E Interacting Systems

30 Virial Expansion

This is an expansion for small densities starting from an expansion in powers of $e^{\beta\mu}$.

30.a Grand canonical potential

We expand the grand canonical partition function by summing the contributions for various particle-numbers

$$Y = \sum_N Z(T,V,N)e^{N\mu/k_BT} = 1 + Z(T,V,1)e^{\mu/k_BT} + Z(T,V,2)e^{2\mu/k_BT} + ... \tag{30.1}$$

This is not a good expansion, since one has to sum up to very large particle numbers. It is much better to expand its logarithm

$$\ln Y = \underbrace{Z(1)e^{\mu/k_BT}}_{\text{one-particle problem}} + \underbrace{(Z(2) - \frac{1}{2}Z^2(1))e^{2\mu/k_BT}}_{\text{two-particle problem}} + ... \tag{30.2}$$

The potential energy be a sum of two-particle interactions,

$$H_{\text{pot}} = \sum_{i<j} W(x_i - x_j). \tag{30.3}$$

Then one obtains for the classical system

$$Z_{\text{kl}}(1) = \frac{V}{\lambda^3}, \tag{30.4}$$

$$Z_{\text{kl}}(2) = \frac{1}{2\lambda^6}\int d^3x_1 d^3x_2 e^{-\beta W(x_1-x_2)} \tag{30.5}$$

$$\begin{aligned} Z_{\text{kl}}(2) - \frac{1}{2}Z_{\text{kl}}^2(1) &= \frac{1}{2\lambda^6}\int d^3x_1 d^3x_2 \left(e^{-\beta W(x_1-x_2)} - 1\right) \\ &= \frac{V}{2\lambda^6}\int d^3x \left(e^{-\beta W(x)} - 1\right). \end{aligned} \tag{30.6}$$

One calls

$$b_{\text{kl}}(T) = -\frac{1}{2}\int d^3x (e^{-\beta W(x)} - 1) \tag{30.7}$$

the second virial coefficient and writes generally (including the quantum case)

$$Z(2) - \frac{1}{2}Z^2(1) = -\frac{V}{\lambda^6}b(T). \tag{30.8}$$

30.b Equation of state

From this expression we can determine the equation of state

$$\frac{PV}{k_{\mathrm{B}}T} = \ln Y = \frac{V\mathrm{e}^{\beta\mu}}{\lambda^3} - \frac{V\mathrm{e}^{2\beta\mu}}{\lambda^6}b(T) + O(\frac{\mathrm{e}^{3\beta\mu}}{\lambda^9}), \tag{30.9}$$

$$N = \frac{1}{\beta}\frac{\partial \ln Y}{\partial \mu} = \frac{V}{\lambda^3}\mathrm{e}^{\beta\mu} - 2\frac{V\mathrm{e}^{2\beta\mu}}{\lambda^6}b(T) + ... \tag{30.10}$$

$$\frac{V}{\lambda^3}\mathrm{e}^{\beta\mu} = N + 2V\left(\frac{\mathrm{e}^{\beta\mu}}{\lambda^3}\right)^2 b(T) + ... = N + 2b(T)\frac{N^2}{V} + ... \tag{30.11}$$

and therefore

$$\frac{P}{k_{\mathrm{B}}T} = \frac{N}{V} + b(T)\frac{N^2}{V^2} + O(\frac{N^3}{V^3}) \tag{30.12}$$

This expansion is called virial expansion. We note that we obtained for the ideal quantum gas in eq.(17.3)

$$b_{\mathrm{id.qu.}} = \mp\frac{\lambda^3}{\sqrt{32}(2S+1)} \tag{30.13}$$

A simple approximation for $b_{\mathrm{kl}}(T)$ is the following: The potential be strongly repelling for $|x_{12}| < c$ and weakly attractive for $|x_{12}| > c$

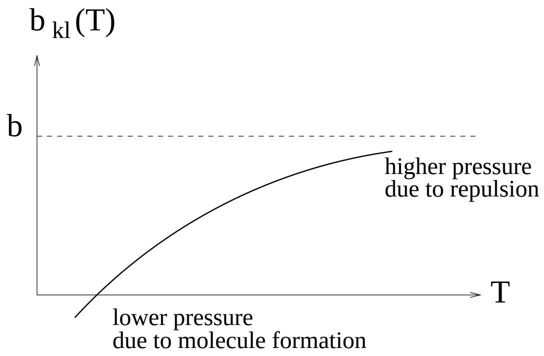
$$\mathrm{e}^{-\beta W(x)} - 1 = \begin{cases} -1 & |x| \le c, \\ -\beta W(x) & |x| > c. \end{cases} \tag{30.14}$$

Then one obtains

$$b_{\mathrm{kl}}(T) = b - \frac{a}{k_{\mathrm{B}}T}, \tag{30.15}$$

where $b = \frac{1}{2}\frac{4\pi}{3}c^3$ is four times the volume of the hard sphere and $a = -\frac{1}{2}\int_{r>c}\mathrm{d}^3 r W(r)$. In case of attraction one has $W < 0$, $a > 0$.

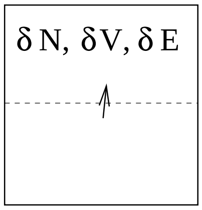
$b_{\mathrm{kl}}(T)$ *versus* T.



31 Phase Equilibria

31.a One component

The state of a homogeneous body in equilibrium is normally determined by giving the extensive quantities, e.g. energy, volume and particle number. It can happen that given these quantities the body is not homogeneous but consists of two states in touch with each other, which have different properties, as e.g. different density. Such states are called different phases of a component.



These phases have as all substances in equilibrium the same temperature, the same pressure and the same chemical potential. This is due to the fact that the entropy of the total system assumes its maximum.If one increases the energy of one phase by δE, its particle number by δN, and its volume by δV, then the change of the total entropy is

$$\delta S_{\text{tot}} = \underbrace{\left(\frac{1}{T} - \frac{1}{T'}\right)}_{0} \delta E - \underbrace{\left(\frac{\mu}{T} - \frac{\mu'}{T'}\right)}_{0} \delta N + \underbrace{\left(\frac{P}{T} - \frac{P'}{T'}\right)}_{0} \delta V, \tag{31.1}$$

which yields

$$T = T', \quad P = P', \quad \mu = \mu'. \tag{31.2}$$

If one expresses the chemical potentials as function of pressure and temperature, then one obtains the condition of equilibrium

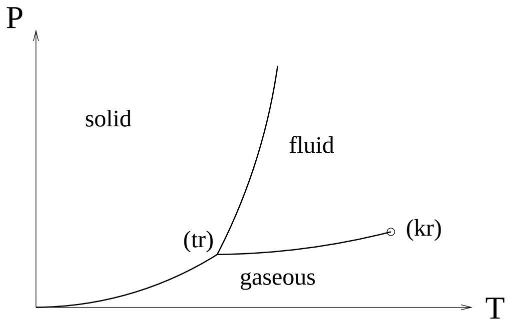
$$\mu(P,T) = \mu'(P,T). \tag{31.3}$$

This equation defines the coexistence curve $P(T)$ of two phases, as for example for the gaseous and the liquid phase. If there are three phases in equilibrium as at the triple point, then one has

$$\mu(P,T) = \mu'(P,T) = \mu''(P,T). \tag{31.4}$$

These two equations define the triple point

Schematic phase diagram



Latent heat We consider the transition of δN particles from the primed phase to the unprimed one. Then the system absorbs the heat

$$\delta Q = T \left(\left.\frac{\partial S}{\partial N}\right|_{P,T} - \left.\frac{\partial S'}{\partial N'}\right|_{P,T} \right) \delta N = T \left(\frac{S}{N} - \frac{S'}{N'} \right) \delta N \tag{31.5}$$

and its volume increases by

$$\delta V = \left(\left.\frac{\partial V}{\partial N}\right|_{P,T} - \left.\frac{\partial V'}{\partial N'}\right|_{P,T} \right) \delta N = \left(\frac{V}{N} - \frac{V'}{N'} \right) \delta N \tag{31.6}$$

Now we have

$$N \mathrm{d}\mu + S \mathrm{d}T - V \mathrm{d}P = 0, \tag{31.7}$$

thus

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP = -\frac{S'}{N'}dT + \frac{V'}{N'}dP = d\mu', \tag{31.8}$$

thus

$$\left(\frac{S}{N} - \frac{S'}{N'}\right) dT = \left(\frac{V}{N} - \frac{V'}{N'}\right) dP \tag{31.9}$$

along the coexistence curve. From this we obtain the relation of Clausius and Clapeyron

$$\frac{\delta Q}{\delta V} = T\frac{dP(T)}{dT}, \tag{31.10}$$

which gives a connection between the latent heat δQ, the volume change δV and the change of pressure along the coexistence curve as the temperature is changed.
Example: We consider the equilibrium of a substance with its vapor. The volume of the solid or liquid state be negligible. If we assume the ideal gas equation $PV = Nk_BT$ for the vapor phase, which implies for the transition $P\delta V = k_BT\delta N$, then we obtain with $q = \delta Q/\delta N$

$$\frac{dP}{dT} = \frac{q\delta N}{T\delta V} = \frac{qP}{k_BT^2}. \tag{31.11}$$

If q is approximately constant, then one has

$$P(T) = P_0 e^{-q/(k_BT)}. \tag{31.12}$$

31.b Several components

For n different substances (components) (with total particle numbers N_1, ... N_n) and m phases, one has

$$\mu_1 = \mu_1' = ... = \mu_1^{(m-1)}, \tag{31.13}$$

$$... \tag{31.14}$$

$$\mu_n = \mu_n' = ... = \mu_n^{(m-1)}. \tag{31.15}$$

These are in total $n(m-1)$ equations. Variables are P and T and the $m(n-1)$ independent concentrations. Then there remain

$$f = 2 + m(n-1) - n(m-1) = 2 + n - m \tag{31.16}$$

free independent variables. (Gibbs' phase rule). For one component ($n = 1$) we already found this. If we consider a saturated solution, that is a solution in equilibrium with its solute, then one has $n = 2$, $m = 2$, $f = 2$; the saturation concentration is a function of the two variables pressure and temperature, $c_s(P,T)$.

32 Dilute Solutions

32.a Osmotic pressure

Let us denote the particle number and the chemical potential of the solvent by $\bar{N}$ and by $\bar{\mu}$ and those of the solute by N_1 and μ_1 then the grand canonical partition function can be written

$$Y = \sum_{N_1} Y_{N_1}(\bar{\mu}, T, V) \mathrm{e}^{\beta\mu_1 N_1} = Y_0(\bar{\mu}, T, V) + Y_1(\bar{\mu}, T, V)\mathrm{e}^{\beta\mu_1} + ... \tag{32.1}$$

Y_{N_1} is the grand canonical partition function for the solvent with N_1 particles of the solute. Then one obtains

$$\ln Y = \ln Y_0 + V y_1(\bar{\mu}, T)\mathrm{e}^{\beta\mu_1} + O(\mathrm{e}^{2\beta\mu_1}) \tag{32.2}$$

with

$$V y_1 = \frac{Y_1}{Y_0}. \tag{32.3}$$

From this one obtains the particle number of the solute

$$N_1 = \frac{\partial \ln Y}{\beta \partial \mu_1} = V y_1(\bar{\mu}, T)\mathrm{e}^{\beta\mu_1} + O(\mathrm{e}^{2\beta\mu_1}), \tag{32.4}$$

from which one obtains the pressure

$$P(\bar{\mu}, T, N_1) = \frac{k_\mathrm{B} T}{V} \ln Y = P(\bar{\mu}, T, 0) + k_\mathrm{B} T \frac{N_1}{V} + O(\frac{N_1^2}{V^2}) \tag{32.5}$$

Note that the function y_1 does not appear in this order. Thus if two solutions are separated by a semipermeable membrane which is permeable for the solvent, but not for the solute, then the pressure difference

$$\Delta P = k_\mathrm{B} T \frac{\Delta N_1}{V} \tag{32.6}$$

acts on the membrane. This is van't Hoff's formula for the osmotic pressure. In this and the following calculations we take only the terms in lowest order in the concentration of the solute into account. Therefore they are only valid for dilute systems.

32.b Equilibrium shift

Now we will consider how the melting and boiling curve of the solvent is displaced. For this purpose we consider for fixed V and T the change of pressure

$$\mathrm{d}P = \left.\frac{\partial P}{\partial \bar{\mu}}\right|_{V,T,N_1=0} \mathrm{d}\bar{\mu} + \frac{k_\mathrm{B} T}{V}\mathrm{d}N_1 = \frac{\bar{N}}{V}\mathrm{d}\bar{\mu} + \frac{k_\mathrm{B} T}{V}\mathrm{d}N_1 \tag{32.7}$$

Thus one obtains for fixed pressure

$$\mathrm{d}\bar{\mu} = -\frac{k_\mathrm{B} T}{\bar{N}}\mathrm{d}N_1 \tag{32.8}$$

and thus for the chemical potential

$$\bar{\mu}(P, T, N_1) = \bar{\mu}(P, T, 0) - \frac{k_\mathrm{B} T}{\bar{N}} N_1 = \mu(P, T) - k_\mathrm{B} T c_1, \tag{32.9}$$

where μ is the chemical potential of the pure solvent and $c_1 = N_1/\bar{N}$ the concentration of the solute. For two phases in equilibrium one has $\bar{\mu} = \bar{\mu}'$, thus

$$\mu(P, T) - k_\mathrm{B} T c = \mu'(P, T) - k_\mathrm{B} T c'. \tag{32.10}$$

For the shift we introduce

$$P = P_0 + \Delta P, \quad T = T_0 + \Delta T, \tag{32.11}$$

and use

$$\mu(P,T) = \mu(P_0,T_0) + \underbrace{\left.\frac{\partial \mu}{\partial P}\right|_T}_{\frac{V}{N}=v} \Delta P + \underbrace{\left.\frac{\partial \mu}{\partial T}\right|_P}_{-\frac{S}{N}=-s} \Delta T \tag{32.12}$$

and obtain

$$(v - v')\Delta P - (s - s')\Delta T = k_\mathrm{B} T(c - c'). \tag{32.13}$$

As a special case we consider the lowering of vapor pressure. The unprimed phase be the vapor ($c = 0$ is assumed), the primed phase the liquid ($v' \ll v$). With $\Delta T = 0$ one obtains

$$v\Delta P = -k_\mathrm{B} T c', \quad \to \quad \frac{\Delta P}{P_0} = -c'. \tag{32.14}$$

This is Raoult's law.
Another special case is the lowering of the freezing point. Now we keep the pressure unchanged, $\Delta P = 0$. The unprimed phase be liquid, the primed solid. The solute be not solved in the solid phase, $c' = 0$. Since $q = T(s - s')$ is the heat disposed at freezing, then one obtains the lowering of the freezing point

$$\Delta T = -\frac{k_\mathrm{B} T^2 c}{q}. \tag{32.15}$$

32.c Saturation concentration and the heat of dilution

The solution of a solute be in equilibrium with the solute, so that the solution is saturated. The chemical potential of the solute in the solution is given by

$$\mu_1 = k_\mathrm{B} T \ln \frac{N_1}{V y_1(\mu, T)} = k_\mathrm{B} T \ln c_1 + g_1(P,T) + O(c_1) \tag{32.16}$$

with

$$g_1(P,T) = -k_\mathrm{B} T \ln y_1(\mu(P,T),T) + k_\mathrm{B} T \ln(\bar{n}(P,T)), \tag{32.17}$$

where $\bar{n}$ is the particle density of the solvent. Denoting the chemical potential of the pure solute by $\mu'(P,t)$ we obtain

$$\mu'(P,T) = \mu_1(P,T,c_\mathrm{s}) \tag{32.18}$$

and therefore the saturation concentration c_s is given by

$$c_\mathrm{s} = \mathrm{e}^{(\mu'(P,T) - g_1(P,T))/(k_\mathrm{B} T)}. \tag{32.19}$$

The heat of dilution is the heat which has to be removed from a system, if the pure solute is solved in the solvent at constant pressure and then the system is brought back to the initial temperature. If the energy is initially given by E_a and finally by E_e (at given temperature) and if the volume changes from V_a to V_e (at external pressure P) then the heat to be removed is the energy gain $E_\mathrm{a} - E_\mathrm{e}$ minus the work $P(V_\mathrm{e} - V_\mathrm{a})$ done against the external pressure,

$$\delta Q = (E_\mathrm{a} + PV_\mathrm{a}) - (E_\mathrm{e} + PV_\mathrm{e}) = I_\mathrm{a} - I_\mathrm{e}, \tag{32.20}$$

thus equal to the difference of the enthalpies: Enthalpy of solution (analogously reaction enthalpy). We determine now the enthalpy as function of $\bar{N}$, N_1, P, and T. We begin with the free enthalpy

$$G = \bar{N}\bar{\mu} + N_1\mu_1 = \bar{N}(\mu(P,T) - k_\mathrm{B} T \frac{N_1}{\bar{N}}) + N_1(k_\mathrm{B} T \ln \frac{N_1}{\bar{N}} + g_1(P,T)) = \bar{N}\mu + N_1 g_1(P,T) + k_\mathrm{B} T N_1 \ln \frac{N_1}{\mathrm{e}\bar{N}} \tag{32.21}$$

Thus we obtain the entropy

$$S = -\left.\frac{\partial G}{\partial T}\right|_{\bar{N},N_1,P} = -\bar{N}\frac{\partial \mu}{\partial T} - N_1\frac{\partial g_1}{\partial T} - k_\mathrm{B} N_1 \ln\frac{N_1}{\mathrm{e}\bar{N}} \tag{32.22}$$

and the enthalpies

$$I_\mathrm{e} = G + TS = \bar{N}(\mu - T\frac{\partial \mu}{\partial T}) + N_1(g_1 - T\frac{\partial g_1}{\partial T}), \tag{32.23}$$

$$I_\mathrm{a} = \bar{N}(\mu - T\frac{\partial \mu}{\partial T}) + N_1(\mu' - T\frac{\partial \mu'}{\partial T}). \tag{32.24}$$

Here I_e is the enthalpy of the solution and I_a the enthalpy of solvent plus solute. Then we obtain the heat of dilution (per particle)

$$q = (\mu' - T\frac{\partial \mu'}{\partial T}) - (g_1 - T\frac{\partial g_1}{\partial T}) = -k_\mathrm{B}T^2\frac{\partial \ln c_\mathrm{s}}{\partial T}. \tag{32.25}$$

Similarly the change of volume can be determined. It is given by the change of the free enthalpy with respect to pressure

$$\delta V = \frac{\partial (G_\mathrm{e} - G_\mathrm{a})}{\partial P} = N_1\frac{\partial (g_1 - \mu')}{\partial P} = -N_1 k_\mathrm{B} T\frac{\partial \ln c_\mathrm{s}}{\partial P}. \tag{32.26}$$

33 Chemical Equilibrium

33.a Equilibrium Condition

The particle numbers cannot arbitrarily change in a chemical reaction. Considering the reaction

$$2H_2 + O_2 \leftrightarrow 2H_2O \tag{33.1}$$

the number of particles will change by

$$\delta N_{H_2} = -2\delta n, \quad \delta N_{O_2} = -\delta n, \quad \delta N_{H_2O} = 2\delta n. \tag{33.2}$$

If generally the particle numbers change by

$$\delta N_i = \nu_i \delta n \tag{33.3}$$

then the reaction reads

$$\sum_i \nu_i A_i \leftrightarrow .\text{reaction enthalpy}\, q \tag{33.4}$$

One calls δn the number of elementary reactions,
The equlibrium state has a maximum of entropy for fixed E and V, similarly for fixed I and P. From

$$\sum_i \left.\frac{\partial S}{\partial N_i}\right|_{E,V} \delta N_i = 0 \quad \text{as well as from} \quad \sum_i \left.\frac{\partial S}{\partial N_i}\right|_{I,P} \delta N_i = 0 \tag{33.5}$$

one obtains

$$T\mathrm{d}S = -\sum_i \mu_i \delta N_i = -\sum_i \nu_i \mu_i \delta n = 0. \tag{33.6}$$

Thus the equilibrium condition reads

$$\sum_i \nu_i \mu_i = 0. \tag{33.7}$$

For our example we have $-2\mu_{H_2} - \mu_{O_2} + 2\mu_{H_2O} = 0$. The reaction enthalpy is obtained by

$$\mathrm{d}I = T\mathrm{d}S + \sum_i \mu_i \mathrm{d}N_i + V\mathrm{d}P \tag{33.8}$$

and thus

$$\delta I = \sum_i \nu_i (T\frac{\partial S}{\partial N_i} + \mu_i)\delta n = -T\sum_i \nu_i \frac{\partial \mu_i}{\partial T}\delta n, \tag{33.9}$$

where we have used eq. (33.7) and

$$\left.\frac{\partial S}{\partial N_i}\right|_{P,T,\text{other } N\text{s}} = -\left.\frac{\partial \mu_i}{\partial T}\right|_{P,\text{all } N} \tag{33.10}$$

and consequently we obtain the reaction enthalpy

$$q = -\frac{\delta I}{\delta n} = T\frac{\partial}{\partial T}(\sum_i \nu_i \mu_i). \tag{33.11}$$

33.b Dilute (ideal) gases

For dilute (ideal) gases the grandcanonical partition function Y can be written

$$Y = \prod_i Y_i = \prod_i \left(\sum_{N_i} \frac{1}{N_i!} Z_i^{N_i}(T,V) \mathrm{e}^{\beta\mu_i N_i} \right) \tag{33.12}$$

where Z_i is the partition function for one-particle of component i. It reads

$$Z_i = \frac{V}{\lambda_i^3} Z_i^{\mathrm{in}}(T) \tag{33.13}$$

with the thermal de Broglie-wavelength λ_i. For atoms without spin one has $Z_i^{\mathrm{in}} = 1$, for other atoms the internal degrees of freedom have to be taken into account (spin, rotation and vibration of molecules). One has to sum over all bound states (binding energy!). Then one obtains

$$Y = \exp\left(\sum_i \frac{V}{\lambda_i^3} Z_i^{\mathrm{in}}(T) \mathrm{e}^{\beta\mu_i} \right) \tag{33.14}$$

and therefore

$$N_i = \frac{\partial \ln Y}{\beta \partial \mu_i} = \frac{V}{\lambda_i^3} Z_i^{\mathrm{in}}(T) \mathrm{e}^{\beta\mu_i}, \tag{33.15}$$

$$PV = k_{\mathrm{B}} T \ln Y = k_{\mathrm{B}} T \sum N_i \tag{33.16}$$

thus

$$\mu_i = k_{\mathrm{B}} T \ln\left(P c_i \chi_i(T)\right), \quad \chi_i = \frac{\lambda_i^3}{k_{\mathrm{B}} T Z_i^{\mathrm{in}}(T)}, \quad c_i = \frac{N_i}{\sum_j N_j}. \tag{33.17}$$

Using the equilibrium condition $\sum_i \nu_i \mu_i = 0$ one obtains the the law of mass action

$$\prod_i c_i^{\nu_i} = \frac{A(T)}{P^{\sum_i \nu_i}}, \quad A(T) = \frac{1}{\prod_i \chi_i^{\nu_i}(T)}. \tag{33.18}$$

The heat of reaction is given by

$$q = T \sum_i \nu_i \frac{\partial \mu_i}{\partial T} = T \sum \nu_i \frac{\mu_i}{T} + k_{\mathrm{B}} T^2 \sum_i \nu_i \frac{\mathrm{d} \ln \chi_i}{\mathrm{d}T} = -k_{\mathrm{B}} T^2 \frac{\mathrm{d} \ln A(T)}{\mathrm{d}T}. \tag{33.19}$$

33.c Dilute solutions

The equilibrium condition for dilute solutions reads

$$\bar{\nu}\bar{\mu} + \sum_i \nu_i \mu_i = 0, \tag{33.20}$$

where it is assumed, that the solvent $\bar{A}$ participates in the reaction, $\bar{\nu}\bar{A} + \sum_i \nu_i A_i \leftrightarrow q$. With

$$\bar{\mu} \approx \mu(P,T), \quad \mu_i = k_{\mathrm{B}} T \ln c_i + g_i(P,T) \tag{33.21}$$

one obtains from

$$\mathrm{e}^{(\bar{\nu}\bar{\mu} + \sum_i \nu_i \mu_i)/(k_{\mathrm{B}} T)} = 1 \tag{33.22}$$

the law of mass action

$$\prod_i c_i^{\nu_i} = K(P,T) = \mathrm{e}^{-(\bar{\nu}\mu + \sum_i \nu_i g_i))/(k_{\mathrm{B}} T)}. \tag{33.23}$$

The enthalpy is given by

$$I = \bar{N}(\mu - T\frac{\partial \mu}{\partial T}) + \sum_i N_i (g_i - T\frac{\partial g_i}{\partial T}) \tag{33.24}$$

and thus the heat of reaction by

$$q = -I(\bar{N} = \bar{\nu}, N_i = \nu_i) = -k_{\mathrm{B}} T^2 \frac{\partial \ln K(P,T)}{\partial T}. \tag{33.25}$$

34 Van der Waals Equation

34.a Derivation

In section 30 we have considered a classical gas with an interacting potential

$$W(x) = \begin{cases} +\infty & |x| < c \quad \text{strongly repellend} \\ W_a(x) & |x| \geq c \quad \text{weakly attractive} \end{cases} \tag{34.1}$$

If only the repulsiv interaction is present then the partition function reads approximately

$$Z_0 = \frac{(V - V_0(N))^N}{N!\lambda^{3N}} \tag{34.2}$$

where $V_0 = V_0(N)$ is the excluded volume. Then the pressure reads

$$\frac{P}{k_\mathrm{B}T} = \frac{\partial \ln Z_0}{\partial V} = \frac{N}{V - V_0} = \frac{N}{V} + \frac{NV_0}{V^2} + ... \tag{34.3}$$

Comparison with the virial expansion in sect. 30 yields $V_0 = Nb(T)$. Together with an attractive potential we replace

$$P = k_\mathrm{B}T\frac{N}{V}(1 + b\frac{N}{V}) - \frac{N^2 a}{V^2} + O(\frac{N^3}{V^3}) \tag{34.4}$$

by

$$P = k_\mathrm{B}T\frac{N}{V - Nb} - \frac{N^2 a}{V^2}. \tag{34.5}$$

This is the van der Waals-equation.

34.b Discussion

We will now discuss the pressure as a function of volume at constant temperature (isotherms), $P = P(V, T)$. At first we determine

$$\frac{\partial P}{\partial V} = -k_\mathrm{B}T\frac{N}{(V - Nb)^2} + \frac{2N^2 a}{V^3}, \tag{34.6}$$

$$\frac{\partial^2 P}{\partial V^2} = k_\mathrm{B}T\frac{2N}{(V - Nb)^3} - \frac{6N^2 a}{V^4} \tag{34.7}$$

If both $\frac{\partial P}{\partial V}$ and $\frac{\partial^2 P}{\partial V^2}$ vanish, then the isotherm has a horizontal point of inflection. From both equations one obtains initially $\frac{2}{V - Nb} = \frac{3}{V}$ and then

$$V_\mathrm{c} = 3Nb, \quad k_\mathrm{B}T_\mathrm{c} = \frac{8a}{27b}, \quad P_\mathrm{c} = \frac{a}{27b^2}. \tag{34.8}$$

Thus one has for the critical point $\frac{Nk_\mathrm{B}T_\mathrm{c}}{P_\mathrm{c}V_\mathrm{c}} = \frac{8}{3}$. For spherical molecules one finds experimentally $\approx 3,4$. For $T > T_\mathrm{c}$ one has always $\frac{\partial P}{\partial V} < 0$, and thus

$$\kappa_T^{-1} = -V\frac{\partial P}{\partial V} = k_\mathrm{B}T\frac{NV}{(V - Nb)^2} - \frac{2N^2 a}{V^2} > 0, \tag{34.9}$$

For $T < T_\mathrm{c}$ there are regions, in which κ_T^{-1} is negative, which is unphysically. For $T < T_\mathrm{c}$ there are two phases, a dilute one which is gaseous and a denser fluid one, which can be in equilibrium. For this equilibrium $\mu_1 = \mu_2$ has to hold with $\mu = (F + PV)/N$. From $N\mathrm{d}\mu = V\mathrm{d}P - S\mathrm{d}T$ one obtains for fixed N and T

$$N(\mu_2 - \mu_1) = \int_{V_1}^{V_2} V\mathrm{d}P = VP|_{V_1}^{V_2} - \int_{V_1}^{V_2} P(T, V, N)\mathrm{d}V = 0, \tag{34.10}$$

thus

$$\int_{V_1}^{V_2} P(T,V,N)\mathrm{d}V = P(V_2 - V_1). \tag{34.11}$$

This is called the Maxwell-construction.
We now consider the coexistence curve in the vicinity of the critical point. For this purpose we write

$$P = P_\mathrm{c}(1+p), \quad V = V_\mathrm{c}(1+v), \quad T = T_\mathrm{c}(1+t). \tag{34.12}$$

Then the equation of state reads

$$p = \frac{8(t+1)}{3v+2} - \frac{3}{(v+1)^2} - 1 = -\frac{3}{2}v^3 + O(v^4) + t(4 - 6v + O(v^2)). \tag{34.13}$$

For the coexisting phases $p_1 = p_2$ must hold,

$$-\frac{3}{2}v_1^3 - 6tv_1 = -\frac{3}{2}v_2^3 - 6tv_2 \tag{34.14}$$

or equivalently

$$\underbrace{(v_1 - v_2)}_{A}\underbrace{(6t + \frac{3}{2}(v_2^2 + v_1v_2 + v_1^2))}_{B} = 0 \tag{34.15}$$

On the other hand one obtains from

$$\int_{v_1}^{v_2}(1+p(v))\mathrm{d}v = (1+p_2)v_2 - (1+p_1)v_1 \tag{34.16}$$

the equation

$$\left(v + 4tv - 3tv^2 - \frac{3}{8}v^4\right)_{v_1}^{v_2} = \left(v + 4tv - 6tv^2 - \frac{3}{2}v^4\right)_{v_1}^{v_2}, \tag{34.17}$$

from which one obtains

$$3t(v_1^2 - v_2^2) + \frac{9}{8}(v_1^4 - v_2^4) = 0 \tag{34.18}$$

or equivalently

$$3\underbrace{(v_1 - v_2)}_{A}\underbrace{(v_1 + v_2)}_{B'}\underbrace{(t + \frac{3}{8}(v_1^2 + v_2^2))}_{C} = 0 \tag{34.19}$$

Both equations can be solved by
α) $A = 0$. This yields $v_1 = v_2$, that is the same phase and thus describes a trivial solution.
β) $B = B' = 0$. Then we have $v_2 = -v_1$, $t + \frac{1}{4}v_1^2 = 0$, thus for $t < 0$.

$$v_1 = -2\sqrt{-t}, \quad v_2 = 2\sqrt{-t}, \quad p = 4t. \tag{34.20}$$

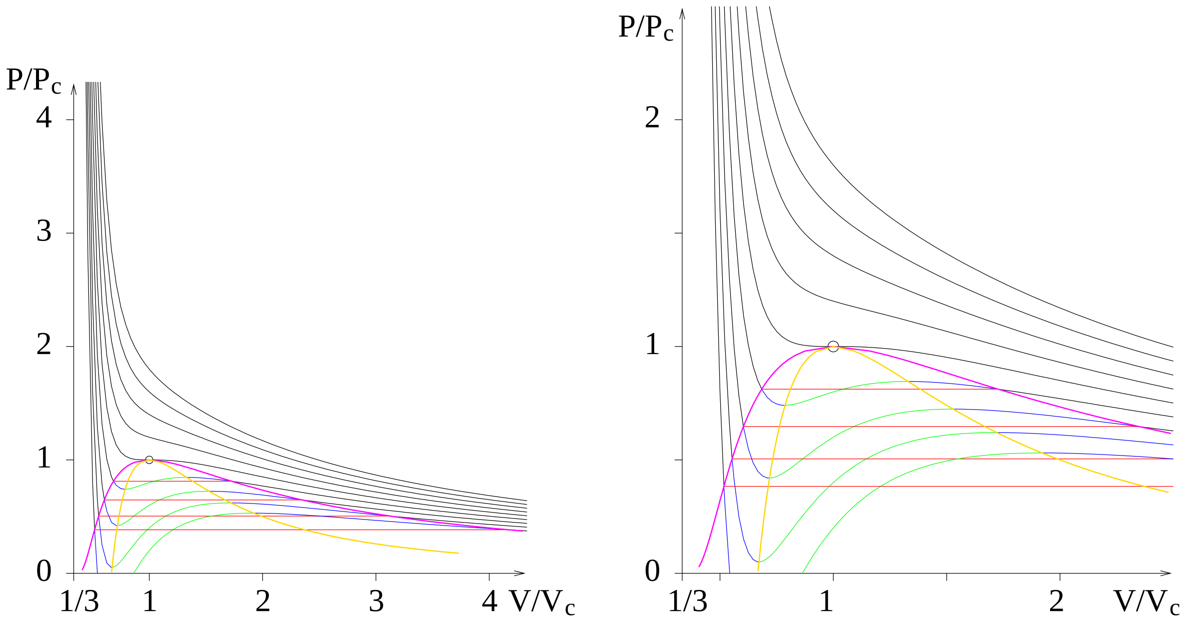
γ) There remains $B = C = 0$. Then one obtains $B - 6C = -\frac{3}{4}(v_1 - v_2)^2 = 0$, which again yields the trivial solution.
Thus we have close to the critical point

$$\delta V = \pm 2V_\mathrm{c}\sqrt{1 - \frac{T}{T_\mathrm{c}}} \quad T < T_\mathrm{c}. \tag{34.21}$$

The system is not stable between these two δV. Instead the system will separate in two phases, the liquid and the gaseous one. One also considers the curves along which κ_T^{-1} vanishes. One obtains for these

$$\frac{\partial p}{\partial v} = -\frac{9}{2}v^2 - 6t = 0, \quad v = \pm\sqrt{-\frac{4}{3}t} \tag{34.22}$$

and calls the curves spinodals. The compressibility is positive between coexistence curve and spinodal curve. In this region the system can be metastable (undercooled, overheated).



Isotherms of the Van der Waals gas: From top to bottom for T/T_c from 1.20 to 0.80 in steps of 0.05. The critical point is indicated by a small circle. The coexistence curve is shown in magenta, the spinodal in light brown. The two-phase region extends below the coexistence curve. In this region part of the system is fluid, the other gaseous. Both coexisting phases are connected by horizontal red lines.

35 Weiss Molecular Field Approximation

35.a Weiss Approximation

In this approximation it is assumed that each magnetic moment ($S = 1/2$)

$$m = \pm\mu_\mathrm{B} \tag{35.1}$$

senses an effective magnetic field (mean field, molecular field)

$$H_\mathrm{eff} = H + WM. \tag{35.2}$$

Here H is the external field, WM an internal field due to the interaction (actually short-range), M is the magnetization, W the Weiss factor. Then one obtains for the energy-levels

$$\epsilon_\pm = \mp\mu_\mathrm{B} H_\mathrm{eff} \tag{35.3}$$

for the magnetic moment and the averaged magnetic moment

$$\langle m\rangle = \mu_\mathrm{B}\frac{\mathrm{e}^{\beta\mu_\mathrm{B} H_\mathrm{eff}} - \mathrm{e}^{-\beta\mu_\mathrm{B} H_\mathrm{eff}}}{\mathrm{e}^{\beta\mu_\mathrm{B} H_\mathrm{eff}} + \mathrm{e}^{-\beta\mu_\mathrm{B} H_\mathrm{eff}}} = \mu_\mathrm{B}\tanh(\beta\mu_\mathrm{B} H_\mathrm{eff}) \tag{35.4}$$

and thus the equation for the magnetization (magnetic moment per volume)

$$M = \frac{N}{V}\langle m\rangle = \frac{N}{V}\mu_\mathrm{B}\tanh(\beta\mu_\mathrm{B}(H + WM)). \tag{35.5}$$

35.b Ising Model

In reality the interaction is short range, e.g. due to the overlapp of the electronic wave-functions

$$\hat{H} = -\frac{1}{2}\sum_{r,r'} I_{r,r'}\frac{m_r m_{r'}}{\mu_\mathrm{B}^2} - H\sum_r m_r \tag{35.6}$$

With the Ising-spins

$$\frac{m_r}{\mu_\mathrm{B}} = S_r = \pm 1 \tag{35.7}$$

one obtains the Ising model

$$\hat{H} = -\frac{1}{2}\sum_{r,r'} I_{r,r'} S_r S_{r'} - H\mu_\mathrm{B}\sum_r S_r. \tag{35.8}$$

35.c Infinitely long-ranged interaction

If one replaces the interaction by an infinitely long-ranged one, where $I_{r,r'} = I/N$ is equal for all pairs m_r, $m_{r'}$ (only division by the number N of spins yields a reasonable limit for $N \to \infty$), then one obtains

$$\hat{H} = -\frac{I}{2N}\sum_{r,r'} S_r S_{r'} = -\frac{I}{2N\mu_\mathrm{B}^2}\sum_{r,r'} m_r m_{r'} = -\frac{IV^2}{2N\mu_\mathrm{B}^2}M^2 \tag{35.9}$$

with the magnetic moment $M = \sum_r m_r/V$. With an external field H the Hamiltonian $\hat{H}$ reads

$$\hat{H} = -I\frac{V^2}{2N\mu_\mathrm{B}^2}M^2 - HMV \tag{35.10}$$

What is the free energy $F(M,T)$ without external field? From this one obtains the partition function

$$Y = \sum_M \mathrm{e}^{-\beta F(M,T) + \beta HMV} \tag{35.11}$$

Then the magnetization is obtained from the maximum

$$\frac{\partial(F - HMV)}{\partial M} = 0, \tag{35.12}$$

from which one obtains

$$H = \frac{1}{V}\frac{\partial F}{\partial M}. \tag{35.13}$$

We have now to calculate F,

$$F(M,T) = E(M) - TS(M), \quad E(M) = -\frac{IV^2}{2N\mu_{\rm B}^2}M^2. \tag{35.14}$$

There remains the determination of the entropy. Thus we have to determine how many spin configurations yield a given magnetization. If N_+ spins are up and N_- spins are down, then one obtains

$$N = N_+ + N_-, \quad MV = \mu_{\rm B}(N_+ - N_-), \tag{35.15}$$

and thus

$$N_\pm = \frac{1}{2}(N \pm \frac{MV}{\mu_{\rm B}}) \tag{35.16}$$

From this we obtain the entropy

$$S = k_{\rm B}\ln W = k_{\rm B}\ln\frac{N!}{N_+!N_-!} = k_{\rm B}\ln\left(\frac{N}{N_+}\right)^{N_+}\left(\frac{N}{N_-}\right)^{N_-}, \tag{35.17}$$

therefore

$$S(M) = -k_{\rm B}\left(\frac{N + \frac{MV}{\mu_{\rm B}}}{2}\right)\ln\left(\frac{1+\frac{MV}{N\mu_{\rm B}}}{2}\right) - k_{\rm B}\left(\frac{N - \frac{MV}{\mu_{\rm B}}}{2}\right)\ln\left(\frac{1-\frac{MV}{N\mu_{\rm B}}}{2}\right) \tag{35.18}$$

From $H - \frac{1}{V}\frac{\partial F}{\partial M} = 0$ we obtain

$$H_{\rm eff} = H + \underbrace{\frac{IV}{N\mu_{\rm B}^2}}_{W}M = \frac{k_{\rm B}T}{2\mu_{\rm B}}\ln\frac{1+\frac{MV}{N\mu_{\rm B}}}{1-\frac{MV}{N\mu_{\rm B}}} \tag{35.19}$$

from which one obtains

$$M = \frac{N}{V}\mu_{\rm B}\tanh(\beta\mu_{\rm B}(H+WM)), \tag{35.20}$$

and thus the Weiss approximation follows.

35.d Critical Behavior

We consider now the critical behavior, that is the behavior in the vicinity of the Curie-temperature. At this point $T = T_{\rm c}$, $H = 0$, the spontaneous magnetization vanishes. In its vicinity the magnetization is small. Thus we expand in powers of the magnetization

$$E = -\frac{1}{2}WVM^2, \tag{35.21}$$

$$S = k_{\rm B}N\ln 2 - \frac{k_{\rm B}N}{2}[(1+x)\ln(1+x) + (1-x)\ln(1-x)], \tag{35.22}$$

$$x = \frac{MV}{N\mu_{\rm B}} = \frac{M}{n\mu_{\rm B}}, \quad n = \frac{N}{V}, \tag{35.23}$$

$$S = k_{\rm B}N\ln 2 - k_{\rm B}N(\frac{x^2}{2} + \frac{x^4}{12} + ...) \tag{35.24}$$

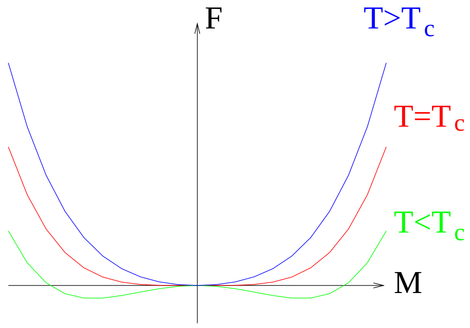
and thus obtain the free energy

$$F = -k_{\mathrm{B}}TN\ln 2 + VM^2\left(-\frac{1}{2}W + \frac{k_{\mathrm{B}}T}{2n\mu_{\mathrm{B}}^2}\right) + VM^4\frac{k_{\mathrm{B}}T}{12n^3\mu_{\mathrm{B}}^4} + ... \tag{35.25}$$

with $n = N/V$. For temperatures $T > T_{\mathrm{c}}$ mit $k_{\mathrm{B}}T_{\mathrm{c}} = n\mu_{\mathrm{B}}^2W$ the minimum of the free energy is at $M = 0$. This is the paramagnetic phase. We may now write

$$F = F_0(T) + \frac{1}{2}a(T)VM^2 + \frac{1}{4}b(T)VM^4 + ..., \quad a(T) = a_0\cdot(T - T_{\mathrm{c}}), \quad b(T) \approx b(T_{\mathrm{c}}) = b_0. \tag{35.26}$$

Sketch of the free energy



We obtain the equation of state from $\frac{\partial F}{\partial M} = HV$

$$a(T)M + b_0M^3 = H \tag{35.27}$$

This yields ($H = 0$, $T < T_{\mathrm{c}}$) the spontaneous magnetization

$$M = \pm\sqrt{-\frac{a(T)}{b(T)}} \approx \sqrt{\frac{a_0}{b_0}(T_{\mathrm{c}} - T)} \tag{35.28}$$

Taking the derivative of the equation of state with respect to the field H we obtain the susceptibility

$$(a(T) + 3b(T)M^2)\underbrace{\frac{\mathrm{d}M}{\mathrm{d}H}}_{\chi_T} = 1 \tag{35.29}$$

and thus

$$\chi_T = \frac{1}{a(T) + 3b(T)M^2}. \tag{35.30}$$

At vanishing external field $H = 0$ one obtains

$$\chi(T) = \begin{cases} \frac{1}{a_0(T-T_{\mathrm{c}})}, & T > T_{\mathrm{c}}, \\ \frac{1}{a(T)-3a(T)} = \frac{1}{2a_0(T_{\mathrm{c}}-T)}, & T < T_{\mathrm{c}}. \end{cases} \tag{35.31}$$

For $T = T_{\mathrm{c}}, H \neq 0$ one obtains

$$H = b_0M^3, \quad M = \left(\frac{H}{b_0}\right)^{1/3}. \tag{35.32}$$

As one approaches the critical point the susceptibility increases like

$$\chi = \frac{1}{3b_0M^2} = \frac{1}{3b_0}\left(\frac{H}{b_0}\right)^{-2/3}. \tag{35.33}$$

Finally for the specific heat at $H = 0$ one obtains

$$C_{H=0} = T\left.\frac{\partial S}{\partial T}\right|_{H=0} = T\frac{\partial S}{\partial M^2}\left.\frac{\partial M^2}{\partial T}\right|_{H=0} = \begin{cases} 0 & T > T_{\mathrm{c}}, \\ \frac{TVa_0^2}{2b_0} & T < T_{\mathrm{c}}. \end{cases} \tag{35.34}$$

Thus one finds a jump in the specific heat.

36 Landau Theory of Phase Transitions

36.a Landau Theory for critical phenomena

In a more general formulation the free energy is written as a volume integral over a density f

$$F = \int \mathrm{d}^3 r f(r) \tag{36.1}$$

where this density is again expanded in powers of the now local order-parameter $m(r)$,

$$f(r) = f_0(T) - h(r)m(r) + \frac{1}{2}a(T)m^2(r) + \frac{1}{4}b(T)m^4(r) + \frac{1}{2}c(T)(\nabla m(r))^2. \tag{36.2}$$

Here we allow an r-dependent magnetic field $h(r)$. The gradient-term is new in this expression. I t takes into account, that the interaction between spins is of short range and that it is energetically advantegeous, if the magnetization does not vary in space. The most probable state is obtained by taking the minimum of the free energy. If we vary $m(r) \to m(r) + \delta m(r)$, then we obtain in linear order in $\delta m(r)$

$$\delta F = \int \mathrm{d}^3 r \delta m(r)[-h(r) + am(r) + bm^3(r) - c\triangle m(r)] \tag{36.3}$$

where we used partial integration for the gradient term. Thus we obtain for the minimum

$$(a + bm(r)^2 - c\triangle)m(r) = h(r) \tag{36.4}$$

For a homogeneous magnetic field $h(r) = H$ one obtains the same space independent solution $M = \langle m(r)\rangle$ as above. But we may also obtain expressions for the correlations

$$g(r, r') = \langle((m(r) - M)(m(r') - M)\rangle. \tag{36.5}$$

Therefore we consider how the expectation value $\langle A\rangle$ changes if a perturbation δH is added to the Hamiltonian

$$\begin{aligned}
\langle A\rangle &= \frac{\mathrm{tr}(A\mathrm{e}^{-\beta(H_0+\delta H)})}{\mathrm{tr}(\mathrm{e}^{-\beta(H_0+\delta H)})} = \frac{\mathrm{tr}(A\mathrm{e}^{-\beta H_0}) - \beta\mathrm{tr}(A\delta H\mathrm{e}^{-\beta H_0})}{\mathrm{tr}(\mathrm{e}^{-\beta H_0}) - \beta\mathrm{tr}(\delta H\mathrm{e}^{-\beta H_0})} \\
&= \frac{\mathrm{tr}(A\mathrm{e}^{-\beta H_0})}{\mathrm{tr}(\mathrm{e}^{-\beta H_0})} - \frac{\mathrm{tr}(A\delta H\mathrm{e}^{-\beta H_0})}{\mathrm{tr}(\mathrm{e}^{-\beta H_0})} + \frac{\mathrm{tr}(A\mathrm{e}^{-\beta H_0})}{\mathrm{tr}(\mathrm{e}^{-\beta H_0})}\frac{\mathrm{tr}(\delta H\mathrm{e}^{-\beta H_0})}{\mathrm{tr}(\mathrm{e}^{-\beta H_0})} \\
&= \langle A\rangle_0 - \beta(\langle A\delta H\rangle_0 - \langle A\rangle_0\langle\delta H\rangle_0),
\end{aligned} \tag{36.6}$$

where we have kept all contributions linear in δH. We see that the reaction of the system to a perturbation is described by a correlation. One obtains with $A = m(r)$ and $\delta H = -\int \mathrm{d}^3 r'\delta h(r')m(r')$

$$\langle\delta m(r)\rangle = \beta\int \mathrm{d}^3 r'\delta h(r')(\langle m(r)m(r')\rangle - \langle m(r)\rangle\langle m(r')\rangle) = \beta\int \mathrm{d}^3 r'\delta h(r')g(r, r') \tag{36.7}$$

If we perform the variation in (36.4) then we obtain

$$(a + 3bM^2 - c\triangle)\delta m(r) = \delta h(r). \tag{36.8}$$

This differential equation can be solved by means of the Fourier transform

$$(a + 3bM^2 + cq^2)\delta m_q = \delta h_q \tag{36.9}$$

from which one obtains

$$\delta m(r) = \frac{1}{(2\pi)^3}\int \mathrm{d}^3 q\mathrm{d}^3 r'\frac{\mathrm{e}^{-iq(r-r')}}{a + 3bM^2 + cq^2}\delta h(r') = \frac{1}{4\pi}\int \mathrm{d}^3 r'\frac{\exp(-|r - r'|/\xi)}{|r - r'|}\delta h(r') \tag{36.10}$$

with the correlation length

$$\xi = \sqrt{\frac{c}{a+3bM^2}} = \begin{cases} (c/a_0)^{1/2}(T-T_\mathrm{c})^{-1/2} & \text{für for } T > T_\mathrm{c},\ h=0, \\ (c/2a_0)^{1/2}(T_\mathrm{c}-T)^{-1/2} & \text{für for } T < T_\mathrm{c},\ h=0. \end{cases} \tag{36.11}$$

Thus the correlation becomes of long range at the critical point. There it does not decay exponentially but algebraically. The correlation length increases with $\xi \propto 1/\sqrt{|T-T_\mathrm{c}|}$ as one approaches the critical point.

36.b Range of validity of the Landau theory

This theory assumes, that the free energy can be expanded in powers of the order-parameter. This holds for many approximations like the van der Waals equation for a fluid or for the molecular field theory by Weiss. These theories yield normally reasonable results as long as one is not too close to the critical point. In the vicinity of this point they yield wrong results.
Ginzburg has given a criterion when molcular field theory is good. He uses the following argument: There are considerable fluctuations in the order-parameter. However, one may average over some region. The largest distance across which this is reasonable is the correlation-length. Thus one requires, that the correlation is small in comparison to the square of the order-parameter,

$$\langle \delta m(\mathbf{r})\delta m(\mathbf{r}')\rangle_{|\mathbf{r}-\mathbf{r}'|=\xi} \ll m^2. \tag{36.12}$$

For simplicities' sake we leave now aside pure number factors, but consider the problem for general dimensionality d of space

$$\frac{k_\mathrm{B}T_\mathrm{c}}{c\xi^{d-2}} \ll \frac{|a|}{b}. \tag{36.13}$$

We denote the correlation length at temperature 0 by ξ_0 and introduce the relative temperature difference $\tau = \frac{T-T_\mathrm{c}}{T_\mathrm{c}}$. Then we may write $\xi = \xi_0/|\tau|^{1/2}$ and $a = a_0T_\mathrm{c}\tau$, so that the inequality reads

$$\frac{k_\mathrm{B}T_\mathrm{c}|\tau|^{d/2-1}}{c\xi_0^{d-2}} \ll \frac{a_0T_\mathrm{c}|\tau|}{b} \text{ oder } |\tau|^{2-d/2} \gg \frac{k_\mathrm{B}b}{ca_0\xi_0^{d-2}}. \tag{36.14}$$

We may now eliminate a_0, b, and c, by expressing the correlation length at temperature 0 and the jump ΔC of the specific heat by these quantities,

$$\xi_0 = \sqrt{\frac{c}{a_0T_\mathrm{c}}}, \quad \Delta C = T_\mathrm{c}\frac{a_0^2}{b}. \tag{36.15}$$

Then we obtain

$$|\tau|^{2-d/2} \gg \frac{k_\mathrm{B}}{\xi_0^d\Delta C}. \tag{36.16}$$

For $d = 3$ one should multiply by a numerical factor. According to the preceeding calculation this would be $1/(16\pi\mathrm{e})$ for $d = 3$. Ginzburg and Levanyuk gave a more careful argument and find, that the Landau-theory should be valid for $|\tau|$ larger then

$$\tau_\mathrm{c} = \frac{1}{32\pi^2}\left(\frac{k_\mathrm{B}}{\Delta C\xi_0^3}.\right)^2 \tag{36.17}$$

The factor ξ_0^6 in the denominator of τ_c indicates that with increasing range of the interaction, which yields a larger correlation length ξ_0, the region inside which Landau theory is invalid can become very small. This holds in particular for conventional superconductors. In tin one finds $\xi_0 = 2300$ Å and $\Delta C = 0.8 \times 10^4$ erg/cm^{3}K, from which $\tau_\mathrm{c} \approx 10^{-14}$ follows. In liquid helium one has a ξ_0, which corresponds to the distance of the atoms. As a result $\tau_\mathrm{c} \approx 1$. The jump of the specific heat in iron is $\Delta C \approx 3 \times 10^7$erg/cm^3 K and $\xi_0 = 2$ Å, from which one obtains $\tau_\mathrm{c} \approx 10^{-2}$. The magnetic fields of the spins in antiferromagnets have the tendency, to cancel each other. Thus τ_c is relatively large.

Ginzburg has estimated $\tau_c \approx 10^{-4}$ for ferroelectrica. For antiferroelectrica one expects larger values of τ_c.
We have performed the calculation for general dimension. This does not only yield an estimate for two-dimensional layers. We realize: If $d > 4$, then on the left hand side of equation (36.16) $|\tau|$ appears with a negative exponent. That is in such high dimensions the immediate vicinity of the critical point is no longer excluded from Landau theory. In four dimensions one has $|\tau|^{2-d/2} = 1$. Since below this dimension the critical phenomena differ from molecular field theory, $d = 4$ is called upper critical dimension.

36.c Power laws and critical exponents

Already at the turn of the century (1900) it was known, that the molecular field behavior as e.g. of the van der Waals equation does not describe the behavior in the vicinity of the critical point correctly. (For the history of critical phenomena see J.M.H. Levelt-Sengers, Physica 73 (1974) 73.) For example one had observed experimentally that the density of a gas or a liquid is not desribed by $\rho - \rho_c \propto (T - T_c)^\beta$ with $\beta = 1/2$, but by $\beta = 0.3434$ (Verschaffelt 1900). Similarly other quantities like susceptibility, specific heat, correlations showed laws with different powers,

$$\begin{array}{lc}
\text{specific heat} & C \propto \tau^{-\alpha} \\
\text{order parameter at } h = 0 & m \propto \tau^{\beta} \\
\text{susceptibility} & \chi \propto \tau^{-\gamma} \\
\text{order parameter at } T = T_c & m \propto h^{1/\delta} \\
\text{correlation at } T_c & g(\mathbf{r}, \mathbf{r}') \propto |\mathbf{r} - \mathbf{r}'|^{2-d-\eta} \\
\text{correlation length} & \xi \propto \tau^{-\nu}.
\end{array} \tag{36.18}$$

One calls α, β, γ, δ, η, and ν critical exponents. In the following table we show some values of critical exponents

Exponent	molecular field	Ising-M. $d = 2$	Ising-M. $d = 3$	Heisenberg-M. $d = 3$	spherical model $d = 3$
α	0(jump)	0(ln)	0.109	−0.116	−1
β	1/2	1/8	0.325	0.365	1/2
γ	1	7/4	1.241	1.387	2
δ	3	(15)	4.82	4.80	5
η	0	1/4	0.031	0.033	0
ν	1/2	1	0.630	0.705	1

(36.19)

First we have given the molecular field values. Next those of the two-dimensional Ising model. Onsager was able to give the solution of the model in 1944. He found, that the specific heat has a logarithmic singularity. Further calculations, in particular those by Yang (1952) determined the spontaneous magnetization and the susceptibility. However, the solution is only known for $h = 0$. One realized from these calculations as well as from those for the spherical model (Berlin and Kac 1952), that the critical exponents can be different from those of molecular field theory. It should be noted, that the values for the three-dimensional Ising model should also apply to liquids at the critical point. One sees, that Verschaffelt's exponent $\beta = 0.3434$, which was actually not measured that precisely, agrees well with $\beta = 0.325$ for the Ising model.
Within this course we cannot derive this behavior. But we would like to indicate shortly, what has to be done: In (36.1, 36.2) we had introduced the free energy for the system. The interpretation given was to simple. Actually it is something intermediate between free energy and Hamiltonian function. If we consider it as a Hamiltonian, then one has to integrate all $m(r)$. These integration may lead to problems with divergencies. In Fourier space one has to confine oneself to the Brillouin zone.
In Fourier space one has to confine oneself to the Brillouin zone. One may proceed in such a way, that one integrates the Fourier components with the largest wave-vectors q. Then there remains an interaction approximately of the same form as in (36.2), only the coefficients a, b and c will change. If one multiplies $m(r)$ with an appropriate factor and rescales the length, so that one again obtains the same region of wave-vectors for those Fourier components, which are not yet integrated, then it

is possible to find a set of interaction constants a, b and c, which stay constant. For these constants the system is self-similar. Upon rescaling it looks similar to itself at all scales. Then it describes the critical point and for example the algebraic decay of the correlation $\langle m(r)m(r')\rangle$.
If one deviates a little bit from these coupling constants, then one can pursue, how these deviations change. They describe the critical behavior with its critical exponents. The procedure of integration over the Fourier components with the largest wave-vectors and the rescaling is called the renormalization group.