m}{h^2} k_B T\right)^{3/2} \right] + \frac{5}{2} \right\}$$

- the same “volume” in the momentum space, smaller accessible volume in the coordinate space.

F
$$F_{vdW} = U - TS = \frac{3}{2} Nk_B T - \frac{N^2 a}{V} - Nk_B T \left\{ \ln\left[\frac{(V - Nb)}{N} \left(\frac{2\pi m}{h^2} k_B T\right)^{3/2} \right] + \frac{5}{2} \right\}$$

$$= -Nk_B T \ln\left[\frac{(V - Nb)}{N} \left(\frac{2\pi m}{h^2} k_B T\right)^{3/2} \right] - Nk_B T - \frac{aN^2}{V}$$

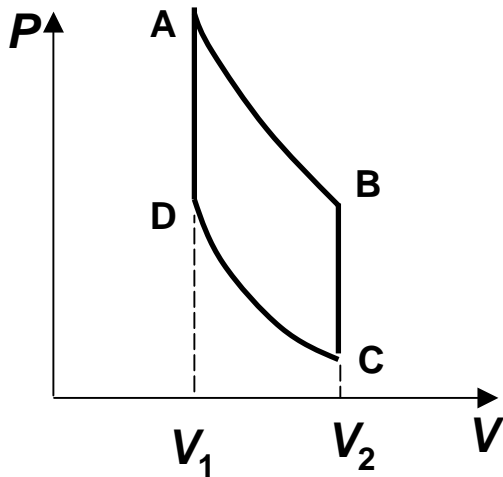


$$F_{vdW} = F_{ideal} - Nk_B T \ln\left(1 - \frac{Nb}{V}\right) - \frac{N^2 a}{V} \quad P_{vdW} = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2}$$

G
$$G_{vdW} = F + PV = -Nk_B T \ln\left[\frac{(V - Nb)}{N} \left(\frac{2\pi m}{h^2} k_B T\right)^{3/2} \right] - Nk_B T - \frac{2aN^2}{V} + \frac{Nk_B TV}{V - Nb}$$

Problem (vdW+heat engine)

The working substance in a heat engine is the vdW gas with a known constant b and a temperature-independent heat capacity c_V (the same as for an ideal gas). The gas goes through the cycle that consists of two isochors (V_1 and V_2) and two adiabats. Find the efficiency of the heat engine.



$$e = 1 - \frac{\delta Q_C}{\delta Q_H}$$

A-D

$$\Delta Q_H = c_V(T_A - T_D)$$

B-C

$$\Delta Q_C = c_V(T_B - T_C)$$

$$e = 1 - \frac{(T_B - T_C)}{(T_A - T_D)}$$

The relationship between T_A, T_B, T_C, T_D – from the adiabatic processes **B-C** and **D-A**

$$S_{vdW} = \frac{f}{2} Nk_B \ln T + Nk_B \ln(V - Nb) + const$$

$$\Delta S_{vdW} = \frac{f}{2} Nk_B \ln \frac{T_f}{T_i} + Nk_B \ln \frac{V_f - Nb}{V_i - Nb}$$

$$\frac{f}{2} Nk_B \ln \frac{T_f}{T_i} + Nk_B \ln \frac{V_f - Nb}{V_i - Nb} = 0 \quad T^{\frac{f}{2}} (V - Nb) = const$$

**adiabatic process
for the vdW gas**

$$e = 1 - \frac{\Delta Q_C}{\Delta Q_H} = 1 - \frac{(T_B - T_C)}{(T_A - T_D)} = 1 - \frac{T_A \left(\frac{V_1 - Nb}{V_2 - Nb} \right)^{2/f} - T_D \left(\frac{V_1 - Nb}{V_2 - Nb} \right)^{2/f}}{T_A - T_D} = 1 - \left(\frac{V_1 - Nb}{V_2 - Nb} \right)^{2/f} = 1 - \left(\frac{V_1 - Nb}{V_2 - Nb} \right)^{R/c_V}$$

Problem

One mole of Nitrogen (N_2) has been compressed at $T_0=273$ K to the volume $V_0=1$ liter. The critical parameters for N_2 are: $V_C = 3Nb = 0.12$ liter/mol, $T_C = (8/27)(a/k_B b) = 126$ K. The gas goes through the free expansion process ($\delta Q = 0$, $\delta W = 0$), in which the pressure drops down to the atmospheric pressure $P_{atm}=1$ bar. Assume that the gas obeys the van der Waals equation of state in the compressed state, and that it behaves as an ideal gas at the atmospheric pressure. Find the change in the gas entropy.

$$S_{vdW} = \frac{f}{2} R \ln T + R \ln(V - Nb) + f(N, m)$$

$$\Delta S = \frac{5}{2} R \ln \frac{T_f}{T_0} + R \ln \left(\frac{V_f}{V_0 - Nb} \right) = \frac{5}{2} R \ln \frac{T_f}{T_0} + R \ln \left(\frac{V_f}{V_0 - V_C / 3} \right)$$

$$T_f = T_0 - \frac{9}{20} \frac{T_C V_C}{V_0} = 266.2 \text{ K} \quad V_f = \frac{RT_f}{P_{atm}} = 2.2 \cdot 10^{-2} \text{ m}^3$$

$$\Delta S = \frac{5}{2} R \ln \frac{266.2}{273} + R \ln \left(\frac{2.2 \cdot 10^{-2}}{1 \cdot 10^{-3} - 0.04 \cdot 10^{-3}} \right) = -5.24 \cdot 10^{-1} + 26 \approx 25.5 \text{ J/K}$$

Phase Separation in the vdW Model

$T = \text{const} (< T_c)$

The phase transformation in the vdW model is easier to analyze by minimizing $F(V)$ rather than $G(P)$ (dramatic changes in the term PV makes the dependence $G(P)$ very complicated, see below).

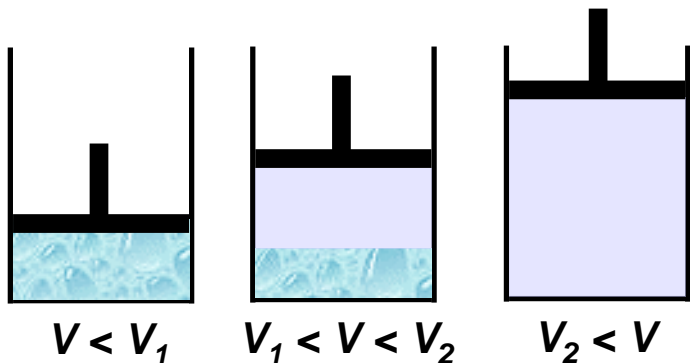
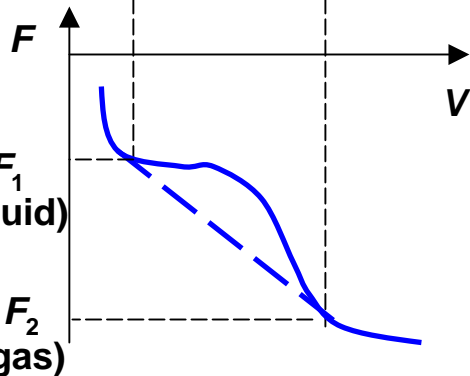
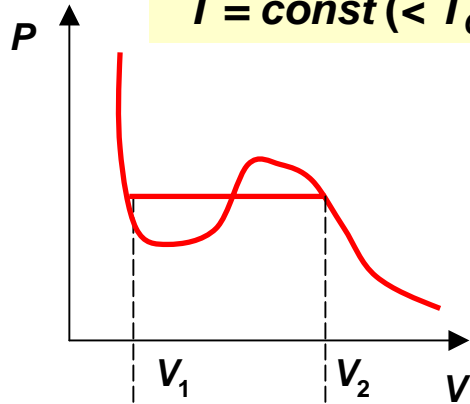
At $T < T_c$, there is a region on the $F(V)$ curve in which F makes a concave protrusion ($\partial^2 F / \partial V^2 < 0$) – unlike its ideal gas counterpart. Due to this protrusion, it is possible to draw a common tangent line so that it touches the bottom of the left dip at $V = V_1$ and the right dip at $V = V_2$. Since the common tangent line lies **below** the free energy curve, molecules can minimize their free energy by refusing to be in a single homogeneous phase in the region between V_1 and V_2 , and by preferring to be in **two coexisting phases**, gas and liquid:

$$N = N_{\text{gas}} + N_{\text{liquid}} \quad \frac{N_{\text{gas}}}{N} = \frac{V - V_1}{V_2 - V_1} \quad \frac{N_{\text{liquid}}}{N} = \frac{V_2 - V}{V_2 - V_1}$$

$$F = \frac{F_1}{N} N_{\text{liquid}} + \frac{F_2}{N} N_{\text{gas}} = F_1 \frac{V - V_2}{V_1 - V_2} + F_2 \frac{V_1 - V}{V_1 - V_2}$$

- we recognize this as the common tangent line.

As usual, the minimum free energy principle controls the way molecules are assembled together.



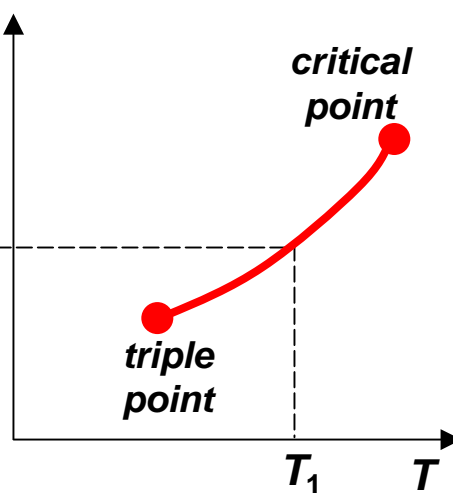
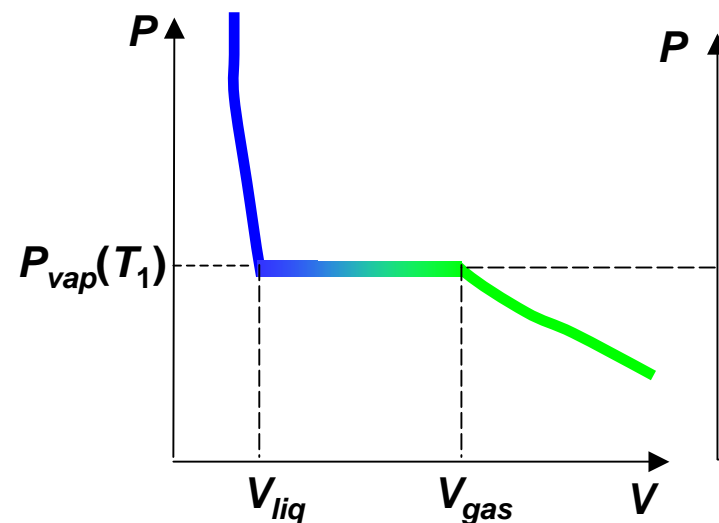
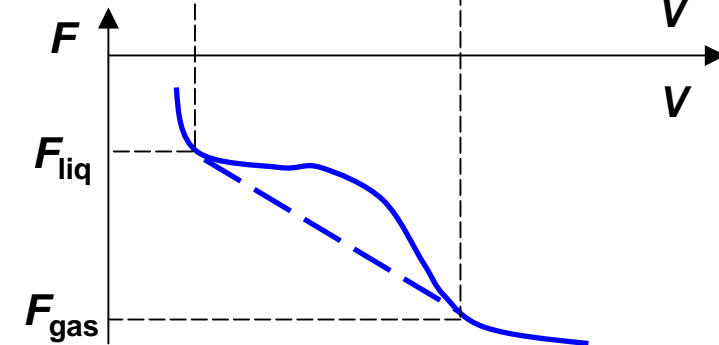
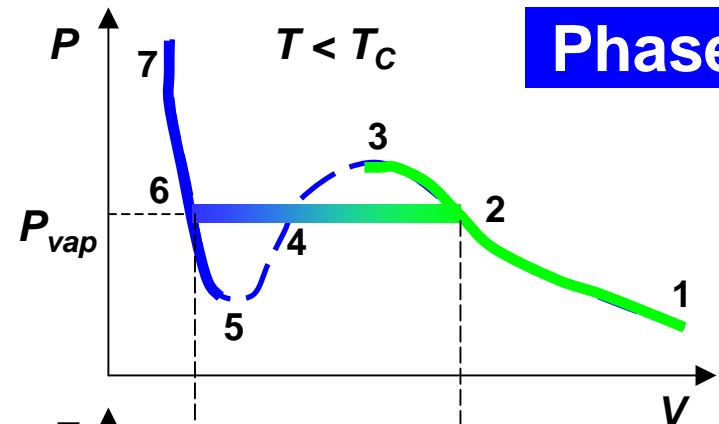
Phase Separation in the vdW Model (cont.)

Since the tangent line $F(V)$ maintains the same slope between V_1 and V_2 , the pressure remains constant between V_1 and V_2 :

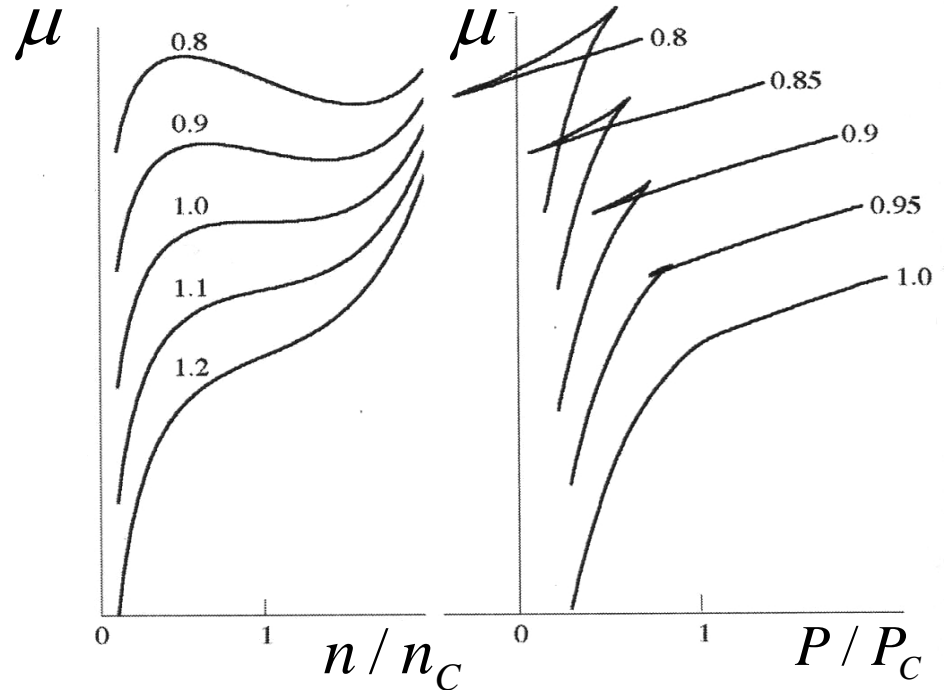
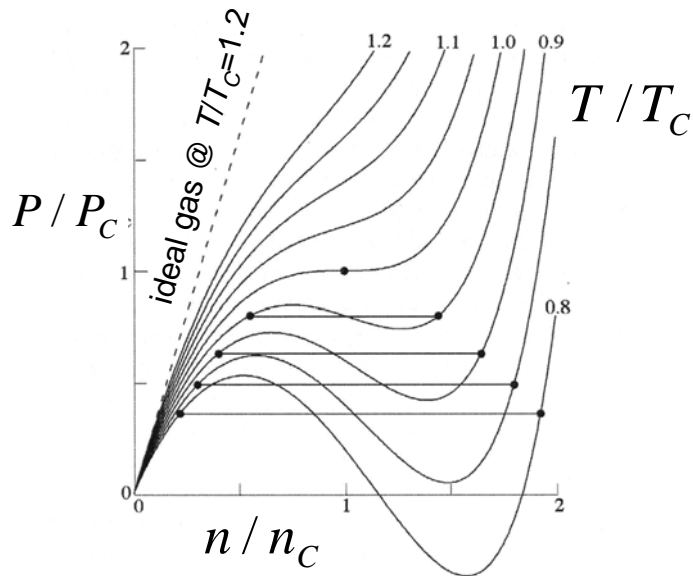
$$\left(\frac{\partial F}{\partial V}\right)_{T,N} = -P$$

In other words, the line connecting points on the PV plot is horizontal and the two coexisting phases are in a mechanical equilibrium. For each temperature below T_C , the phase transformation occurs at a well-defined pressure P_{vap} , the so-called **vapor pressure**.

Two stable branches 1-2-3 and 5-6-7 correspond to **different phases**. Along branch 1-2-3 V is large, P is small, the density is also small – gas. Along branch 5-6-7 V is small, P is large, the density is large – liquid. Between the branches – **the gas-liquid phase transformation**, which starts even before we reach 3 moving along branch 1-2-3.



Phase Separation in the vdW Model (cont.)

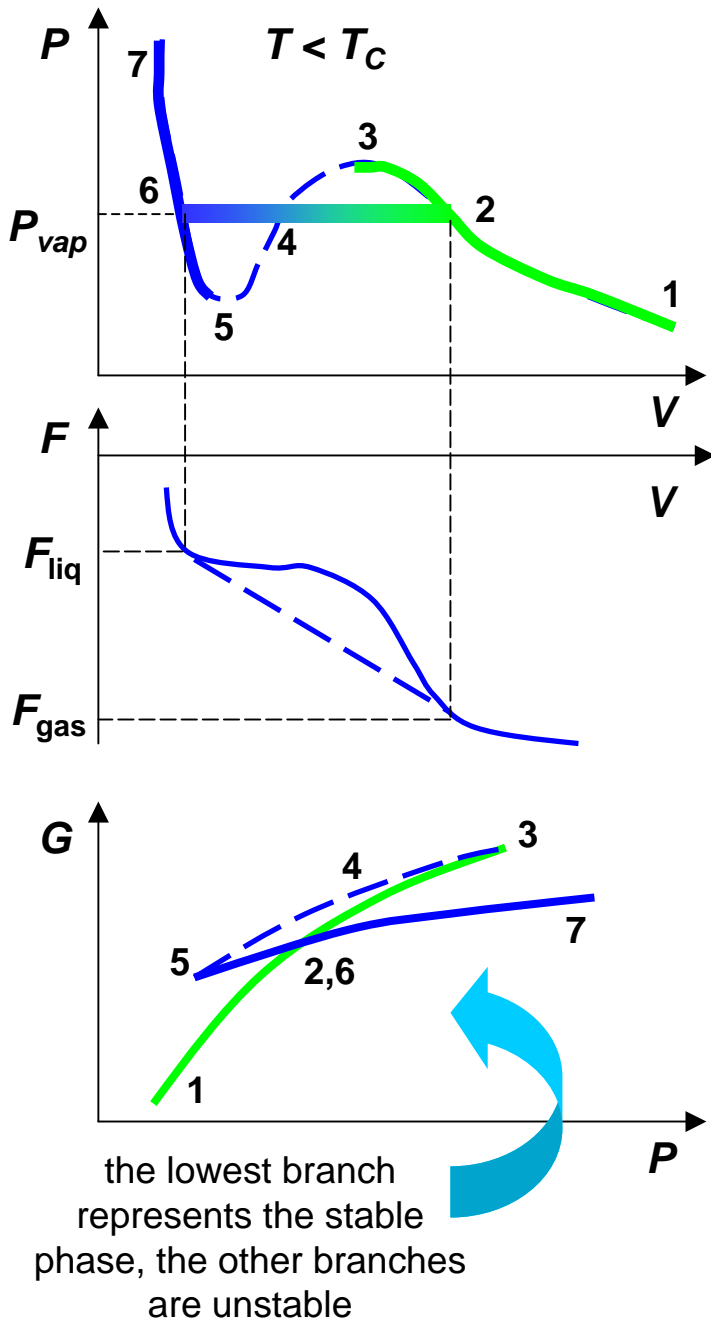


$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = k_B T \left[\ln \left(\frac{3n_C}{n_Q} \right) - \ln \left(\frac{3n_C}{n} - 1 \right) + \frac{1}{3n_C/n - 1} \right] - \frac{9}{4} k_B T_C \left(\frac{n}{n_C} \right)$$

For $T < T_C$, there are three values of n with the same μ . The outer two values of n correspond to two stable phases which are in equilibrium with each other.

The kink on the $\mathbf{G}(\mathbf{V})$ curve is a signature of the 1st order transition. When we move along the gas-liquid coexistence curve towards the critical point, the transition becomes less and less abrupt, and at the critical point, the abruptness disappears.

The Maxwell Construction



[finding the position of line 2-6 without analyzing $F(V)$]

On the one hand, using the dashed line on the $F-V$ plot:

$$F_{gas} - F_{liquid} = \int_{V_6}^{V_2} \left(\frac{\partial F}{\partial V} \right)_{T,N} dV = \left(\frac{\partial F}{\partial V} \right)_{T,N} (V_2 - V_6)$$

$$= -P_{vap} (V_2 - V_6)$$

On the other hand, the area under the vdW isotherm 2-6 on the $P-V$ plot:

$$\int_{V_6}^{V_2} P dV = - \int_{V_6}^{V_2} \left(\frac{\partial F}{\partial V} \right)_{T,N} dV = -(F_{gas} - F_{liquid})$$

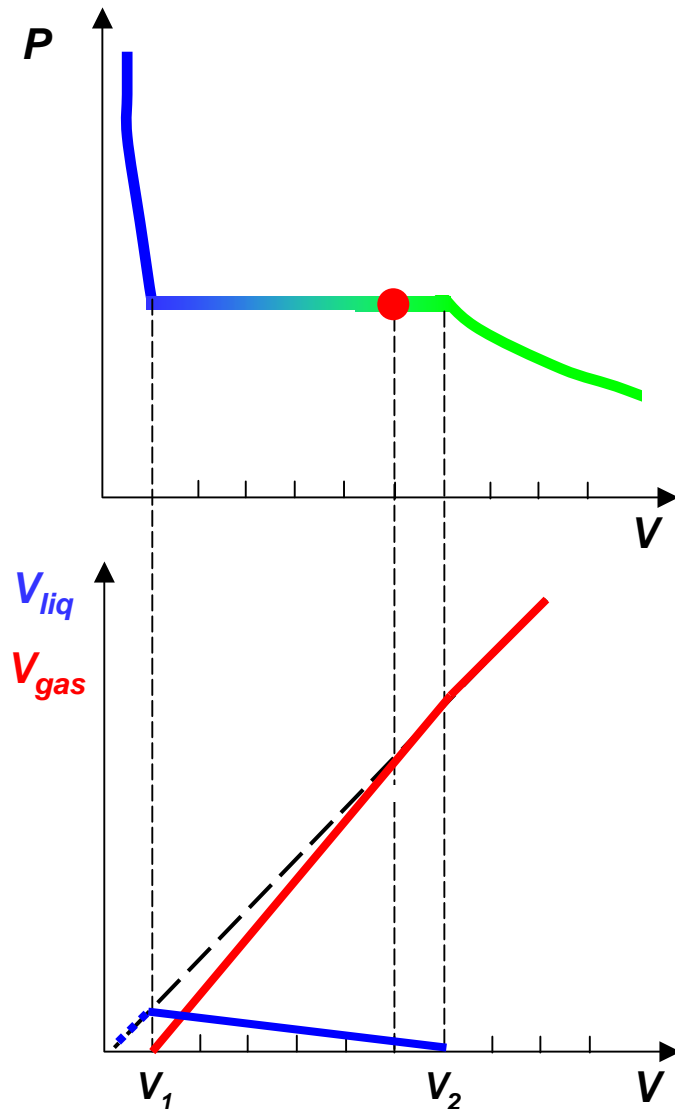
Thus,

$$\int_{V_6}^{V_2} P_{vdW}(V) dV = P_{vap} (V_2 - V_6)$$

the areas 2-3-4-2 and 4-5-6-4 **must be equal!**

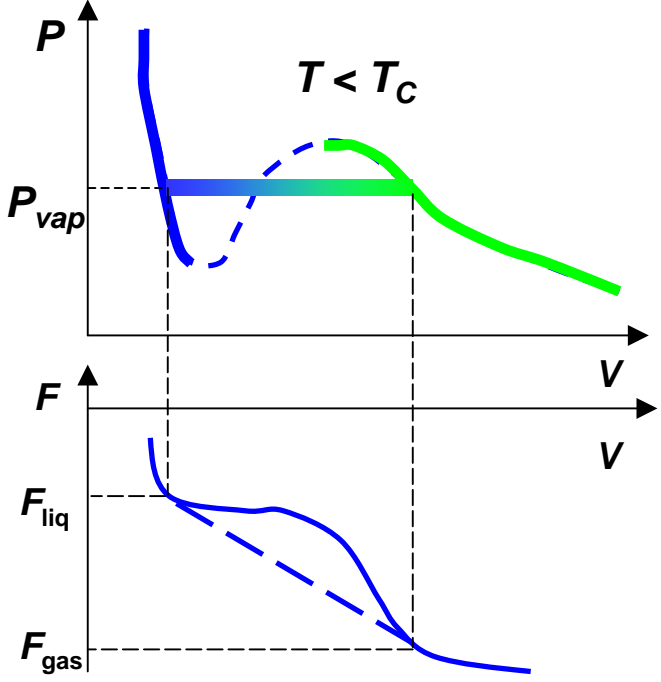
Problem

The total mass of water and its saturated vapor (gas) $m_{total} = m_{liq} + m_{gas} = 12$ kg. What are the masses of water, m_{liq} , and the gas, m_{gas} , in the state of the system shown in the Figure?



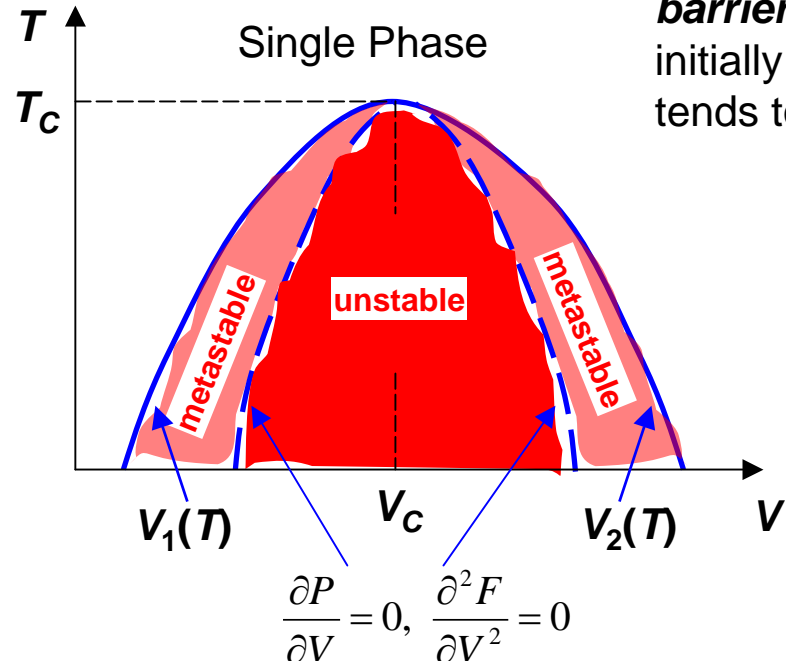
V_{liq} increases from 0 to V_1 while the total volume decreases from V_2 to V_1 . V_{gas} decreases from V_2 to 0 while the total volume decreases from V_2 to V_1 . When $V = V_1$, $m_{total} = m_{liq}$. Thus, in the state shown in the Figure, $m_{liq} \approx 2$ kg and $m_{gas} \approx 10$ kg.

Phase Diagram in T - V Plane



At $T > T_C$, the N molecules can exist in a single phase in any volume V , with any density $n = N/V$. Below T_C , they can exist in a homogeneous phase either in volume $V < V_1$ or in volume $V > V_2$. There is a gap in the density allowed for a homogeneous phase.

There are two regions within the two-phase “dome”: metastable ($\partial P / \partial V < 0$) and unstable ($\partial P / \partial V > 0$). In the unstable region with negative compressibility, nothing can prevent phase separation. In two metastable regions, though the system would decrease the free energy by phase separation, it should **overcome the potential barrier** first. Indeed, when small droplets with radius R are initially formed, an associated with the surface energy term tends to increase F . The F loss (gain) per droplet:

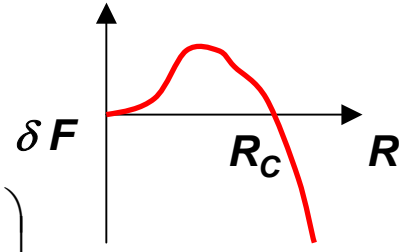


condensation:
$$-\Delta F \frac{N_1}{N} \left(\frac{4}{3} \pi R^3 / V_1 \right)$$

interface:
$$\gamma 4\pi R^2$$

Total balance:

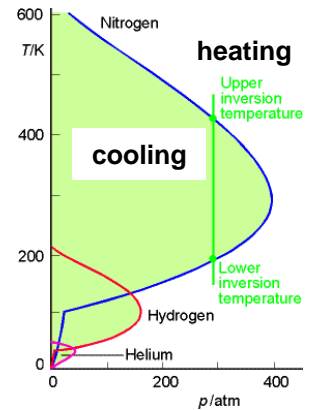
$$\delta F = \gamma 4\pi R^2 - \Delta F \frac{N_1}{N} \left(\frac{4}{3} \pi R^3 / V_1 \right)$$



Joule-Thomson Process for the vdW Gas

The JT process corresponds to an *isenthalpic expansion*:

$$\Delta H = \left(\frac{\partial H}{\partial T} \right)_P \Delta T + \left(\frac{\partial H}{\partial P} \right)_T \Delta P = 0 \quad \left(\frac{\partial H}{\partial T} \right)_P = C_P \quad C_P \Delta T = - \left(\frac{\partial H}{\partial P} \right)_T \Delta P$$



$$\boxed{\left(\frac{\Delta T}{\Delta P} \right)_H = \frac{- \left(\frac{\partial H}{\partial P} \right)_T}{C_P} = \frac{T \left(\frac{\partial V}{\partial T} \right)_P - V}{C_P}} \quad \left(\begin{array}{l} \Delta H = T\Delta S + V\Delta P \quad \left(\frac{\partial H}{\partial P} \right)_T = T \left(\frac{\partial S}{\partial P} \right)_T + V \\ \left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \quad \text{(see Pr. 5.12)} \end{array} \right)$$

This is a pretty general (model-independent) result. By applying this result to the vdW equation, one can qualitatively describe the shape of the inversion curve (requires solving cubic equations...).

We'll consider the vdW gas at **low densities**: $P \gg \frac{N^2 a}{V^2}$ $V \gg Nb$

$$\left(P + \frac{N^2 a}{V^2} \right) (V - Nb) = Nk_B T \quad PV + \frac{N^2 a}{V} - PNb = Nk_B T \left[\frac{\partial}{\partial T} (\dots) \right]_P$$

$$P \left(\frac{\partial V}{\partial T} \right)_P - \frac{N^2 a}{V^2} \left(\frac{\partial V}{\partial T} \right)_P = Nk_B \quad \left(\frac{\partial V}{\partial T} \right)_P = \frac{Nk_B}{P - \frac{N^2 a}{V^2}} \quad \boxed{\left(\frac{\Delta T}{\Delta P} \right)_H \approx \frac{2 \frac{Na}{k_B T} - Nb}{C_P}}$$

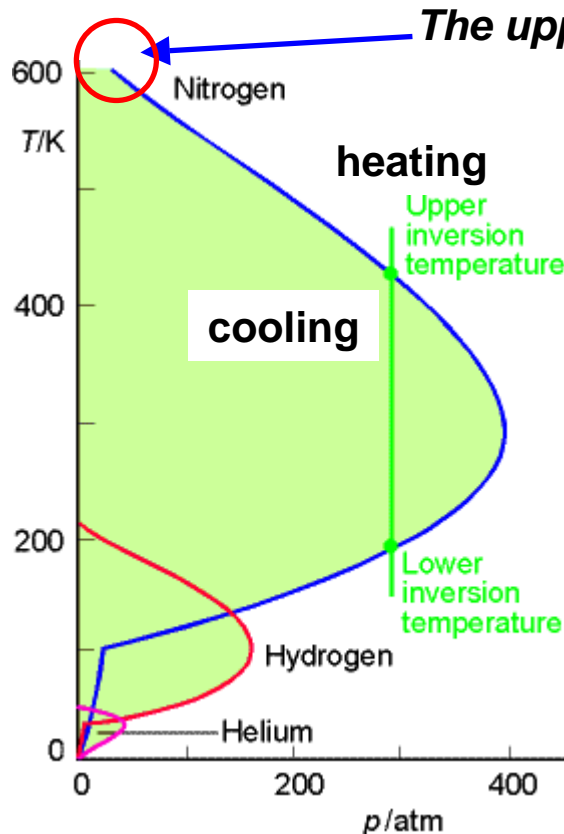
Joule-Thomson Process for the vdW Gas (cont.)

Cooling: $\frac{2a}{k_B T} - b > 0$

Heating: $\frac{2a}{k_B T} - b < 0$

If $b = 0$, T always **decreases** in the JT process: an increase of U_{pot} at the expense of K .
 If $a = 0$, T always **increases** in the JT process (despite the work of molecular forces is 0):

$$P(V - Nb) = RT \quad PV = RT - PNb \quad H = U + PV = (C_V + R)T + PNb = C_p T + PNb$$



**The upper inversion temperature:
(at low densities)**

$$\frac{2a}{k_B T_{INV}} - b = 0$$

$$T_{INV} = \frac{2a}{k_B b} = \frac{27}{4} T_C$$

(T_C – the critical temperature of the vdW gas, see below)

Substance	T_{INV} (P=1 bar)
CO ₂	(2050)
CH ₄	(1290)
O ₂	893
N ₂	621
H ₂	205
⁴ He	51
³ He	(23)

Thus, **the vdW gas can be liquefied by compression only if its $T < 27/4 T_C$.**

Problem

The vdW gas undergoes an *isothermal* expansion from volume V_1 to volume V_2 . Calculate the change in the Helmholtz free energy.

In the isothermal process, the change of the Helmholtz free energy is

$$(dF)_{T,N} = (-SdT - PdV + \mu dN)_{T,N} = -PdV$$

$$\Delta F = -\int_{V_1}^{V_2} PdV = -\int_{V_1}^{V_2} \left(\frac{RT}{V - Nb} - \frac{N^2 a}{V^2} \right) dV = N^2 a \left(\frac{1}{V_1} - \frac{1}{V_2} \right) - RT \ln \left(\frac{V_2 - Nb}{V_1 - Nb} \right)$$

compare with $F = U - TS$

$$(\Delta U_{vdW})_T = N^2 a \left(\frac{1}{V_1} - \frac{1}{V_2} \right) \quad (T\Delta S_{vdW})_T$$