

Chapter 6

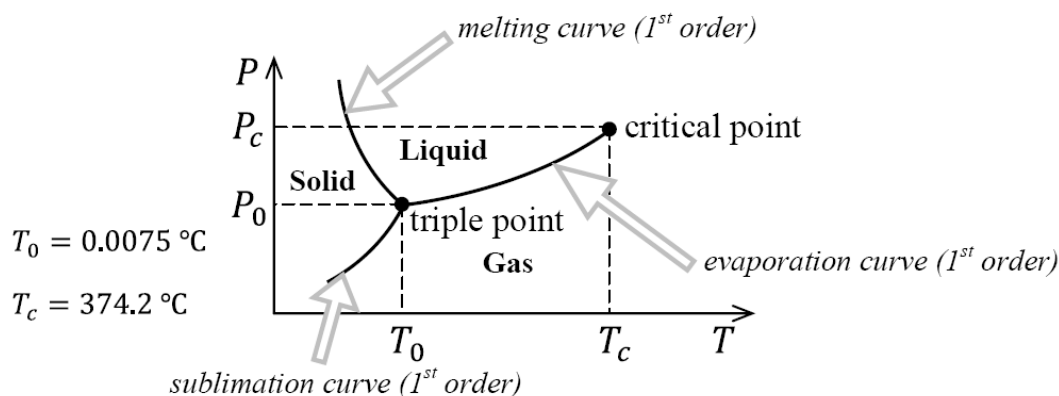
Phase transitions

6.1 Concept of phase

Phases are states of matter characterized by distinct macroscopic properties. Typical phases we will discuss in this chapter are liquid, solid and gas. Other important phases are superconducting and magnetic states.

First and second order phase transitions. States of matter come with their stability regions, the *phase diagram*. The properties of the microscopic state change by definition at the *phase boundary*. This change is

$\left. \begin{array}{l} \text{discontinuous} \\ \text{continuous} \end{array} \right\}$ for a $\left\{ \begin{array}{l} \text{first order} \\ \text{second order} \end{array} \right\}$ phase transition



The appropriate variables for phase diagram of water are the pressure P and the temperature T .

critical point : The first-order phase boundary between gas and liquid becomes second order right at the critical point. The two phases have then equal densities and specific entropies (entropy per particle).

★ There is no critical point for the liquid-solid transition.

triple point : The point at which gas, liquid and solid *coexist*.

Skating on ice. The melting curve of water has *negative slope*. Ice does hence melt at constant temperature $T < T_0$ when increasing the pressure P . This happens during skating on ice.

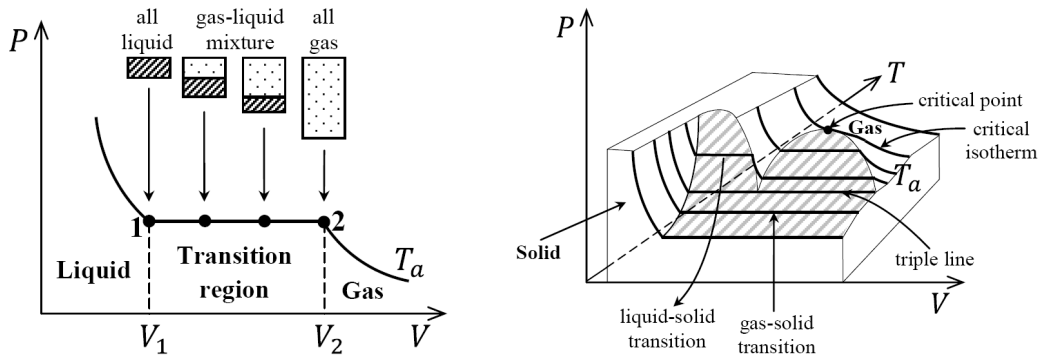
6.2 First-order phase transition

When water starts boiling, it undergoes a phase transition from a liquid to a gas phase. For both phases independently, the equation of state is a well-defined regular function, continuous, with continuous derivatives. However, while going from liquid to gas one function “abruptly” changes to the other function. Such a transition is of *first-order*.

Gibbs enthalpy. Phase transitions in the $P - T$ phase diagram are described by the Gibbs enthalpy $G(T, P, N)$, as defined by (5.11), which is itself a function of the pressure P and of the temperature T . $G(T, P, N)$ changes *continuously* across the phase boundary when the transition is of first order. The entropy S and volume V , which are given by the derivatives

$$S = - \left(\frac{\partial G}{\partial T} \right)_P, \quad V = \left(\frac{\partial G}{\partial P} \right)_T, \quad dG = -SdT + VdP + \mu dN$$

of the Gibbs potential, are in contrast *discontinuous*.



Latent heat. Let us consider an instead of the $P - T$ the $P - V$ diagram, which is a projection of the equation of state for water.

Two phases **1** and **2** coexisting at a temperature T_0 have *different* entropies S_1 and S_2 . The system must therefore absorb or release heat, the *latent heat* ΔQ_L ,

$$\Delta Q_L = T_0(S_2 - S_1) ,$$

during a phase transition of first order.

6.2.1 Condition for phase coexistence

We consider a system composed by one species of particles at given conditions of P and T (constant). Let us assume coexistence of two phases in our system. In this case, the

Gibbs potential is the sum of Gibbs potentials of the two phases,

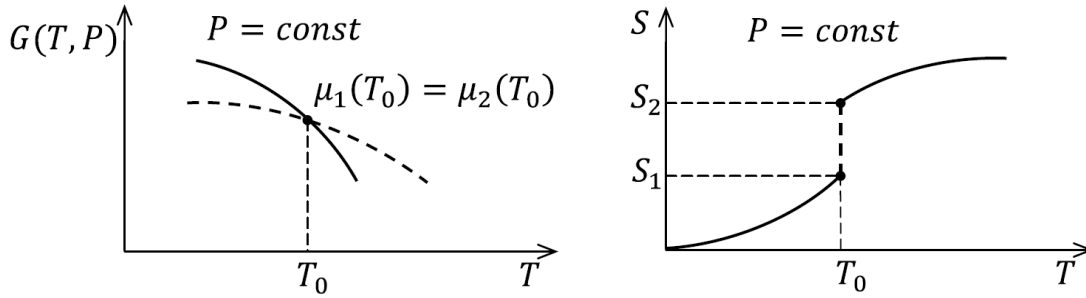
$$\begin{aligned} G(T, P, N) &= G_1(T, P, N_1) + G_2(T, P, N_2) \\ &= N_1\mu_1(T, P) + N_2\mu_2(T, P) , \end{aligned}$$

where we have used the Gibbs-Duhem relation (5.17). N_i and μ_i are the number of particles and the chemical potential in phase i and $N = N_1 + N_2$.

Principle of minimal Gibbs energy. The principle of minimal Gibbs energy discussed in Sect. 5.5.2 states that Gibbs potential has to be at its *minimum*, i.e. $dG = 0$, when P , T and $N = N_1 + N_2$ are fixed. G has to be therefore in equilibrium with respect to particle transfer from one phase to the other. This implies that

$$dG = \mu_1 dN_1 + \mu_2 dN_2 = 0, \quad \boxed{\mu_1(T, P) = \mu_2(T, P)} , \quad (6.1)$$

with $dN_1 = -dN_2$. The condition of *coexistence* (6.1), tells us that the two phases **1** and **2** must have identical chemical potentials.



6.2.2 Clausius-Clapeyron equation

We denote the discontinuities across the phase boundary with

$$\begin{aligned} \Delta G &= G_2(T, P, N_1) - G_1(T, P, N_2) \\ \Delta S &= S_2 - S_1 = - \left(\frac{\partial(\Delta G)}{\partial T} \right)_P, \quad \Delta V = V_2 - V_1 = \left(\frac{\partial(\Delta G)}{\partial P} \right)_T, \end{aligned} \quad (6.2)$$

where we assume that $S_2 > S_1$.

Cyclic chain rule. The discontinuities ΔG , ΔS and ΔV are functions of V , T and P , which are in turn related by the equation of state $f(P, V, T) = 0$. There must hence exist a function \tilde{f} such that

$$\tilde{f}(\Delta G, T, P) = 0 .$$

This condition allows to apply the cyclic chain rule discussed in Sect. 4.5. It leads to

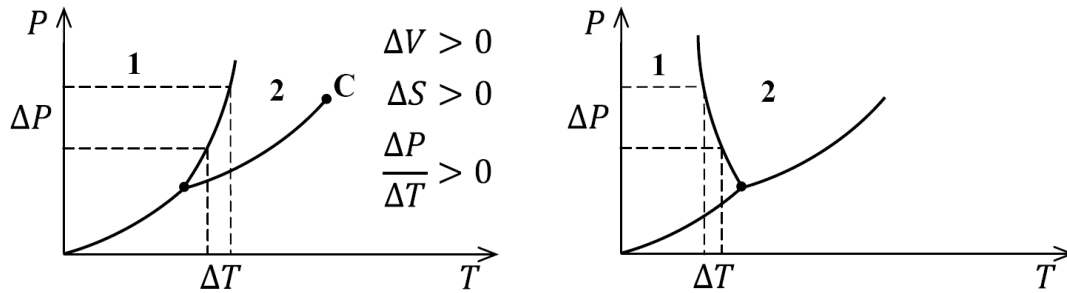
$$\underbrace{\left(\frac{\partial(\Delta G)}{\partial T} \right)_P}_{-\Delta S} \left(\frac{\partial T}{\partial P} \right)_{\Delta G} \underbrace{\left(\frac{\partial P}{\partial(\Delta G)} \right)_T}_{1/\Delta V} = -1 , \quad (6.3)$$

where we have used (6.2).

Vapor pressure. We note that P is the vapor pressure (Dampfdruck) for the gas-liquid transition. It changes with temperature along the phase transition line as

$$\boxed{\frac{dP}{dT} \equiv \left(\frac{\partial P}{\partial T}\right)_{\Delta G=0}}, \quad (6.4)$$

where we have used with $\Delta G = 0$ when the two phases are in equilibrium with each other. $(\partial P/\partial T)_{\Delta G=0}$ is hence slope of the transition line in the $P - T$ diagram.



The slope $\Delta P/\Delta T$ along the solid-liquid interface is positive when the substance contract upon freezing, the standard situation. Water does however expands upon freezing due to the Hydrogen bonding between molecules. $\Delta P/\Delta T$ is in this case negative.

Clausius-Clapeyron relation. We rewrite (6.3) as

$$\left(\frac{dP}{dT}\right)_{\Delta G=0} = \frac{\Delta S}{\Delta V}, \quad \boxed{\frac{dP}{dT} = \frac{\Delta Q_L}{T\Delta V}}, \quad (6.5)$$

where $\Delta Q_L = T\Delta S$ is the latent heat. All quantities entering the *Clausius-Clapeyron* relation (6.5) can be measured. It can be used either as a consistency check or to determine the latent heat ΔQ by measuring T , ΔV and the slope dP/dT .

Second order transitions. In a second-order phase transition the first derivatives of G vanish and the Clapeyron equation is replaced by a condition involving second derivatives.

6.3 Ehrenfest classification of phase transitions

For the following discussion, let us denote the two phases in equilibrium at a given coexistence curve as α and β . Following Ehrenfest we define next the *order of the phase transition*.

The order of the lowest derivative of the Gibbs enthalpy G showing a *discontinuity* upon crossing the coexistence curve is the order of a phase transition.

This definition quantifies the preliminary discussion of Sect. 6.1.

Phase transitions of order n . Explicitly, a phase transition between phases α and β is of order n if

$$\left(\frac{\partial^m G_\alpha}{\partial T^m}\right)_P = \left(\frac{\partial^m G_\beta}{\partial T^m}\right)_P, \quad \left(\frac{\partial^m G_\alpha}{\partial P^m}\right)_T = \left(\frac{\partial^m G_\beta}{\partial P^m}\right)_T$$

for $m = 1, 2, \dots, n-1$ and if

$$\left(\frac{\partial^n G_\alpha}{\partial T^n}\right)_P \neq \left(\frac{\partial^n G_\beta}{\partial T^n}\right)_P, \quad \left(\frac{\partial^n G_\alpha}{\partial P^n}\right)_T \neq \left(\frac{\partial^n G_\beta}{\partial P^n}\right)_T$$

In practice, only phase transitions of first- and second-order are of importance. Their properties are listed below.

1st order:

- 1) $G(T, P)$ continuous;
- 2) $S = -\left(\frac{\partial G}{\partial T}\right)_P$ and $V = \left(\frac{\partial G}{\partial P}\right)_T$ discontinuous;
- 3) \exists latent heat.

2nd order:

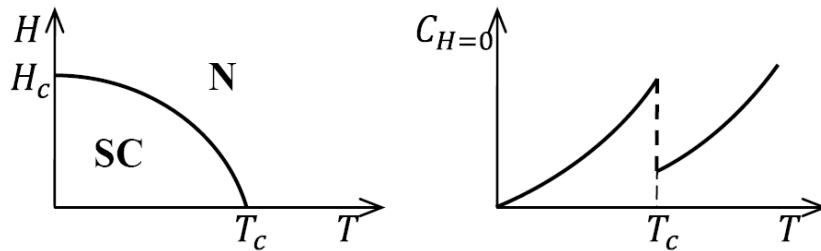
- 1) $G(T, P)$ continuous;
- 2) $S(T, P)$ and $V(T, P)$ continuous;
- 3) the discontinuities in the second order derivative of $G(T, P, N)$ leads to discontinuities of the *response functions*

$$C_P = T \left(\frac{\partial S}{\partial T}\right)_P = -T \left(\frac{\partial^2 G}{\partial T^2}\right)_P$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V} \left(\frac{\partial^2 G}{\partial P^2}\right)_T$$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right) = \frac{1}{V} \left(\frac{\partial^2 G}{\partial T \partial P}\right)$$

(susceptibilities) across the transition Here we have used the definition (4.19) for the heat C_P at constant pressure. κ_T is the isothermal compressibility, α the thermal expansion coefficient, as defined in Sect. 4.5, and $dG = -SdT + VdP + \mu dN$.



Specific heat jump. Phase transitions of the second order show a *finite discontinuity* in the specific heat C_P . An example is the transition to a superconducting state at zero magnetic field \mathcal{H} .

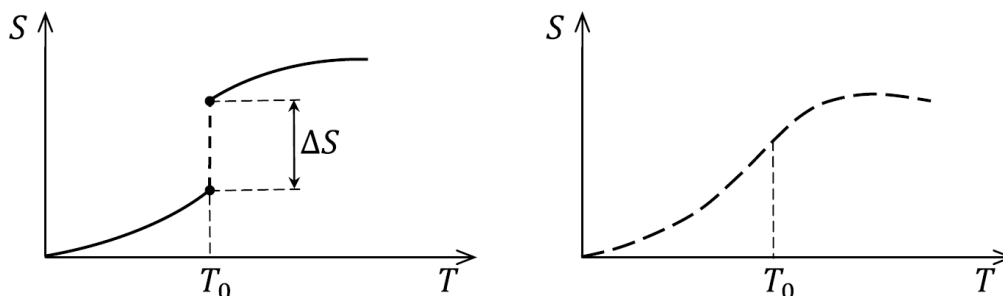
Diverging correlation length at criticality. The Ehrenfest classification is only valid if the motion of far away particles is not correlated, viz that the *correlation length* is finite. The correlation length diverges however at criticality for second order phase transition i.e. when $T \rightarrow T_c$. This leads in turn also to diverging response functions. The magnetic susceptibility χ of a magnetic system diverges f.i. as

$$\chi = \left(\frac{\partial M}{\partial H} \right)_T, \quad \chi(T) \sim \frac{1}{(T - T_c)^\gamma}, \quad (6.6)$$

where γ is the *critical exponent*. Critical exponents are evaluated using advanced statistical mechanics methods, such as the *renormalization group theory*. Note, however, that (6.6) is observed in most cases only very close to the transition.

The entropy for a discontinuous transition. Discounting the exact order of transition we may classify a phase transition in any case with regard to the continuity of the entropy. For a *discontinuous transition* we have:

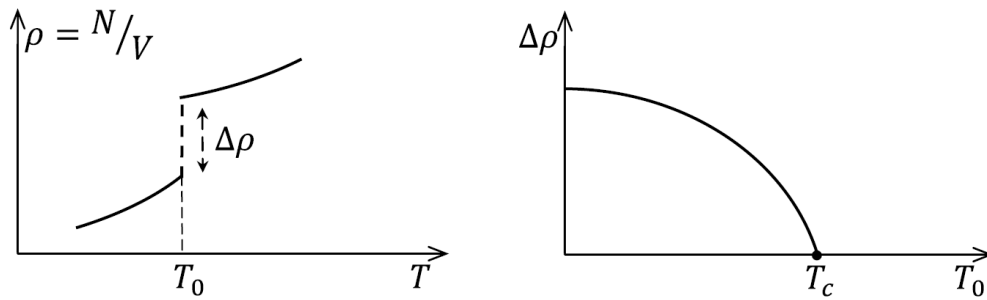
- (i) $\Delta S \neq 0$; \exists latent heat;
- (ii) $C_P = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_P$ is finite for $T \neq T_0$; no condition exists for $T = T_0$.



The entropy for a continuous transition. In this case we find:

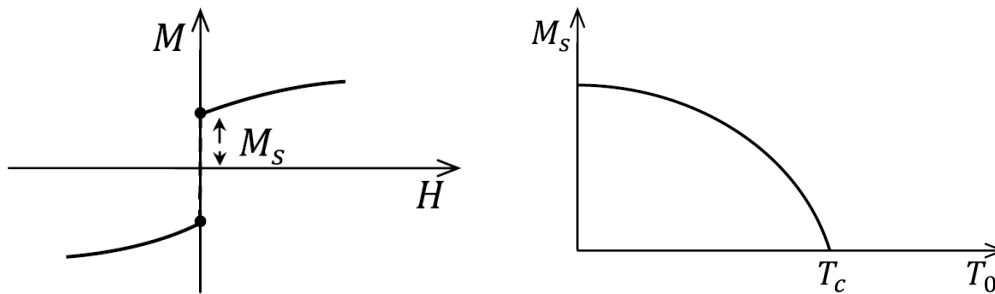
- (i) S continuous \Rightarrow no latent heat;
- (ii) \exists critical point T_c ;
- (iii) singularities in C_V, κ_T, χ_T

Density jumps. Consider a fluid system for which the volume $V = (\partial G / \partial P)_T$ shows a finite discontinuity ΔV at a 1st order phase transition, such as the liquid-gas line below the critical point. The corresponding densities particle density $\rho = N/V$ is then likewise discontinuous.



The density jump $\Delta\rho$ diminishes along the liquid-gas transition line, when the temperature is increased, until it vanishing at T_c . The transition becomes continuous at the critical point $T = T_c$.

Spontaneous magnetic ordering. The magnetization M of a magnetic compound is in part induced by an external magnetic field and in part due to the spontaneous ordering, viz by the alignment of the microscopic moments.



The magnetic work entering the internal energy $dU = \delta Q + \delta W$ is $\delta W = \mathcal{H}dM$, as defined by (3.15). With the Gibbs enthalpy $G(T, \mathcal{H})$ being the (two-fold) Legendre transform of the internal energy $U(S, M)$, we then have that

$$M = - \left(\frac{\partial G}{\partial \mathcal{H}} \right)_T, \quad dG = -SdT - Md\mathcal{H}.$$

The magnetization M is discontinuous when spontaneous ordering is present, i.e. when the transition is of 1st order. Following the transition line, by increasing the temperature $T \rightarrow T_c$, the jump $2M_s$ decreases until spontaneous ordering disappears and the phase transition becomes second-order at $T_0 = T_c$.

6.4 Van der Waals equation of state

The equation of state for an ideal gas,

$$PV = Nk_B T, \quad PV = nRT, \quad (6.7)$$

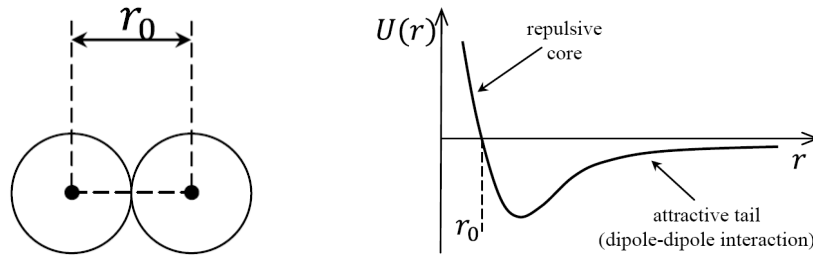
is only valid for very small densities of particles and, therefore, cannot describe the gas-liquid phase transition. This phase transition is due to *intermolecular* interactions. In

this section, we will derive an equation of state for a gas which includes intermolecular interaction in a phenomenological way.

Renormalized ideal gas. We consider with

$$P_{eff}V_{eff} = nRT \quad (6.8)$$

the ansatz that a gas of interacting molecules still obeys the ideal gas equation of state (6.7), albeit with yet to determine effective variables, where the *effective* pressure and temperature, P_{eff} and T_{eff} , are functions of the physical pressure P and temperature T respectively. One can regard (6.8) as a *renormalized* ideal gas equation of state.



Interaction potential. The interaction between molecules is generically composed of a repulsive core (due to the Fermi repulsion between the electrons) and an attractive tail (due to the *van der Waals* dipole-dipole interaction).

The depth of the attractive $U(r)$ is about 1 eV (changes with the gas species). This minimum is responsible for the chemical valence and for the crystal structure of solids.

Effective volume. The repulsive core of the intermolecular interaction leads to a volume exclusion, which can be modeled by considering the individual molecules as hard spheres of radius r_0 . The effective Volume entering (6.8) is then

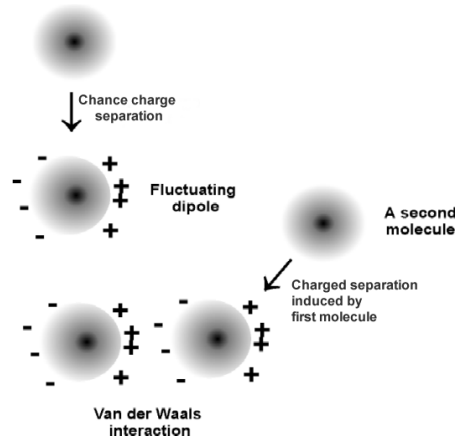
$$\boxed{V_{eff} = V - b'N}, \quad b' \approx \frac{1}{2} \frac{4\pi(2r_0)^3}{3} = \frac{16\pi r_0^3}{3}, \quad (6.9)$$

where $N = n(R/k_B)$ is the overall number of molecules. Note that two hard-core particle of radius r_0 cannot come closer than $2r_0$, with the factor $1/2$ in (6.9) correcting for double counting.

Effective pressure. The interaction between molecules is pairwise and therefore proportional to the square of the density N/V . The van der Waals interaction mediated by induced dipoles is furthermore attractive. We may hence assume with

$$P = P_{eff} - a' \frac{N^2}{V^2}, \quad a' > 0 \quad (6.10)$$

that the physical pressure P is smaller than the effective pressure P_{eff} by an amount proportional to $(N/V)^2$.



Van der Waals equation. We use

$$a = N_a^2 a', \quad b = N_a b', \quad N = N_a n,$$

where N_A is Avogadro's constant, together with the expressions (6.9) and (6.10) for the effective volume $V_{eff} = V - Nb'$ and respectively for the effective pressure $P_{eff} = P + a'N^2/V^2$. We then obtain the van der Waals equation

$$P_{eff}V_{eff} = nRT, \quad \boxed{\left(P + a\left(\frac{n}{V}\right)^2\right)(V - bn) = nRT}. \quad (6.11)$$

6.4.1 Virial expansion

Inter-particle interactions become irrelevant in the low density limit (N/V) $\rightarrow 0$, for which the the van der Waals equation (6.11), reduces consequently to the ideal-gas equation of state $PV = nRT$. It is hence of interest to evaluate the corrections to the ideal-gas equation of state by expanding (6.11) for fixed particle number N systematically in $1/V$.

Rescaling. We start by rescaling the parameters of the van der Waals equation:

$$an^2 = A, \quad B = bn, \quad \bar{R} = nR.$$

We then obtain

$$P = \frac{\bar{R}T}{(V - B)} - \frac{A}{V^2}, \quad \frac{PV}{\bar{R}T} = \left(1 - \frac{B}{V}\right)^{-1} - \frac{A}{\bar{R}TV}. \quad (6.12)$$

for (6.11),

Virial expansions. With the Taylor expansion

$$\left(1 - \frac{B}{V}\right)^{-1} = 1 + \frac{B}{V} + \left(\frac{B}{V}\right)^2 + \dots$$

of the first term in (6.12) with respect to $1/V$ we obtain

$$\frac{PV}{\bar{R}T} = 1 + \frac{1}{V} \left(B - \frac{A}{\bar{R}T}\right) + \left(\frac{B}{V}\right)^2 + \left(\frac{B}{V}\right)^3 + \dots \quad (6.13)$$

This expression has the form of a *virial expansion*:

$$\frac{PV}{\bar{R}T} = 1 + \frac{C_2}{V} + \frac{C_3}{V^2} + \dots, \quad \boxed{C_2 = B - \frac{A}{\bar{R}T}}, \quad (6.14)$$

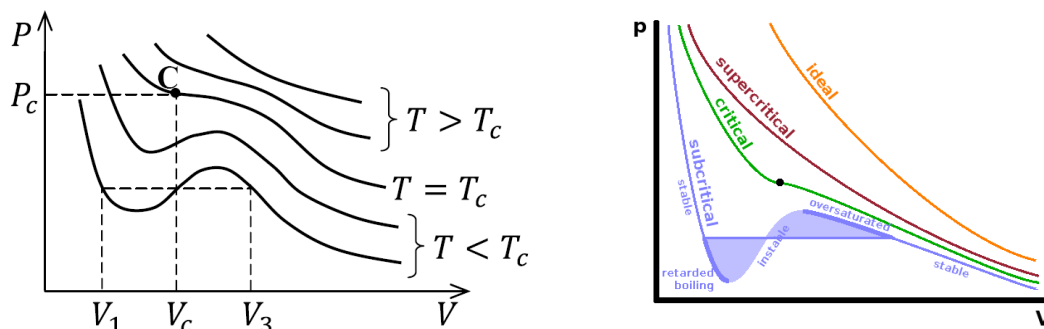
where C_n is the n^{th} virial coefficient. Measuring C_2 and $C_3 = B^2$ by observing experimentally the deviations from the ideal gas law on can extract the parameters A and B of the van der Waals gas. The virial expansion is also important for microscopic calculations.

6.4.2 Critical point

The the isotherms of the pressure P are uniquely defined via the van der Waals equation (6.12) by the Volume P . The reverse is however not true. Rewriting (6.11) we obtain

$$(PV^2 + an^2)(V - bn) = nRTV^2, \quad (6.15)$$

which shows that $V(P)$ is given by the roots of a 3rd-order polynomial.



Roots of the Van der Waals equation. For given T and P there exist either three real roots or one real and two complex roots of (6.15). There exists hence a *critical point* (P_c, V_c, T_c) such that (6.15) has

$$\begin{aligned} T < T_c \quad P < P_c & : \text{ three different real roots} \\ T = T_c \quad P = P_c & : \text{ one three-fold degenerate real root} \\ T > T_c \quad P > P_c & : \text{ one real root} \end{aligned}$$

The van der Waals of equation of the state must be then proportional to

$$(V - V_c)^3 = 0, \quad \boxed{V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0} \quad (6.16)$$

at the critical point (P_c, T_c, V_c) . Comparing (6.15) with (6.16) we find V_c , P_c , and T_c :

$$\left. \begin{aligned} 3V_c &= nb + \frac{nRT_c}{P_c} \\ 3V_c^2 &= \frac{an^2}{P_c} \\ V_c^3 &= \frac{abn^3}{P_c} \end{aligned} \right\} \left\{ \begin{aligned} V_c &= 3bn \\ P_c &= \frac{a}{27b^2} \\ RT_c &= \frac{8a}{27b} \end{aligned} \right. \quad (6.17)$$

Comparison with the ideal gas. Combining the roots found in (6.17) we can define with

$$\boxed{Z_c = \frac{P_c V_c}{nRT_c} = \frac{3}{8} = 0.375}$$

a universal parameter measuring the deviation of a real gas from the ideal gas limit $Z_c \rightarrow 1$. For water we have $Z_c = 0.226$ and $T_c = 324^\circ\text{C}$. Real gases are generically further away from the ideal gas limit than the van der Waals theory would predict.

6.4.3 Maxwell construction

The van der Waals isotherm is a monotonic function of V for $T > T_c$. For $T < T_c$, it has a “kink” with *negative* compressibility:

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T < 0, \quad \left(\frac{\partial P}{\partial V} \right)_T > 0. \quad (6.18)$$

Negative compressibility, if existent for a real gas, would however lead to a *collapse* of the system, with a decreasing volume V and pressure P inducing each other. The system would not be thermodynamically stable.

Phase separation. The working substance avoids the collapse by separating spontaneously into two phases, with each of the two phases being located in a point in the $V - P$ state phase characterized by a positive compressibility κ_T . These two phase will hence have different densities, corresponding respectively to a liquid and to a gas phase.

Coexistence condition. The two phases **1** and **2** are in equilibrium at the vapor pressure P_V , as discussed in Sect. 5.5.2, if the differentials of the Gibbs enthalpies coincide for constant $N_1 + N_2 = N$ and $V_1 + V_2 = V$:

$$\begin{aligned} dG_1(T, P_V, N_1) &= dG_2(T, P_V, N_2), \\ dF_1(T, V_1, N_1) + P_V dV_1 &= dF_2(T, V_2, N_2) + P_V dV_2, \end{aligned} \quad (6.19)$$

where we used that $G(T, P, N) = F(T, V, N) + PV$. Note that both the temperature T and the vapor pressure P_V are constant in (6.19).

Free energy. The free energy $F(T, V, N)$ defined by (5.12),

$$F(V, T) = - \int_{\text{isotherm}} P dV, \quad P = - \left(\frac{\partial F}{\partial V} \right)_{T, N}, \quad (6.20)$$

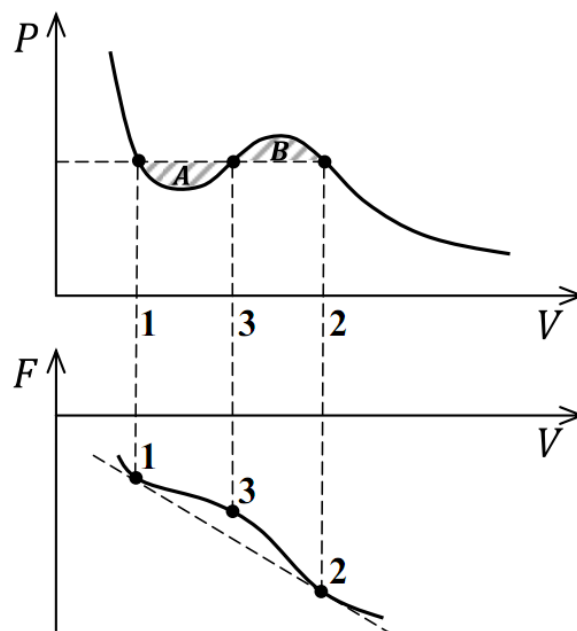
can be obtained as the area under the isotherm.

Integrating the coexistence condition (6.19) one obtains

$$F_1 - F_2 = P_V(V_2 - V_1), \quad (6.21)$$

which implies that the volumes V_1 and V_2 are defined by a double tangent construction.

- The free energy is a weighted mixture of two phases **1** and **2** at any point along the tangent between **1** and **2**. The resulting non-uniform state has the same P and T as the uniform state **3**, but a lower free energy.



Maxwell construction. We note that

$$F_2 - F_1 = \int_{V_1}^{V_2} (-P)dV = \int_{V_1}^{V_3} (-P)dV + \int_{V_3}^{V_2} (-P)dV$$

along any isotherm, according to (6.20). Rewriting the coexistence condition (6.21) as

$$F_2 - F_1 = P_V(V_1 - V_3 + V_3 - V_2)$$

we then obtain with

$$\boxed{\underbrace{P_V(V_3 - V_1) - \int_{V_1}^{V_3} P dV}_{\text{area A}} = \underbrace{\int_{V_3}^{V_2} P dV - P_V(V_2 - V_3)}_{\text{area B}}} \quad (6.22)$$

the *Maxwell construction*. Eq. (6.22) determines the vapor pressure $P_V = P(V_3)$ as the pressure for which the areas *A* and *B* are equal to each other.