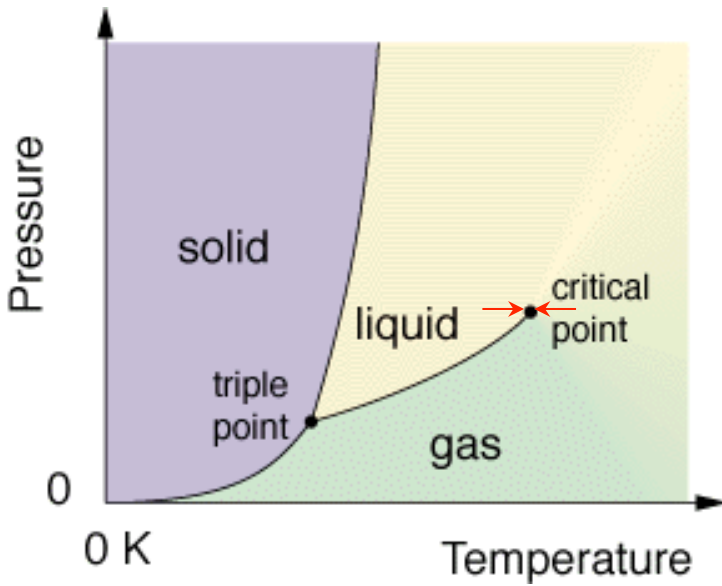


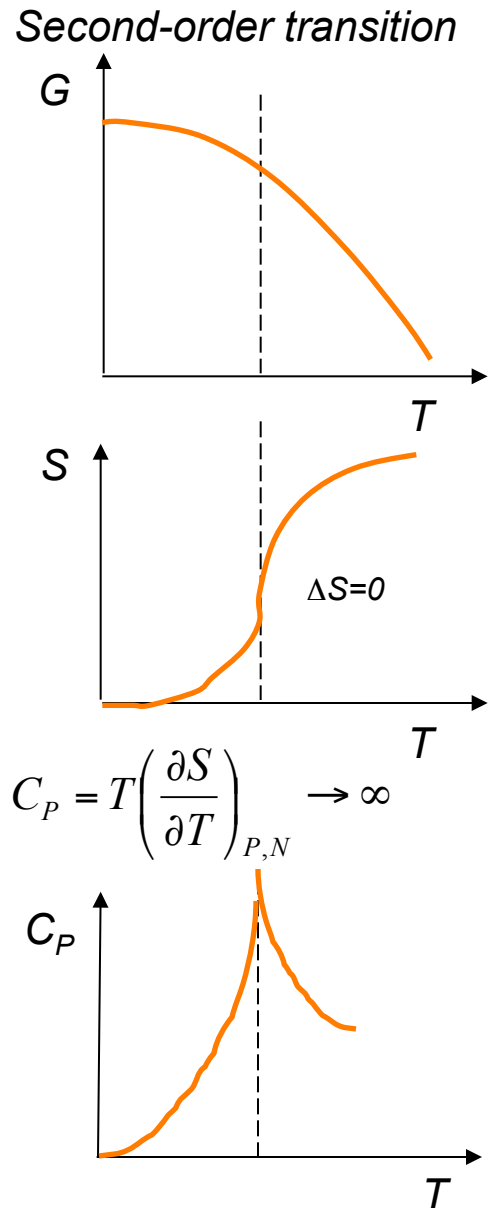
## Second-order phase transitions



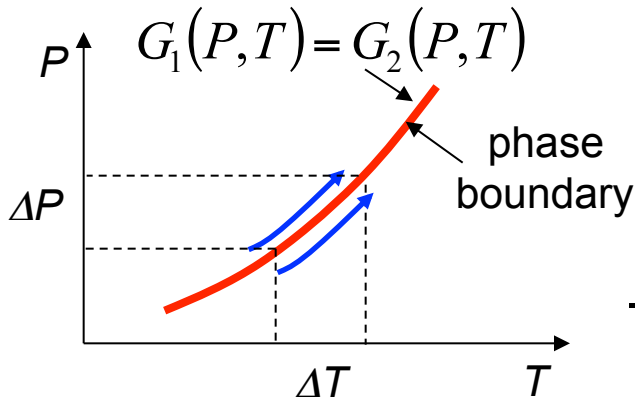
The vaporization coexistence curve ends at a point called the *critical point* ( $T_C, P_C$ ). As one moves along the coexistence curve toward the critical point, the distinction between the liquid phase on one side and the gas phase on the other gradually decreases and finally disappears at  $(T_C, P_C)$ . The  $T$ -driven phase transition that occurs *exactly* at the critical point is called a second-order phase transition. At pressures and/or temperatures beyond the critical point there is no physical distinction between liquid and gas. The density of the gas is so great and the thermal motion of the liquid is so great that gas and liquid are the same.

Unlike the 1<sup>st</sup>-order transitions, the 2<sup>nd</sup>-order transition does not require any latent heat ( $L=0$ ). In the *higher-order transitions* (*order-disorder transitions* or *critical phenomena*) the entropy is continuous across the transition. The specific heat  $C_P = T(\partial S/\partial T)_P$  diverges at the transition (a cusp-like “ $\lambda$ ” singularity).

These include the ferromagnetic phase transition in materials such as iron, where the magnetization, which is the first derivative of the free energy with respect to the applied magnetic field strength, increases continuously from zero as the temperature is lowered below the Curie temperature. The magnetic susceptibility, the second derivative of the free energy with the field, changes discontinuously.



# The Clausius-Clapeyron Relation



Along the phase boundary:

$$G_1(P, T) = G_2(P, T)$$

$$-S_1 dT + V_1 dP = -S_2 dT + V_2 dP$$

For the slope of the boundary we have:

$$\frac{dP}{dT} = \frac{S_1(P, T) - S_2(P, T)}{V_1(P, T) - V_2(P, T)}$$

*Clausius-Clapeyron Relation :*

$$\frac{dP}{dT} = \frac{L(T)}{T \Delta V(T)}$$

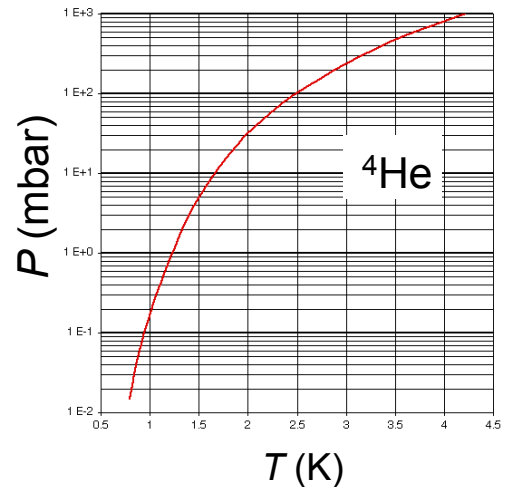
For the *liquid-gas* phase transition, we can make the following reasonable assumptions:

- molar volume of the liquid is much smaller than that of the gas (neglect  $V_{\text{liquid}}$ )
- molar volume of gas is given by the ideal gas law  $V = RT/P$
- latent heat is almost  $T$ -independent,  $L \approx L(T)$

$$\left( \frac{dP}{dT} \right)_{\text{vap}} \approx \frac{L}{TV_{\text{gas}}} = \frac{LP}{RT^2}$$

$$\frac{dP}{P} = \frac{L}{R} \frac{dT}{T^2}$$

$$P_{\text{vap}} \propto \exp\left(-\frac{L}{RT}\right)$$



**The triple point:**

$$G_{\text{liq}}(P_{\text{tr}}, T_{\text{tr}}) = G_{\text{gas}}(P_{\text{tr}}, T_{\text{tr}}) = G_{\text{sol}}(P_{\text{tr}}, T_{\text{tr}})$$

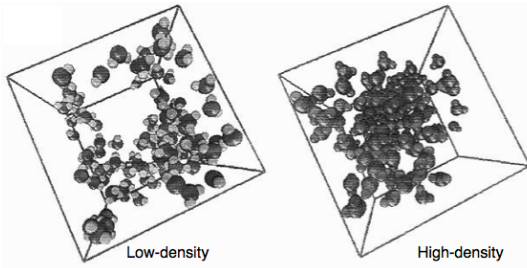
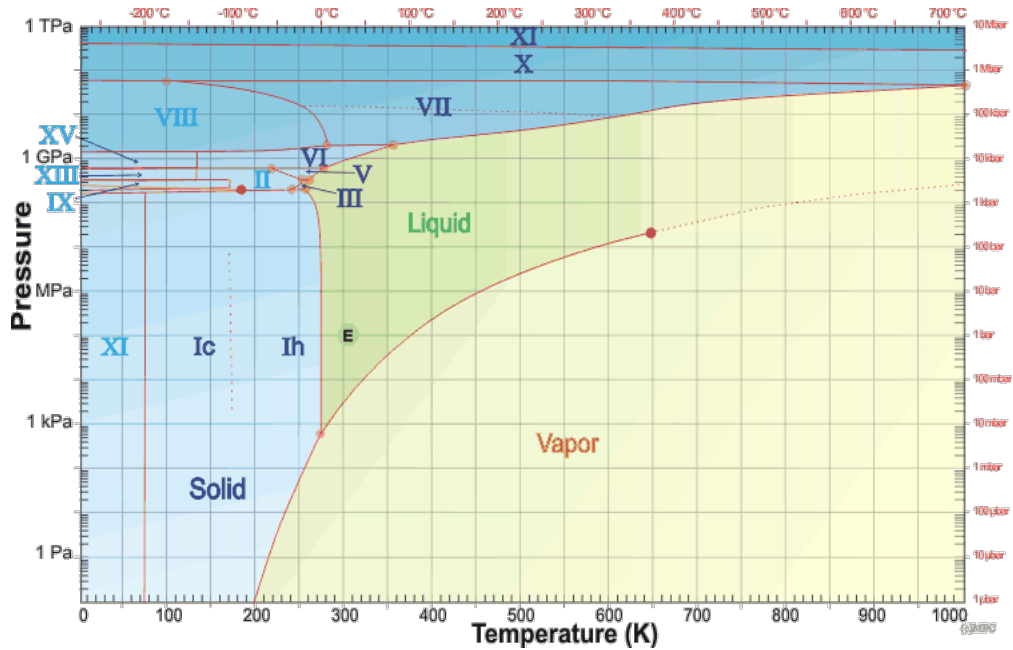
$$L_{\text{vap}} = T_{\text{tr}}(S_{\text{G}} - S_{\text{L}}) \quad L_{\text{melt}} = T_{\text{tr}}(S_{\text{L}} - S_{\text{S}}) \quad L_{\text{sub}} = T_{\text{tr}}(S_{\text{G}} - S_{\text{S}})$$



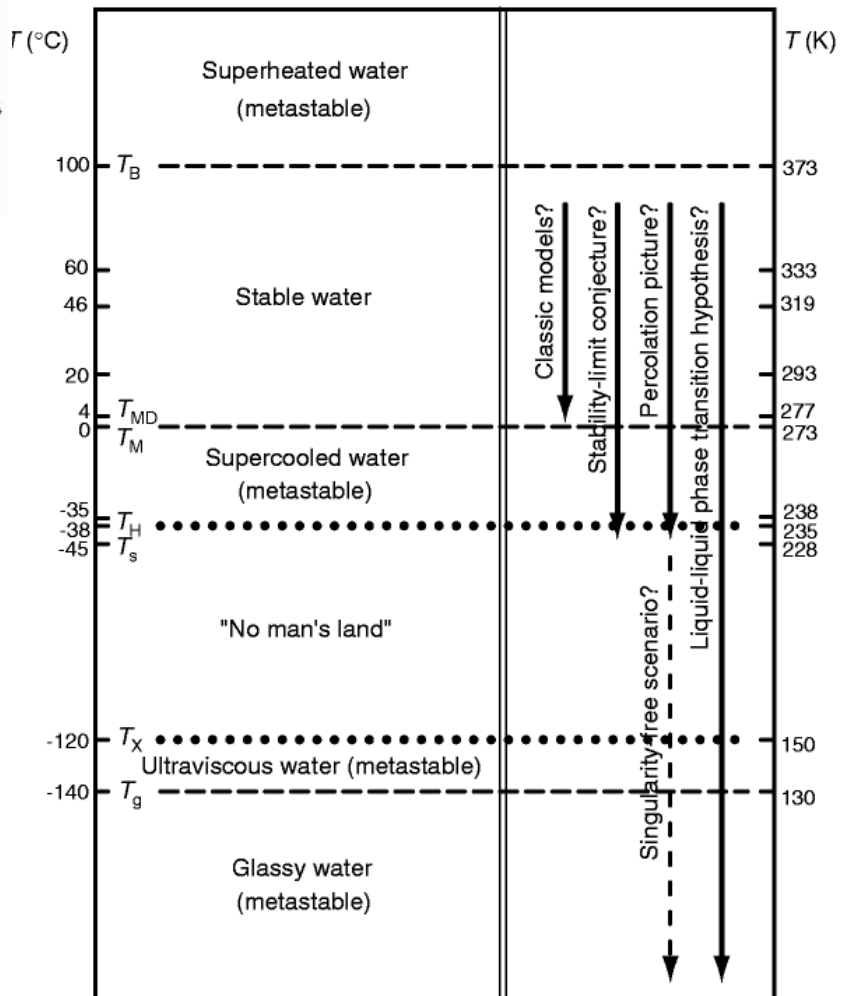
$$L_{\text{melt}}(T_{\text{tr}}) + L_{\text{vap}}(T_{\text{tr}}) = L_{\text{sub}}(T_{\text{tr}})$$

# Phase diagram of water

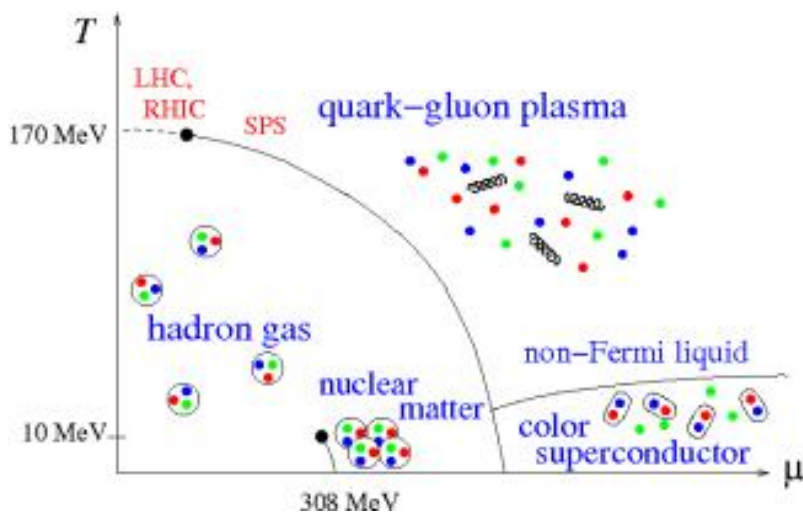
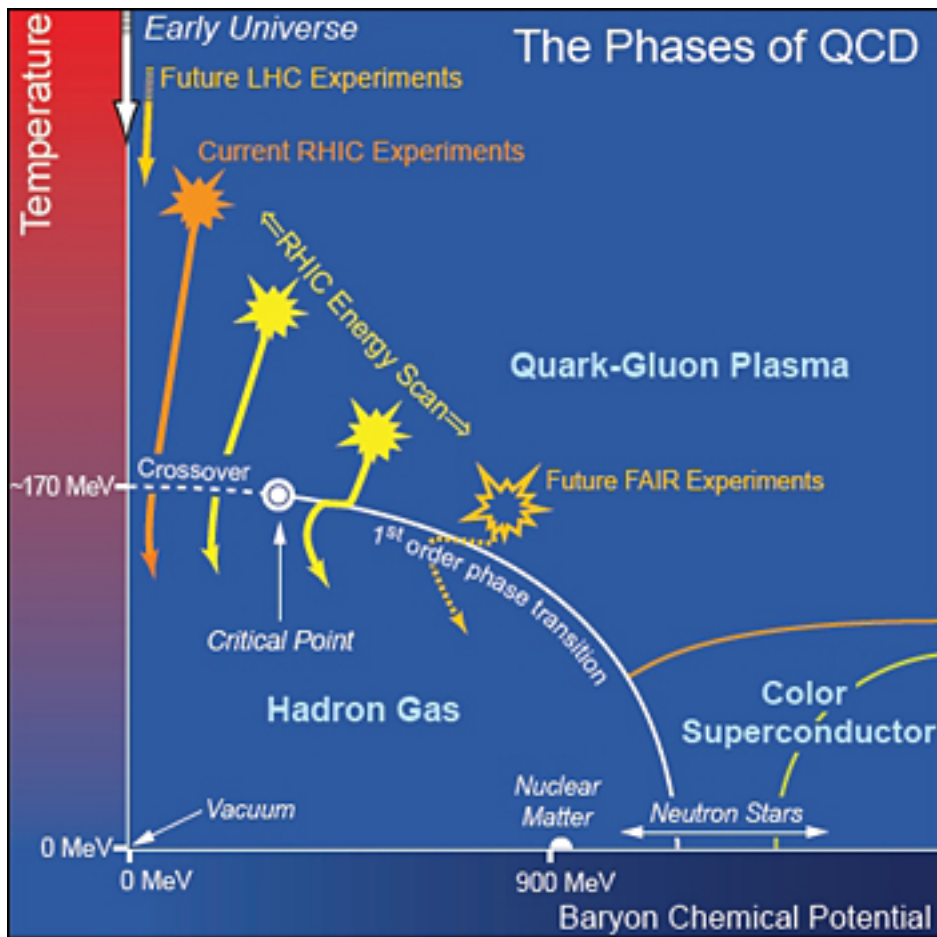
The critical point and the orange line in the ice-one phase space refer to the low-density (LDA) and high-density (HDA) forms of amorphous water (ice)



**Supercritical water** is created in submarine volcanoes. Many lie at such great depths that the tremendous pressure from the weight of the water above them prevents the explosive release of steam and gases. This causes the water to be heated to over 375 degrees C, turning the water in the hottest parts of the vents into a supercritical fluid since the pressure at this depth of over 3 km is over 300 atmospheres, well above the 218 atmospheres required.



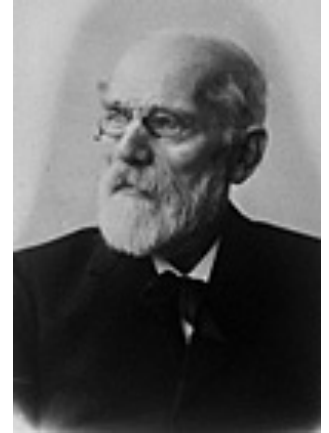
# Phase diagram of quark-gluon matter



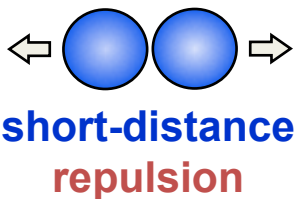
# van der Waals model

Phases exist because the particles interact with each other, in contrast to an ideal gas. The interactions are complicated (quantum mechanics), so we create simplified, effective models of the interparticle interactions in order to figure out what properties of the interactions lead to the observed phase diagrams.

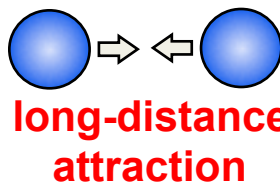
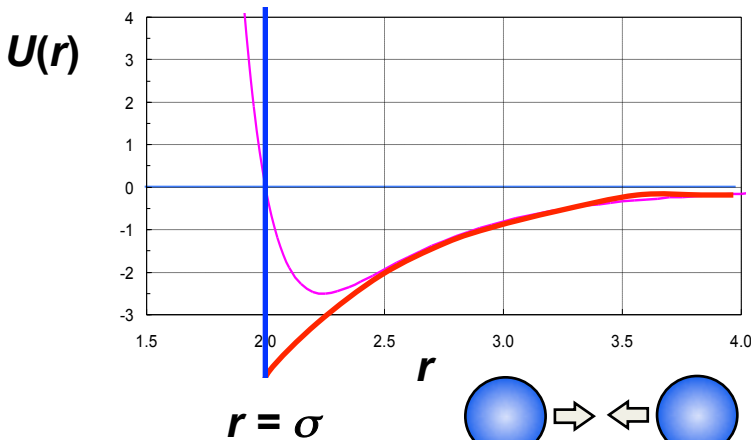
The van der Waals equation is an equation of state for a fluid composed of particles that have a non-zero volume and a pairwise attractive inter-particle force (such as the van der Waals force). It was derived in 1873 by Johannes Diderik van der Waals, who received the Nobel prize in 1910 for "his work on the equation of state for gases and liquids". The equation is based on a modification of the ideal gas law and approximates the behavior of real fluids, taking into account the nonzero size of molecules and the attraction between them.



Johannes van der Waals  
(1837 – 1923)



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



## Lennard-Jones

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

$$\Delta U = -N \cdot \frac{N}{V} \cdot a = -\frac{N^2 a}{V}$$

$$U_{\text{vdW}} = U_{\text{IG}} - \frac{N^2 a}{V} \Rightarrow P_{\text{eff}} = P + \frac{N^2 a}{V^2}$$

$$V_{\text{eff}} = V - Nb$$

the constant  $b$  ( $\sim 4\pi\sigma^3/3$ ) is a measure of the short-range repulsion, the “excluded volume” per particle

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

# The vdW equation of state

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

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

$a$  – 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	$a'$ ( $\text{J} \cdot \text{m}^3/\text{mol}^2$ )	$b'$ ( $\times 10^{-5} \text{ m}^3/\text{mol}$ )	$P_c$ (MPa)	$T_c$ (K)
Air	.1358	3.64	3.77	133 K
Carbon Dioxide ( $\text{CO}_2$ )	.3643	4.27	7.39	304.2 K
Nitrogen ( $\text{N}_2$ )	.1361	3.85	3.39	126.2 K
Hydrogen ( $\text{H}_2$ )	.0247	2.65	1.30	33.2 K
Water ( $\text{H}_2\text{O}$ )	.5507	3.04	22.09	647.3 K
Ammonia ( $\text{NH}_3$ )	.4233	3.73	11.28	406 K
Helium (He)	.00341	2.34	0.23	5.2 K
Freon ( $\text{CCl}_2\text{F}_2$ )	1.078	9.98	4.12	385 K

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

$Nb \ll V$  - low densities

$$PV \approx N \left( kT - \frac{Na}{V} \right)$$

$kT \gg \frac{Na}{V}$  - high temperatures  
(kinetic energy  $\gg$  interaction energy)

# Entropy of monatomic van der Waals gas

Multiplicity of ideal gas:  $\Omega_{\text{IG}}(N, V, U) \approx \frac{1}{N!} \frac{V^N}{(3N/2)!} \left( \frac{2\pi m U}{h^2} \right)^{3N/2} 2\Delta p$

Multiplicity of van der Waals gas:  $\Omega_{\text{vdW}}(N, V, U) \approx \frac{1}{N!} \frac{(V - Nb)^N}{(3N/2)!} \left( \frac{2\pi m \left( U + \frac{N^2 a}{V} \right)}{h^2} \right)^{3N/2} 2\Delta p$

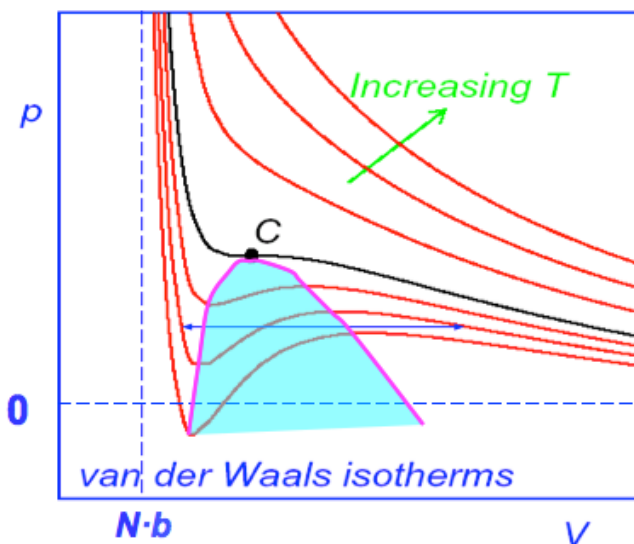
$$S_{\text{vdW}}(N, V, U) = Nk_B \left\{ \ln \left[ \frac{V - Nb}{N} \left( \frac{4\pi m U + \frac{N^2 a}{V}}{3h^2 N} \right)^{3/2} \right] + \frac{5}{2} \right\}$$

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{V, N} \quad U_{\text{vdW}} = \frac{3}{2} NkT - \frac{N^2 a}{V}$$

$$P = T \cdot \left( \frac{\partial S}{\partial V} \right)_{U, N} \quad P = \frac{NkT}{(V - Nb)} - \frac{N^2 a}{V^2}$$

$$\mu = -T \cdot \left( \frac{\partial S}{\partial N} \right)_{U, V} \quad \mu = -k_B T \ln \left[ \frac{V - Nb}{N} \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] - \frac{2Na}{V} + \frac{Nb}{V - Nb}$$

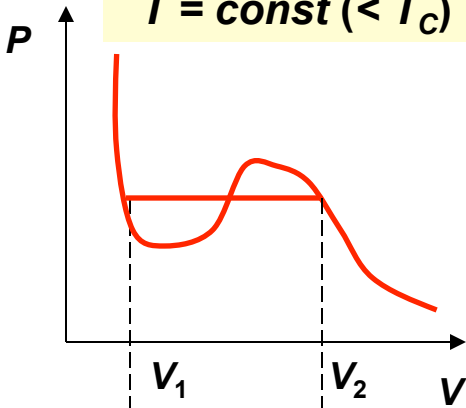
## van der Waals Isotherms



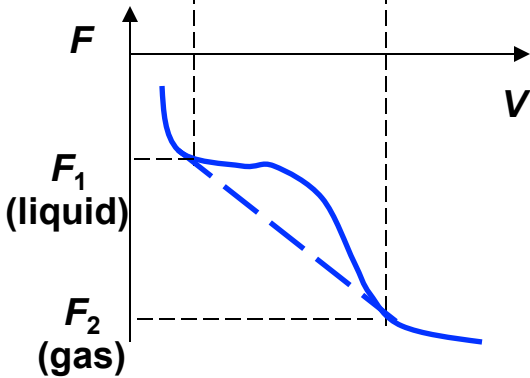
A real isotherm cannot have a negative slope  $dP/dn$  (or a positive slope  $dP/dV$ ), since this corresponds to a negative compressibility. The black isotherm at  $T=T_C$  corresponds to the critical behavior. Below  $T_C$ , the system becomes unstable against the *phase separation* (gas  $\leftrightarrow$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

# Phase Separation in the vdW Model

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



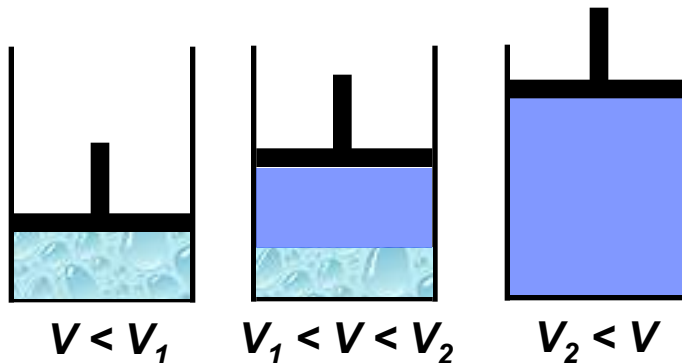
The phase transformation in the vdW model is easier to analyze by minimizing  $F(V)$  rather than  $G(P)$  (dramatic changes in the term  $PV$  makes the dependence  $G(P)$  very complicated, see below).



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:

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

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

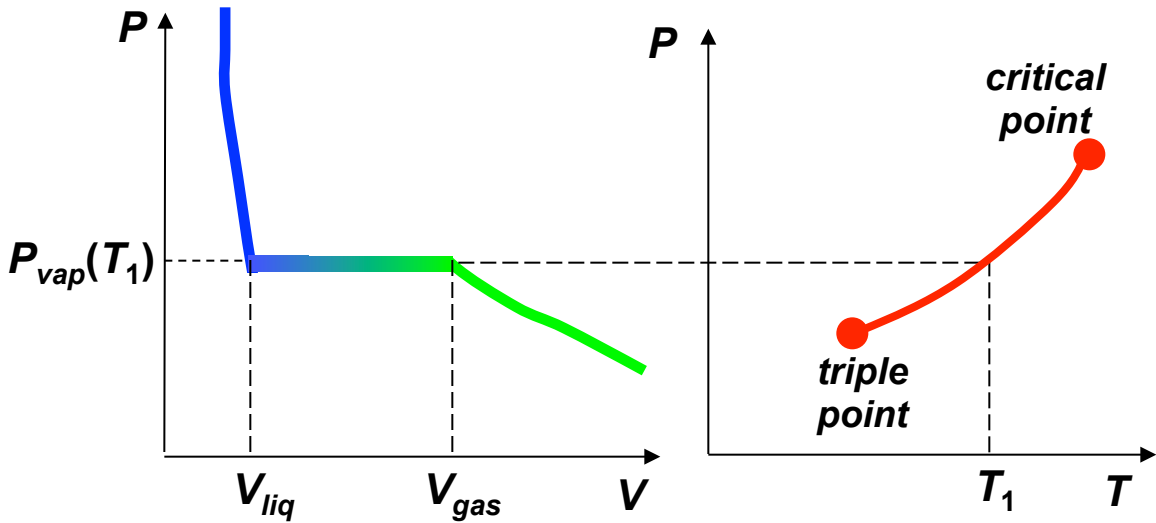
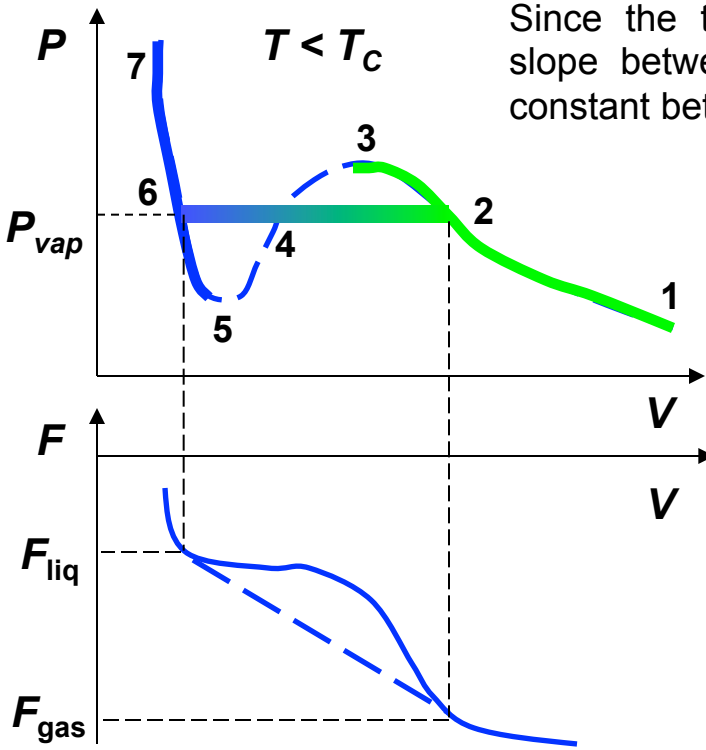




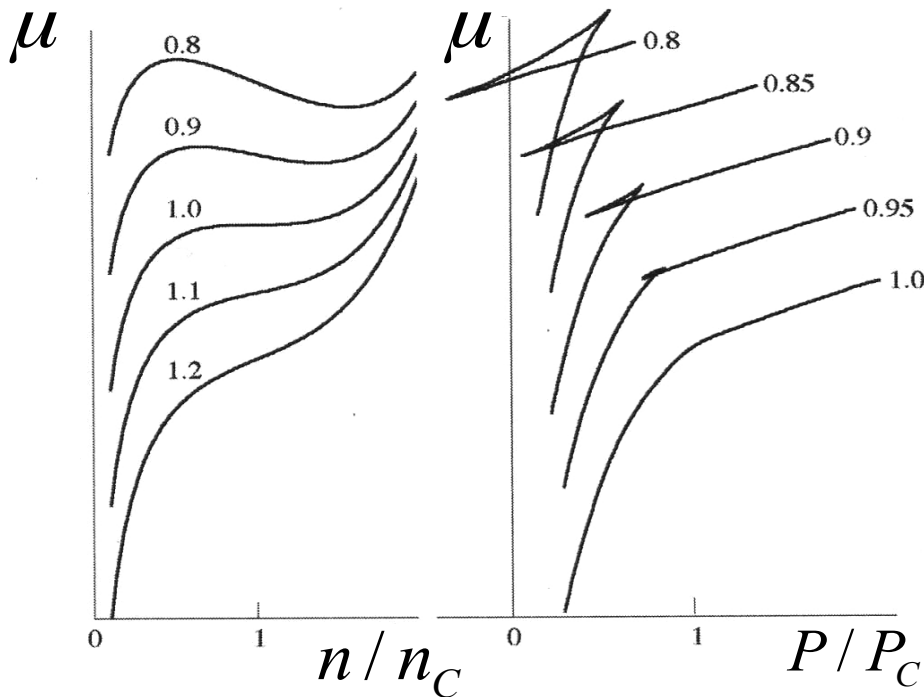
Since the tangent line  $F(V)$  maintains the same slope between  $V_1$  and  $V_2$ , the pressure remains constant between  $V_1$  and  $V_2$ :

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

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*.

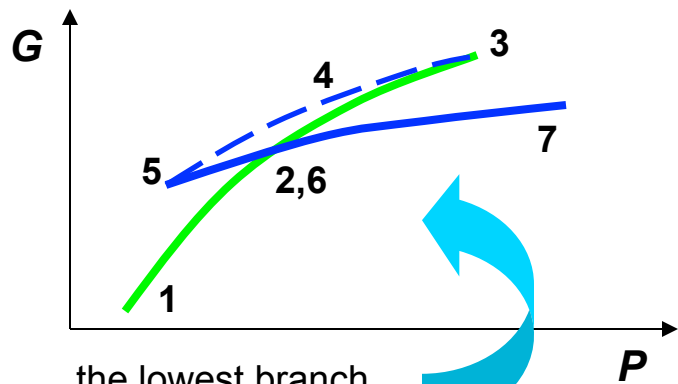


Two stable branches 1-2-3 and 5-6-7 correspond to *different phases*. Along branch 1-2-3  $V$  is large,  $P$  is small, the density is also small – gas. Along branch 5-6-7  $V$  is small,  $P$  is large, the density is large – liquid. Between the branches – *the gas-liquid phase transformation*, which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



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

The kink on the  $G(V)$  curve is a signature of the 1<sup>st</sup> 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 lowest branch represents the stable phase, the other branches are unstable